

**HydroQuakes: PROGETTO DI
MONITORAGGIO DEI POTENZIALI
PRECURSORI SISMICI DI NATURA
IDROGEOLOGICA E IDROGEOCHIMICA
TRAMITE STAZIONI SPERIMENTALI**



Rapporto Finale, Marzo 2021

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Ania
FONDAZIONE

HydroQuakes: PROGETTO DI MONITORAGGIO DEI POTENZIALI PRECURSORI SISMICI DI NATURA IDROGEOLOGICA E IDROGEOCHIMICA TRAMITE STAZIONI SPERIMENTALI

Rapporto Finale (Marzo 2021)



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HydroQuakes

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HydroQuakes, un progetto scientifico finanziato da

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APPENDICE: Articoli Scientifici Derivati dal Progetto HydroQuakes

1. Boschetti, T., Barbieri, M., Barberio, M.D., Billi, A., Franchini, S., Petitta, M., 2019. CO₂ Inflow and element desorption prior to a seismic sequence, Amatrice-Norcia 2016, Italy. *Geochemistry, Geophysics, Geosystems*, 20, 2303-2317, <https://doi.org/10.1029/2018GC008117>
2. Barbieri, M., Boschetti, T., Barberio, M.D., Billi, A., Iacumin, P., Selmo, E.M., Franchini, S., Petitta, M., 2020. Tracing deep fluid source contribution to groundwater in an active seismic area (central Italy): a combined geothermometric and isotopic ($\delta^{13}\text{C}$) perspective. *Journal of Hydrology*, 582, 12449, <https://doi.org/10.1016/j.jhydrol.2019.124495>
3. Barberio, M.D., Gori, F., Barbieri, M., Billi, A., Casalati, F., Franchini, S., Lorenzetti, L., Petitta, M., 2020. Optimization of dissolved Radon monitoring in groundwater to contribute to the evaluation of the seismic activity: an experience in central-southern Italy. *SN Applied Sciences*, 2, 1392, <https://doi.org/10.1007/s42452-020-3185-2>
4. Franchini, S., Agostini, S., Barbieri, M., Barberio, M.D., Billi, A., Boschetti, T., Pennisi, M., Petitta, M., 2021. HydroQuakes, central Apennines, Italy: Towards a hydrogeochemical monitoring network for seismic precursors and the hydro-seismo-sensitivity of boron. *Journal of Hydrology*, in press, <https://doi.org/10.1016/j.jhydrol.2020.125754>.
5. Coppola, M., Correale, A., Barberio, M.D., Billi, A., Cavallo, A., Fondriest, M., Nazzari, M., Paonita, A., Romano, C., Stagno, V., Viti, C., Vona, A., 2021. Micro- to nano-scale structural and geochemical evidence of fluid-assisted coseismic slip along the seismogenic carbonate-hosted Mt. Morrone Fault, Italy: implications for earthquake hydrogeochemical precursors. *Earth and Planetary Science Letters*, under review.
6. Franchini, S., Barberio, M.D., Skelton, A., Stockmann, G., Barbieri, M., Billi, A., Boschetti, T., Gori, F., Giansante, L., Jónsson, S., Petitta, M., 2021. Changes in groundwater trace element concentrations before seismic and volcanic activities occurred in Iceland during 2010-2018. *Science of the Total Environment*, under review.

Progetto HydroQuakes (2017-2020): Sintesi

HydroQuakes è un programma di ricerca scientifica triennale (da dicembre 2017 a dicembre 2020) in collaborazione tra IGAG-CNR (Istituto di Geologia Ambientale e Geoingegneria del Consiglio Nazionale delle Ricerche, www.igag.cnr.it) e Fondazione ANIA (www.fondazioneania.it), volto al monitoraggio idrogeochimico di acque sotterranee e sorgive per l'individuazione di potenziali precursori sismici di natura idrogeochimica. Al progetto partecipano anche ricercatori della Sapienza Università di Roma.

La previsione dei terremoti è stata per secoli un miraggio lontano, impossibile da raggiungere. Ciononostante, da millenni si conoscono le relazioni, quanto meno temporali, tra terremoti forti e variazioni delle proprietà chimico-fisiche delle sorgenti e delle falde acquifere. Negli ultimi due decenni, in alcuni paesi (tra i quali Giappone, Islanda, Italia), si è cominciato a monitorare con costanza tali relazioni ed alcune variazioni chimico-fisiche pre-sismiche sono state interpretate come potenziali precursori sismici. Il Progetto HydroQuakes (2017-2020) ha spostato sensibilmente in avanti il livello delle conoscenze dei precursori sismici in campo idrogeochimico, sia in Italia sia all'estero (Islanda). In sintesi:

- (1) Grazie al Progetto HydroQuakes, ora l'Appennino centro-meridionale (da Sulmona ai Monti del Matese) è coperto da una rete di monitoraggio idrogeochimico per lo studio e l'identificazione di potenziali precursori sismici ([Franchini et al., 2021a](#)). Tale rete è stata da esempio per altre iniziative simili nazionali ed internazionali promosse da vari team di ricerca.
- (2) Nell'ambito del Progetto HydroQuakes, è stato installato, primo al mondo, uno spettrometro di massa (marca Hiden) presso la sorgente di Bojano per il monitoraggio in continuo di alcuni parametri chimici delle acque sorgive ([Franchini et al., 2021a](#)). Tale strumento ha permesso e permetterà di individuare, da remoto, in tempo reale, eventuali variazioni

pre-sismiche nella chimica delle acque sotto osservazione. Anche in questo caso, tale esempio è stato seguito da altri team di ricerca italiani.

- (3) Durante gli anni di monitoraggio del Progetto HydroQuakes, è stato osservato che le anomalie idrogeochimiche pre-sismiche non risultano verificarsi, almeno con significatività statistica, nel caso di terremoti di magnitudo $M_w < 5.0$, mentre sia pure sul numero ridotto di eventi verificatosi nel periodo di studio, le anomalie sono ben visibili per terremoti di magnitudo $M_w > 5.0$. Questo risultato è molto promettente in quanto associa l'identificazione di anomalie idrogeochimiche pre-sismiche a terremoti forti, aprendo la strada alla possibilità futura di poter prevedere un giorno terremoti forti tramite anomalie idrogeochimiche. In ogni caso, l'incremento delle attività di monitoraggio ha consentito anche di osservare variazioni, seppur minime, nel chimismo delle acque sotterranee anche per eventi di entità minore, come il terremoto di Collelongo (1 Gennaio 2019, M_w 4.1), che si è verificato lungo una delle faglie più grandi dell'Appennino centrale, ossia quella che causò il terremoto di Avezzano del 1915. A partire da Novembre 2018, infatti, deboli anomalie geochimiche (variazioni di Boro) nelle acque monitorate hanno annunciato l'imminente movimento sismico ((1 Gennaio 2019) lungo la grande faglia di Avezzano ([Franchini et al., 2021a](#)).
- (4) I cambiamenti osservati nei siti di monitoraggio durante il Progetto HydroQuakes nel chimismo delle acque presentano caratteristiche comuni ma anche particolarità nei diversi siti di monitoraggio, rendendo potenzialmente possibile l'identificazione futura di precursori a largo raggio (anomalie comuni a diversi siti) ma anche di ioni e composti sito-specifici (anomalie riscontrate localmente), correlati alle condizioni geologiche. Ciò favorirebbe lo sviluppo di monitoraggi al contempo generalizzati e mirati, in grado di consentire adeguate previsioni nelle diverse condizioni geologiche del nostro Paese.
- (5) Nell'ambito del Progetto HydroQuakes, sono stati studiati alcuni reperti fossili provenienti dalla Faglia del Monte Morrone (Sulmona), dove nel 2016 le stazioni idrogeochimiche

avevano registrato anomalie geochemiche (incremento di Arsenico e Vanadio nelle acque) 3-4 mesi prima del terremoto di Amatrice. I reperti fossili studiati confermano la presenza di rocce ricche in Vanadio, offrendo dunque una validazione indiretta delle anomalie geochemiche pre-sismiche del 2016. In altre parole, i reperti fossili testimoniano l'occorrenza di eventi passati anomali simili a quelli del 2016 ([Coppola et al., 2021](#)).

(6) Nell'ambito del Progetto HydroQuakes, è stato sviluppato un modello geochemico tramite software dedicati, per la comprensione dei processi idrogeochemici pre-sismici. Il modello sviluppato è in accordo con le anomalie geochemiche pre-sismiche del 2016 (pre-sisma di Amatrice 2016) e le spiega con un apporto pre-sismico di anidride carbonica profonda ([Boschetti et al., 2019](#); [Barbieri et al., 2020](#)). Auspichiamo che questo modello possa essere utilizzato in futuro come strumento predittivo per il tipo di anomalia pre-sismica attesa in aree sismicamente attive d'Italia.

(7) Nell'ambito del Progetto HydroQuakes, è stata sviluppata una collaborazione internazionale per l'analisi delle acque sotterranee campionate in Islanda del Nord. L'analisi dei campioni prelevati settimanalmente nel periodo 2010-2018 ha messo chiaramente in evidenza la presenza di anomalie idrogeochemiche pre-vulcaniche e pre-sismiche, ossia interpretabili come precursori dell'eruzione del Vulcano Bárðarbunga del 2014 e come precursori sismici del terremoto di magnitudo M_w 5.2 del 2018 nel Nord dell'Islanda ([Franchini et al., 2021b](#)).

In conclusione, il Progetto HydroQuakes conferma che l'installazione di reti di monitoraggio idrogeochemico in aree sismiche è una strada corretta per l'identificazione di precursori sismici. In tali aree, lo studio dei reperti fossili e lo sviluppo di modelli geochemici ad hoc possono validare i precursori stessi e permettere di comprenderne i processi chimico-fisici, fino alla previsione del tipo di anomalia attesa in una determinata area sismicamente attiva

d'Italia. Il confronto con i risultati ottenuti da monitoraggi idrogeochimici in altre aree sismicamente attive della Terra conforta e rafforza i risultati ottenuti dal Progetto HydroQuakes.

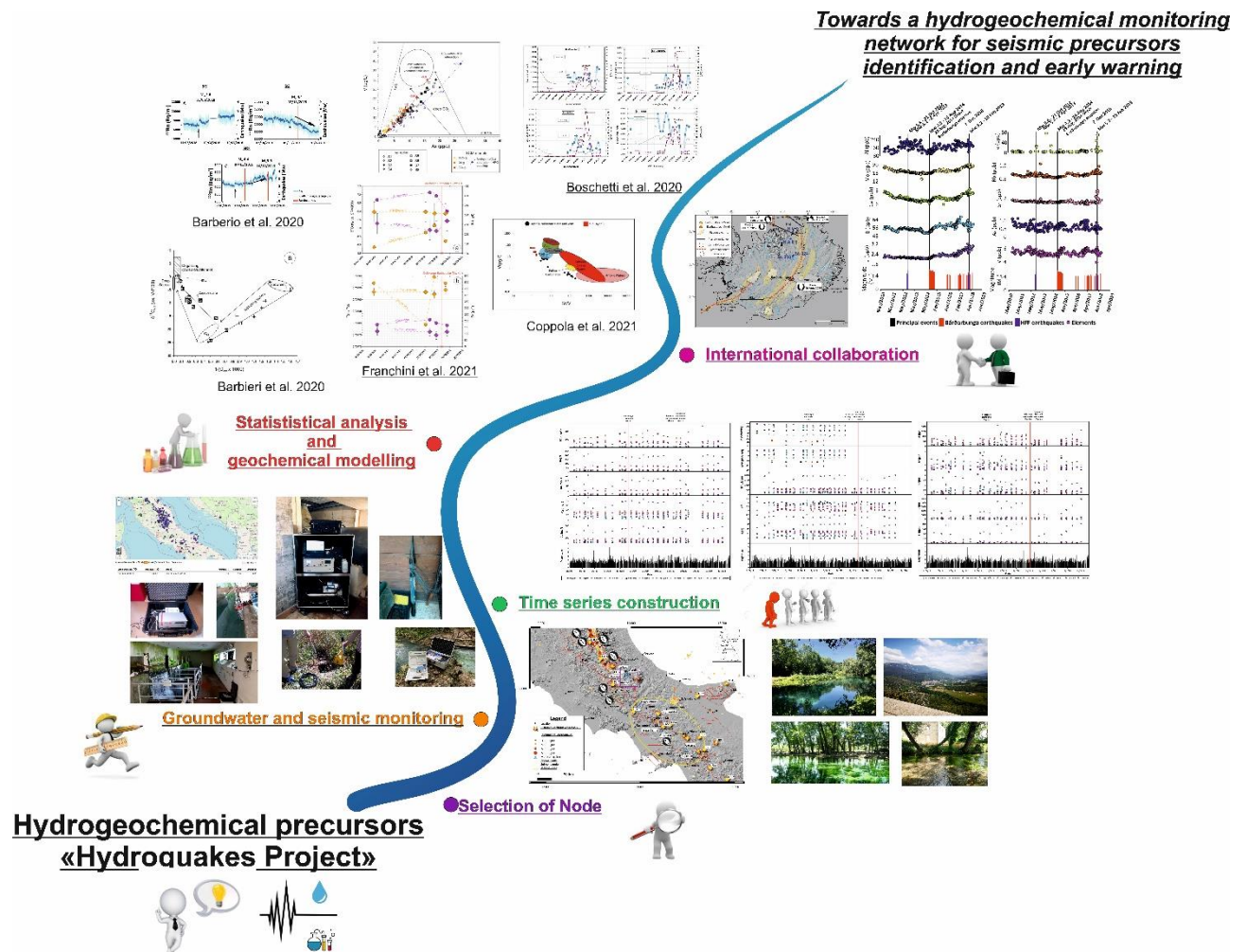


Grafico concettuale e flusso di lavoro del Progetto HydroQuakes

- Barbieri, M., Boschetti, T., Barberio, M.D., Billi, A., Iacumin, P., Selmo, E.M., Franchini, S., Petitta, M., 2020. Tracing deep fluid source contribution to groundwater in an active seismic area (central Italy): a combined geothermometric and isotopic ($\delta^{13}\text{C}$) perspective. *Journal of Hydrology*, 582, 12449, <https://doi.org/10.1016/j.jhydrol.2019.124495>
- Boschetti, T., Barbieri, M., Barberio, M.D., Billi, A., Franchini, S., Petitta, M., 2019. CO_2 Inflow and element desorption prior to a seismic sequence, Amatrice-Norcia 2016, Italy. *Geochemistry, Geophysics, Geosystems*, 20, 2303-2317, <https://doi.org/10.1029/2018GC008117>

- Coppola, M., Correale, A., Barberio, M.D., Billi, A., Cavallo, A., Fondriest, M., Nazzari, M., Paonita, A., Romano, C., Stagno, V., Viti, C., Vona, A., 2021. Micro- to nano-scale structural and geochemical evidence of fluid-assisted coseismic slip along the seismogenic carbonate-hosted Mt. Morrone Fault, Italy: implications for earthquake hydrogeochemical precursors. *Earth and Planetary Science Letters*, under review.
- Franchini, S., Agostini, S., Barbieri, M., Barberio, M.D., Billi, A., Boschetti, T., Pennisi, M., Petitta, M., 2021a. HydroQuakes, central Apennines, Italy: Towards a hydrogeochemical monitoring network for seismic precursors and the hydro-seismo-sensitivity of boron. *Journal of Hydrology*, in press, <https://doi.org/10.1016/j.jhydrol.2020.125754>.
- Franchini, S., Barberio, M.D., Skelton, A., Stockmann, G., Barbieri, M., Billi, A., Boschetti, T., Gori, F., Giansante, L., Jónsson, S., Petitta, M., 2021b. Changes in groundwater trace element concentrations before seismic and volcanic activities occurred in Iceland during 2010-2018. *Science of the Total Environment*, under review.

1. Introduzione, Obiettivi e Gruppo di Lavoro

Hydroquakes è un programma di ricerca scientifica triennale (da dicembre 2017) in collaborazione tra IGAG-CNR (Istituto di Geologia Ambientale e Geoingegneria del Consiglio Nazionale delle Ricerche, www.igag.cnr.it) e Fondazione ANIA (www.fondazioneania.it), volto al monitoraggio idrogeochimico di acque sotterranee e sorgive per l'individuazione di potenziali precursori sismici di natura idrogeochimica. Al progetto partecipano anche ricercatori della Sapienza Università di Roma.

Gli obiettivi principali di Hydroquakes sono i seguenti:

Obiettivo tecnico-scientifico: progettazione, realizzazione e test di stazioni idrogeologiche sperimentali a scala appenninica, finalizzate alla determinazione dei parametri in grado di influire sulle caratteristiche idrogeologiche e idrogeochimiche delle acque sotterranee in funzione della deformazione profonda in grado di innescare terremoti, al fine di utilizzarne i potenziali precursori sismici per l'implementazione di un sistema di early-warning da sottoporre ad integrazione con le reti sismologiche esistenti.

Obiettivo sociale: educazione, informazione e prevenzione per eventi di tipo catastrofico sul territorio italiano inclusi gli eventi sismici, con particolare riguardo alla protezione delle famiglie e delle imprese del paese, con l'obiettivo di realizzare un'azione sociale che intercetti le esigenze di sicurezza dei cittadini reinterprestandole in chiave di protezione.

La presente relazione descrive le attività svolte ed i risultati ottenuti durante il tre anni di progetto dal seguente gruppo di lavoro:

Andrea Billi (Dirigente di Ricerca presso IGAG-CNR);

Marco Petitta (Professore Ordinario di Idrogeologia presso Sapienza Università di Roma);

Maurizio Barbieri (Professore Associato di Geochimica presso Sapienza Università di Roma);

Marino Domenico Barberio (PostDoc in Idrogeologia presso Sapienza Università di Roma);

Stefania Franchini (PostDoc in Idrogeochimica presso Sapienza Università di Roma);

Francesca Gori (Dottoranda in Idrogeochimica presso Sapienza Università di Roma).

Inoltre, al progetto hanno partecipato saltuariamente il Prof. Carlo Doglioni (Professore Ordinario di Geodinamica presso Sapienza Università di Roma e Presidente dell'INGV), che lo ha avviato ed ha sovrinteso agli accordi iniziali, ed il Dott. Tiziano Boschetti dell'Università di Parma. Le ricerche svolte durante il Progetto HydroQuakes si sono spesso avvalse di proficue collaborazioni con colleghi Italiani e stranieri che sono menzionati nell'Appendice di questa relazione come co-autori dei sei articoli scientifici riportati nell'Appendice stessa.

2. Stato dell'Arte

Negli ultimi anni, alcuni studi significativi hanno evidenziato come, prima di un evento sismico, le acque sotterranee subiscano cambiamenti nella concentrazione di alcuni elementi, soprattutto ioni metallici. Ciò è probabilmente correlato alla dilatazione crostale nella fase preparatoria di un terremoto, in particolare lungo le faglie normali, e alla conseguente risalita di fluidi idrotermali profondi arricchiti con metalli e acidi. Studi precedenti condotti in Giappone, Turchia, Islanda, India e Italia ([Fig. 1](#) e [Tab. 1](#)) hanno quindi dimostrato che il monitoraggio e le analisi idrogeochimiche delle acque sotterranee sono uno strumento utile per studiare i precursori sismici ([Wakita et al., 1988](#); [Igarashi et al., 1995](#); [Claesson et al., 2004](#); [Skelton et al., 2008, 2014](#); [Huang et al., 2012](#); [Inan et al., 2012](#); [Wästeby et al., 2014](#); [Andrén et al., 2016](#); [Sano and Wakita, 2016](#); [De Luca et al., 2018](#)). Alcuni di tali esempi sono brevemente descritti nelle righe successive.

In Giappone, furono eseguite analisi chimiche su acque minerali imbottigliate da pozzi situati vicino all'epicentro del terremoto di Kobe (Giappone) di Mw 7.2 nel gennaio 1995. Prima del terremoto, per diversi mesi, si verificò un costante aumento della concentrazione di Cl e SO₄. Tale concentrazione divenne molto alta dopo il terremoto ([Tsunogai et al., 1995](#)). Si registrò anche un aumento della concentrazione di Radon nelle falde acquifere diversi mesi prima del terremoto. In particolare, dieci giorni prima del terremoto, si ebbe un improvviso aumento della concentrazione di Radon, al quale seguì un improvviso decremento una settimana prima del terremoto. Dopo il sisma, la concentrazione di Radon divenne piuttosto stabile ad un livello molto basso ([Igarashi et al., 1995](#)).

Nel 2017, pochi mesi prima del terremoto di Tottori (Giappone) di Mw 6.6 furono registrate, nelle acque sotterranee, anomalie nel rapporto isotopico dell'ossigeno ($\delta^{18}\text{O}$) di + 0,24 ‰ rispetto al background locale (a 5 km dall'epicentro). Tre mesi prima del terremoto fu rilevato anche un piccolo aumento di Cl e SO₄. [Onda et al. \(2018\)](#) ritengono che le deformazioni della crosta prima del terremoto di Tottori possano aver aumentato la permeabilità delle rocce,

dunque favorendo un'interazione acqua-roccia tale da arricchire in $\delta^{18}\text{O}$ l'acqua a contatto con le rocce fratturate (Onda et al., 2018).

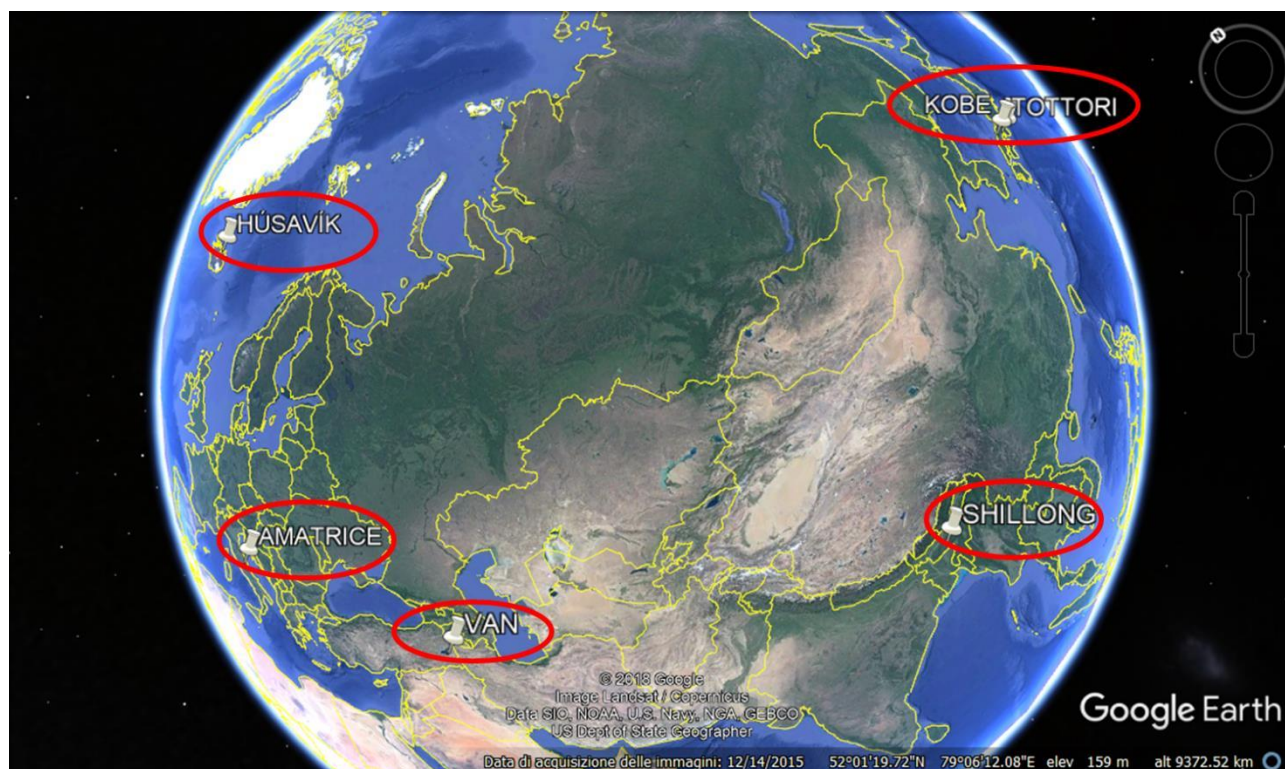


Figura 1. Ubicazione delle aree e stazioni di monitoraggio dove sono stati registrati potenziali precursori idrogeochimici di terremoti medio-forti ($M_w > 5.5$). Vedi anche Tab. 1.

Studi condotti in Islanda hanno dimostrato che la chimica della falda freatica campionata anche ad una grande distanza dall'epicentro del terremoto (80-90 km) può risultare alterata in relazione alla dilatazione crostale pre-sismica avvenuta 4-6 mesi prima di due terremoti $M_w \geq 5.5$ (ottobre 2012 e aprile 2013; Skelton et al., 2014). Nella stessa area, simili cambiamenti idrogeochimici erano già stati registrati nel 2002, quando Claesson et al. (2004) osservarono picchi significativi nelle concentrazioni di Cu, Zn, Mn e Cr, rispettivamente 1, 2, 5 e ≥ 10 settimane prima di un terremoto di $M_w 5.8$. Alcuni giorni dopo il terremoto furono registrati sia un rapido aumento delle concentrazioni di diversi elementi, sia una diminuzione di Na/Ca, $\delta^{18}\text{O}$

e δD . Questi cambiamenti idrogeochimici sono probabilmente legati all'afflusso nel sistema idrologico di fluidi idrotermali profondi arrivati in superficie in seguito alla rottura di una barriera profonda durante le fasi presismiche (Claesson et al., 2004).

SITO	MAGNITUDO	PRECURSORE	QUANDO	DOVE
KOBE – GIAPPONE (1995) Igarashi et al., 1995; Tsunogai & Wakita, 1995	Mw 7.2	aumento delle concentrazioni di Cl e SO_4^{2-} ; aumento della concentrazione di radon nelle acque sotterranee; improvvisa diminuzione della concentrazione di Radon nelle acque sotterranee.	diversi mesi prima diversi mesi prima una settimana prima	20-30 km dall'epicentro
HUSAÐÍK – ISLANDA (2002) Claesson et al., 2004	Mw 5.8	aumento nelle concentrazioni di Cu, Zn, Mn, and Cr.	1, 2, 5, e ≥ 10 settimane prima	circa 90 km dall'epicentro
SHILLONG PLATEAU – INDIA (2004-2005) Skelton et al., 2008	Mw ≥ 5.0	aumento dei rapporti [Na+K]/Si, Na/K, and [Na+K]/Ca; aumento della conducibilità e dell'alcalinità e della concentrazione di Cl; diminuzione del rapporto Ba/Sr.	3-5 settimane prima del terremoto di M_w 5.3	206 km dall'epicentro
VAN – TURCHIA (2011) Inan et al., 2012	Mw 7.2	aumento nelle concentrazioni di Ca, Mg, K e Cl; diminuzione delle concentrazioni di Na e SO_4^{2-}	3-6 giorni prima del terremoto di M_w 5.0 1 mese prima	213 km dall'epicentro < 20 km dall'epicentro
HUSAÐÍK – ISLANDA (2012-2013) Skelton et al., 2014	Mw ≥ 5.5	alterazione della chimica delle acque sotterranee	4-6 mesi prima	circa 90 km dall'epicentro
AMATRICE/NORCIA – ITALIA (2016-2017) Barberio et al., 2017	Mw ≥ 6.0	aumento delle concentrazioni di As, V e Fe e variazione del pH	3-4 mesi prima	circa 90 km dall'epicentro
TOTTORI – GIAPPONE (2017) Onda et al., 2018	Mw 6.6	aumento dello 0.24‰ del rapporto isotopico dell'ossigeno	pochi mesi prima	5 km dall'epicentro

Tabella 1. Dati relativi agli studi precedenti (Fig. 1) nei quali sono stati registrati potenziali precursori idrogeochimici di terremoti medio-forti ($M_w > 5.5$).

In Turchia, analisi chimiche condotte su acqua di sorgente imbottigliata a meno di 20 km dall'epicentro del terremoto di Van (Turchia) di Mw 7.2 dell'ottobre 2011 mostrarono un aumento di Ca, Mg, K e Cl e una diminuzione di Na e SO_4 prima del terremoto. Le analisi su campioni post-sismici evidenziarono una diminuzione di Ca, Mg, K e Cl e un aumento di Na e SO_4 (Inan et al., 2012).

Anomalie idrogeochimiche transitorie sono state rilevate nella falda acquifera situata a nord del Plateau di Shillong (India) prima di due terremoti di $M_w \geq 5.0$ (a 200 km dall'epicentro). I rapporti [Na + K]/Si, Na/K e [Na + K]/Ca oltre alla conduttività, alcalinità e concentrazione di Cl

iniziarono ad aumentare 3-5 settimane prima del terremoto Mw 5.3, mentre il rapporto Ba/Sr iniziò la sua diminuzione 3-6 giorni prima del terremoto Mw 5.0. [Skelton et al. \(2008\)](#) ritengono che la prima di queste anomalie idrogeochimiche sia dovuta ad un mescolamento tra due diversi acquiferi probabilmente a seguito del terremoto di Mw 5.3, mentre la seconda anomalia idrogeochimica potrebbe essere stata causata da microfratture sull'acquifero principale a causa del terremoto di Mw 5.0 ([Skelton et al., 2008](#)).

Un recente studio in Italia ha rilevato anomalie idrogeochimiche e variazioni del pH 3-4 mesi prima dell'inizio della sequenza sismica nell'Italia centrale (Amatrice-Norcia 2016-2017). In particolare, sono state osservate concentrazioni più elevate di As, V e Fe prima dell'inizio della sequenza sismica, mentre all'inizio della sequenza è stato registrato anche un aumento della concentrazione di Cr ([Barberio et al., 2017](#)).

A riprova del grande potenziale dei precursori idrogeochimici nel campo della previsione dei terremoti, nell'ultimo anno (2019-2020) numerosi sono stati gli studi scientifici pubblicati su tale tema ([Nakagawa et al., 2019](#); [Skelton et al., 2019](#); [Barbieri et al. 2020](#); [Hosono and Masaki, 2020](#); [Lutzky et al., 2020](#); [Sato et al., 2020](#); [Singh and Mukherjee, 2020](#); [Shi et al., 2020](#)). Inoltre, il Programma Operativo Nazionale (PON) del Ministero dell'Istruzione, dell'Università e della Ricerca ha di recente finanziato un progetto scientifico infrastrutturale (INGV) per il monitoraggio di emissioni di gas in Italia meridionale al fine dell'identificazione di possibili precursori sismici.

Le similitudini ed analogie tra gli studi precedenti sui precursori idrogeochimici dei forti terremoti ([Wakita et al., 1988](#); [Igarashi et al., 1995](#); [Tsunogai et al., 1995](#); [Claesson et al., 2004](#); [Skelton et al., 2008, 2014](#); [Huang et al., 2012](#); [Inan et al., 2012](#); [Wästeby et al., 2014](#); [Andrén et al., 2016](#); [Sano and Wakita, 2016](#); [De Luca et al., 2018](#); [Onda et al., 2018](#); [Hosono and Masaki, 2020](#); [Shi et al., 2020](#)) suggeriscono che il monitoraggio e le analisi delle proprietà idrogeochimiche delle sorgenti naturali potrebbe essere un campo promettente di ricerca per lo studio dei precursori sismici. Tuttavia, gli elementi coinvolti e il modo in cui cambiano nel tempo secondo il ciclo sismico suggeriscono che tali precursori sismici, se reali, potrebbero essere sito

specifici. Il presente progetto si propone di comprendere meglio i precursori sismici di natura idrogeochimica ed i relativi processi proprio per favorire la comprensione dei fenomeni sito-specifici e la loro eventuale applicabilità ad altri siti o il loro eventuale valore generale e globale. Di seguito viene descritto il processo di selezione dell'area di monitoraggio idrogeochimico del presente progetto.

3. Selezione dell'Area di Monitoraggio

Il gruppo di lavoro sopra menzionato lavora già da alcuni anni nel sito di monitoraggio di Popoli-Sulmona (Barberio et al., 2016; Petitta et al., 2018) e, nel 2018, ha iniziato una collaborazione con ricercatori svedesi ed islandesi per un sito ubicato in Islanda (Húsavík; vedi Fig. 1), dove già da anni è in corso un monitoraggio idrogeochimico (Claesson et al., 2004; Skelton et al., 2014, 2019). Tali siti (Popoli-Sulmona e Húsavík) fanno ora parte del monitoraggio idrogeochimico realizzato per il progetto HydroQuakes (vedi sotto la sezione sui risultati). Inoltre, per il progetto Hydroquakes, è stato selezionato una nuova area di monitoraggio seguendo i criteri di selezione di seguito descritti.

La selezione dell'area si basa su tre criteri principali:

- (1) criterio sismologico, per la conoscenza dei terremoti attuali e recenti registrati da stazioni di misura della rete nazionale sismometrica (<http://terremoti.ingv.it/it/>);
- (2) criterio paleosismologico, per la conoscenza della ricorrenza dei terremoti non solo recenti (registrati dalla rete nazionale sismometrica) ma anche storici (registrati da fonti storiche; <http://istituto.ingv.it/it/archivi-e-banche-dati.html>) e preistorici (determinati tramite metodi paleosismologici);
- (3) criteri idrologici-idrogeochimici, per la conoscenza di sorgenti profonde idonee che siano il meno possibile influenzate dai cicli stagionali e da tutto ciò che succede in superficie.

Una prima selezione dell'area è stata realizzata sulla base di studi statistici precedenti svolti da diversi gruppi di ricercatori.

Cinti et al. (2004) forniscono un modello di distribuzione spazio-temporale dei terremoti distruttivi in Italia ($M_w > 5.5$) basato su una regionalizzazione fondata su parametri tettonici, sul

catalogo sismico degli ultimi 4 secoli e sui dati sismologici e geologici (Fig. 2). In particolare, per regionalizzazione, gli autori intendono la definizione di aree omogenee dal punto di vista del comportamento sismico e della cinematica ed orientamento del campo di stress. La tecnica statistica utilizzata per la definizione della mappa di probabilità dei prossimi terremoti di $M_w > 5.5$ in Italia è in grado di considerare contemporaneamente tutti i fattori tettono-fisici che possono potenzialmente influenzare la distribuzione spazio-temporale degli eventi sismici futuri. L'obiettivo principale di questo studio è quindi quello di fornire una mappa di probabilità per i prossimi terremoti medio-grandi ($M_w > 5.5$) in Italia dipendente dal tempo (Fig. 2). In particolare, la distribuzione dei terremoti futuri di $M_w > 5.5$ è dipendente dal tempo nei primi anni dopo un terremoto medio-grande, dopo di che il processo diventa quasi tempo-indipendente. Poiché i terremoti tendono a verificarsi nelle stesse aree in cui si sono verificati in passato, Cinti et al. (2004) calcolano la probabilità solo per le zone in cui si è verificato almeno un terremoto di $M_w > 5.5$ negli ultimi 4 secoli. L'Italia è stata quindi divisa dagli autori in 61 zone, di cui 34 hanno registrato un evento di $M_w > 5.5$ negli ultimi 4 secoli. Per tali zone, è stata evidenziata una probabilità di possibili terremoti futuri per i 10 anni seguenti il 2004 compresa tra 2% e 27%. Per le restanti zone del territorio italiano viene associata arbitrariamente una probabilità $< 1\%$ perché non si possono escludere eventuali terremoti futuri. Secondo gli autori, le 4 regioni con le probabilità più elevate sono (Fig. 2):

- (1) La regione Friuli, con una probabilità del 27% di un evento sismico prodotto da una faglia orientata E-W con probabile meccanismo di rottura di tipo thrust-faglia inversa;
- (2) Parte dell'Appennino meridionale (Campania-Molise), con una probabilità del 25% di un evento sismico prodotto da una faglia orientata NW-SE con probabile meccanismo di rottura di tipo estensionale;
- (3) La regione Umbria-Marche, con una probabilità del 25% di un evento sismico prodotto

da una faglia orientata NW-SE con probabile meccanismo di rottura di tipo estensionale;

- (4) Parte dell'Arco calabro, con una probabilità del 17% di un evento sismico prodotto da una faglia orientata NE-SW con meccanismo di rottura di tipo estensionale.

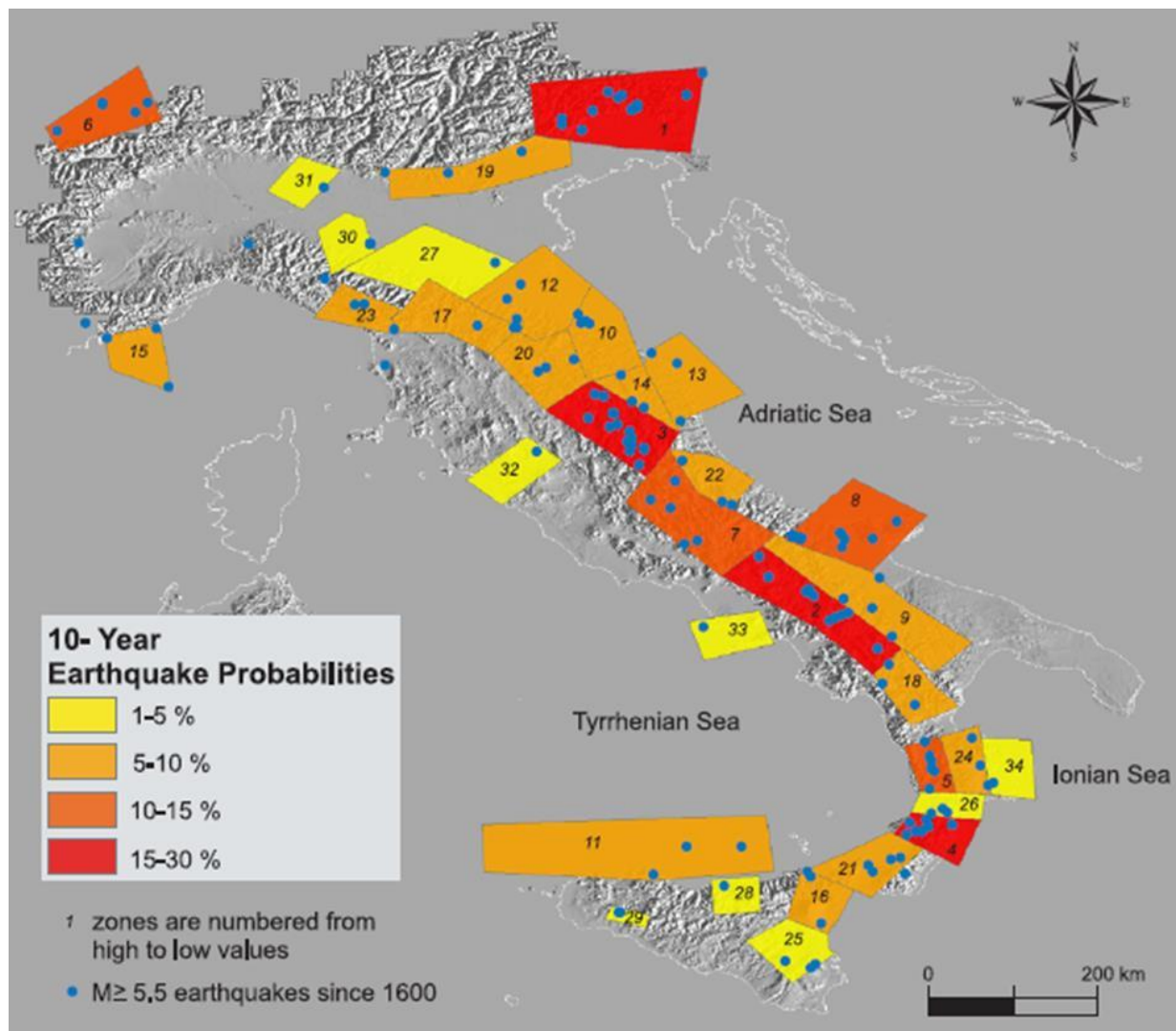


Figura 2. Mappa di probabilità di terremoti da moderati a grandi ($M_w \geq 5.5$) in Italia per 10 anni seguenti il 2004 (Cinti et al., 2004).

Successivamente (ed anche in precedenza), sono stati svolti studi statistico-sismologici da altri gruppi di lavoro che concordano in larga parte con il lavoro di [Cinti et al. \(2004\)](#) sulle aree a maggior rischio sismico futuro ([Galadini et al., 2000](#); [Meletti et al., 2000](#); [Galli et al., 2008, 2017](#); [Slejko et al., 2009](#)). Per esempio, [Slejko et al. \(2009\)](#), utilizzando vincoli geodetici e modellazione geofisica, ricostruiscono una mappa di probabilità per i 30 anni seguenti il 2009 di eventi sismici di $M_w \geq 6.0$ ([Fig. 3](#)) e $M_w \geq 6.5$ ([Fig. 4](#)); in particolare, gli autori vogliono definire il potenziale sismico delle aree sismogeniche in Italia considerando modelli regionali di sismicità e l'attuale strain rate (rateo di deformazione tettonica). La maggior parte delle zone sismogenetiche più "pericolose" in termini di probabilità di terremoti vengono individuate dagli autori nell'Appennino meridionale. Le probabilità basate sia sui vincoli geodetici sia sulla modellazione geofisica sono inferiori al 5% per eventi di $M_w \geq 6.0$ ad eccezione dell'Appennino meridionale (Campania, Molise, Basilicata), dove raggiungono valori tra il 10% e il 20%. La probabilità a 30 anni per eventi di $M_w \geq 6.5$ varia principalmente tra 0.4% e 3%, ad eccezione sempre dell'Appennino meridionale dove sono più elevate anche se rimangono inferiori al 10%. ([Figg. 3 e 4](#); [Slejko et al 2009](#)).

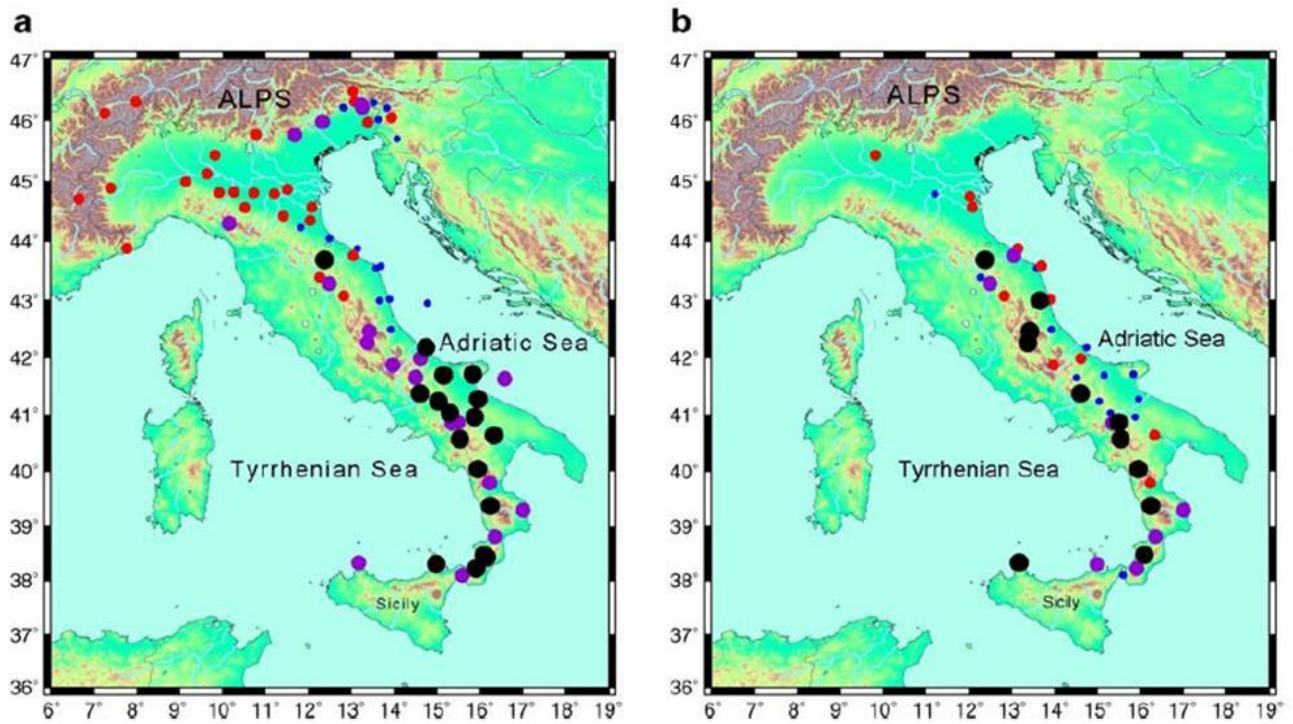


Figura 3. Mappa di probabilità (P) per i 30 anni seguenti il 2009 per terremoti di $M \geq 6.0$: a) probabilità calcolata da vincoli geodetici, b) probabilità calcolata da vincoli geofisici. I punti blu per $P \leq 1\%$; i punti rossi per $1\% < P \leq 2.5\%$; i punti viola per $2.5\% < P \leq 5\%$; i punti neri per $P > 5\%$.

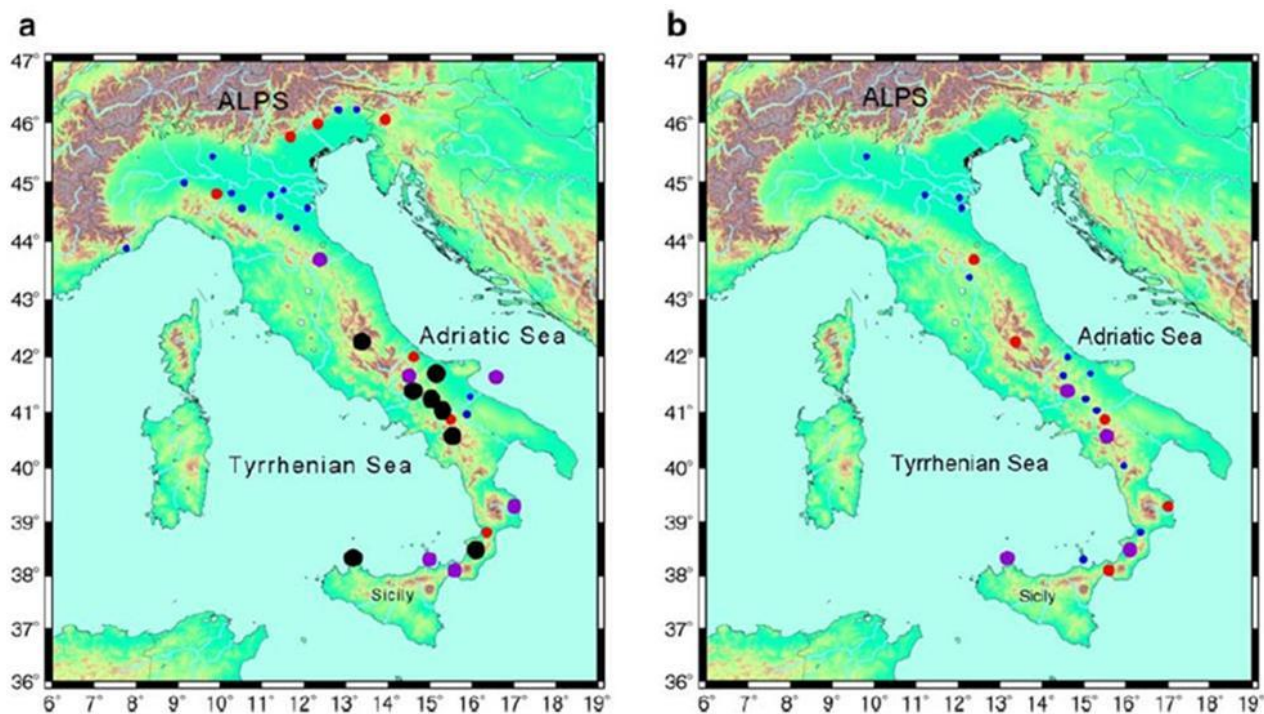


Figura 4. Mappa di probabilità (P) per i 30 anni seguenti il 2009 per terremoti di $M \geq 6.5$: a) probabilità calcolata da vincoli geodetici, b) probabilità calcolata da vincoli geofisici. I punti blu per $P \leq 0.4\%$; i punti rossi per $0.4\% < P \leq 1.5\%$; i punti viola per $1.5\% < P \leq 3\%$; i punti neri per $P > 3\%$.

Quindi, nonostante lo studio di [Cinti et al. \(2004\)](#) sia ormai temporalmente superato, il fatto che nella zona dell'Appennino meridionale non si sia ancora verificato un terremoto di magnitudo $M_w > 5.5$ e che anche altri gruppi di ricercatori concordino nell'individuare in quest'area una delle zone a probabilità più elevata di eventi sismici futuri di $M_w \geq 6$ ([Slejko et al., 2009](#)) ci ha portato a concentrare il nostro lavoro nella zona dell'Appennino meridionale, e abbiamo quindi iniziato a studiare in particolare l'area Beneventana e dei Monti del Matese (Campania-Molise). Quest'area fa parte della cintura sismogenetica dell'Appennino meridionale che ha subito grandi eventi sismici distruttivi sia in epoca storica sia in tempi recenti ([Fig. 5](#); [Galli et al., 2008](#); [Galli e Naso, 2009](#)). L'area, in particolare, è stata colpita da forti terremoti di $M_w \geq 6.5$ con periodicità di circa 100-150 anni, mentre dall'ultimo evento è stata soggetta solo ad eventi sismici di magnitudo moderata, compreso il sisma di $M_w 4.9$ del dicembre 2013 ([D'Amico](#)

et al., 2014; Galli et al., 2017). Questa lunga quiescenza sismica e la distribuzione attuale della sismicità di fondo, rendono questa regione una delle più probabili candidate ad eventi sismici futuri di magnitudo elevata, compresa tra 6.5 e 7.0.

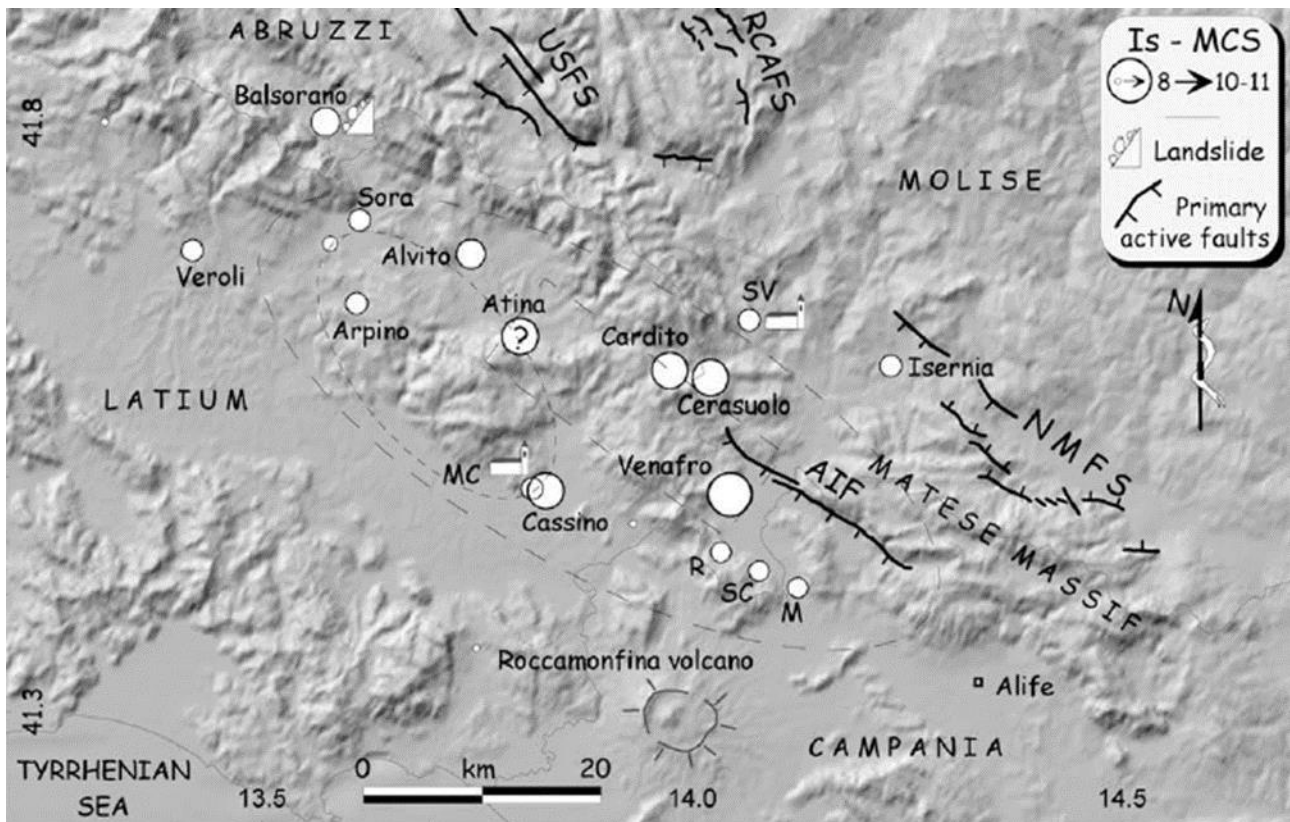


Figura 5. Principali faglie normali attive nell'area dei Monte del Matese ed epicentri di alcuni terremoti storici (Galli e Naso, 2009).

L'area di studio è caratterizzata da eventi sismici dovuti a faglie normali in un regime di stress tensionale orientato tendenzialmente NE-SO. Gli eventi di magnitudo elevata si verificano lungo un segmento di faglia che si estende in direzione NO-SE per 40-50 km. I terremoti si verificano principalmente intorno alla piattaforma calcarea dei Monti del Matese (Fig. 5; Chiarabba et al., 1997). Alcuni ricercatori hanno evidenziato come la faglia delle Aque Iulie e il sistema di faglie N-Matese (Fig. 6) siano tra le strutture sismogenetiche più pericolose della catena appenninica ($M_w \geq 6.6$), con il tempo di ricorrenza più breve (pochi secoli) fra quelli

appenninici, poiché lo slip rate (rateo di movimento della faglia) è uno dei più elevati. Queste due strutture insieme ospitano gran parte dell'estensione NE-SO che attualmente interessa questo settore della catena (Galli e Naso, 2009; Galli et al., 2017).

Inoltre, un recente studio di Cucci (2019) mette in evidenza come, storicamente, le sorgenti ed i processi idrogeochimici dell'Appennino Campano-Molisano abbiano mostrato repentini comportamenti anomali in concomitanza con terremoti nella stessa area. Si tratta non solo di processi contemporanei ad alcuni terremoti maggiori (in particolare, i terremoti del 1805 e 1930 di magnitudo Mw 6.7), ma anche di processi pre-sismici. Tali processi sono elencati e descritti in dettaglio in Cucci (2019).

Anche il DISS, Database Italiano delle Principali Sorgenti Sismogenetiche (<http://diss.rm.ingv.it/diss/index.php/DISS321>), individua nell'area Matese-Beneventana due sorgenti principali (faglie estensionali a direzione NW-WSE) ciascuna in grado di generare terremoti di magnitudo fino a circa 6.7. Coerentemente, nella stessa area, Trippetta et al. (2019) individuano faglie capaci di generare terremoti con magnitudo fino a quasi 7.0.

A valle della selezione dell'area Matese-Beneventana sulla base di criteri (paleo)sismologici, in tale area sono state individuate alcune sorgenti potenzialmente adatte al monitoraggio idrogeochimico volto alla individuazione di possibili precursori sismici. Le sorgenti selezionate preliminarmente in base alle portate annuali e stagionali ed in base ad alcuni parametri idrogeochimici noti in letteratura sono le seguenti (Fig. 7): Bojano, Grassano, Telese Terme, Capo Volturno, Caposele e Cassano Irpino (Figg. 8-11 e Tab. 3). Il metodo utilizzato per la caratterizzazione idrogeochimica e per il monitoraggio di tali sorgenti, ed i relativi risultati sono presentati nelle sezioni seguenti.

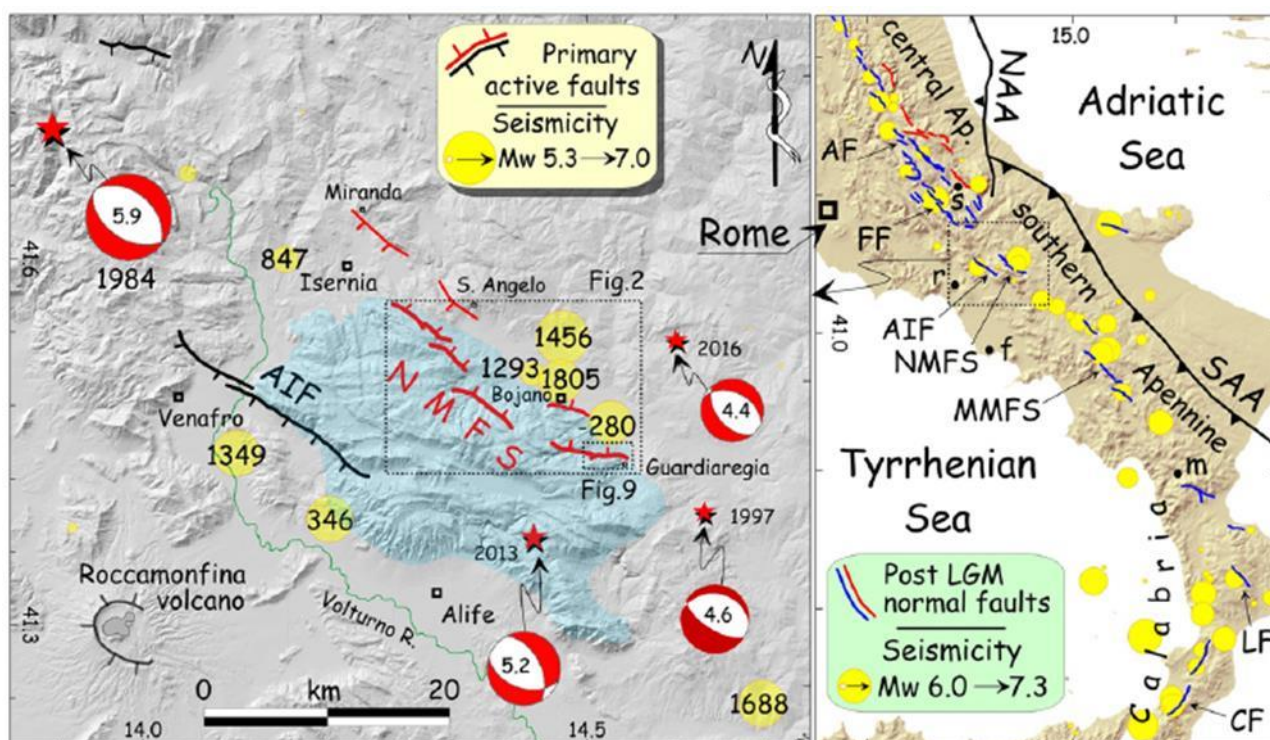


Figura 6. Epicentri (cerchi gialli) dei terremoti storici più forti (Galli e Naso, 2009) attorno al massiccio del Matese (blu area) e sistemi di faglie attive primarie (AIF e NMFS; Galli et al., 2017).

ANNO	MAGNITUDO
1349	M _w 6.6
1456	M _w 6.5
1688	M _w 7.0
1702	M _w 6.5
1805	M _w 6.6

Tabella 2. Terremoti storici (M_w ≥ 6.5) dell'area Matese-Beneventana.



Figura 7. Ubicazione delle sorgenti selezionate per il progetto Hydroquakes nell'Appennino Matese-Beneventano.



Figura 8. Fotografia della sorgente di Rocchetta a Volturno.



Figura 9. Fotografia delle sorgenti di Bojano (sinistra) e Grassano (destra).

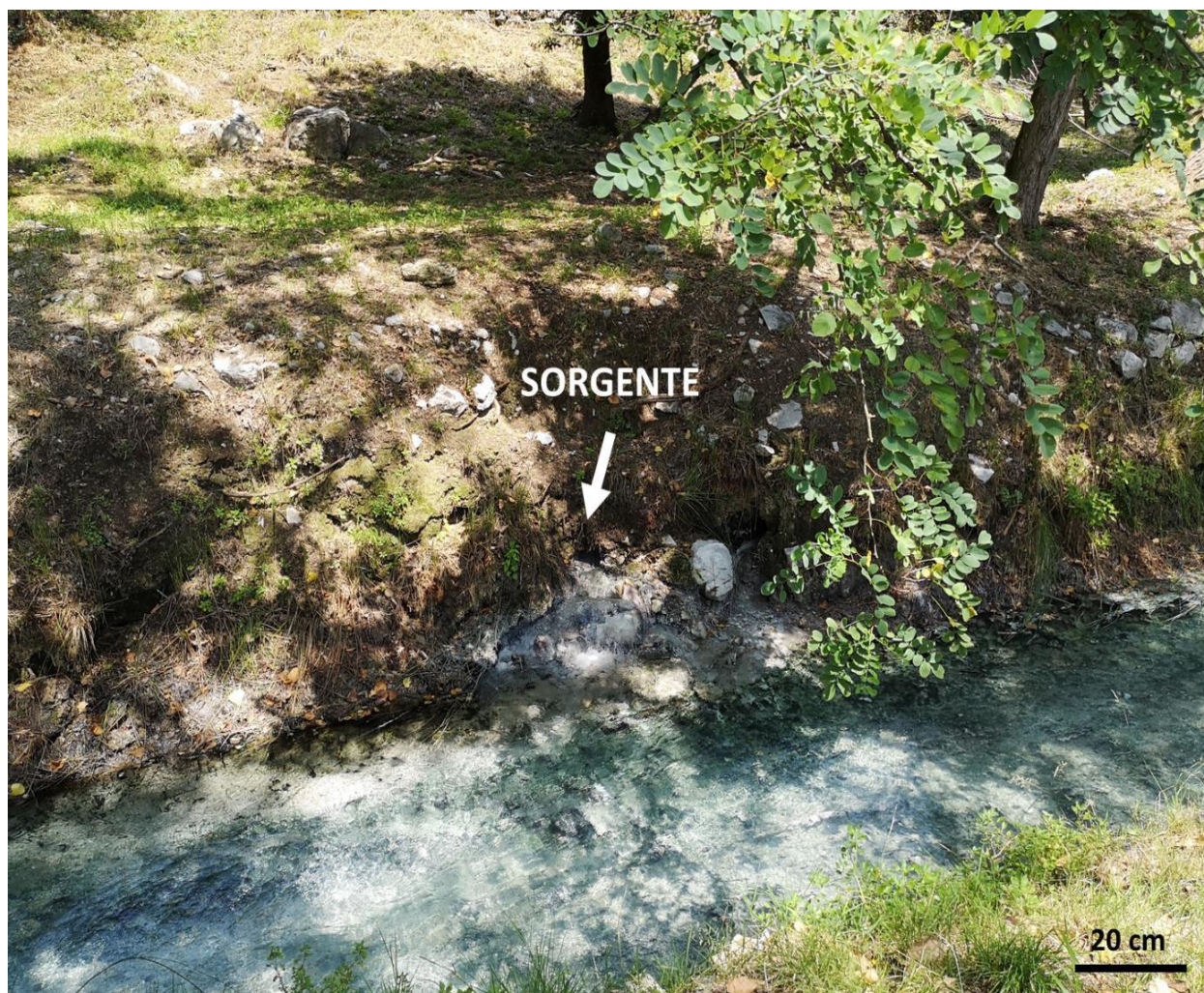


Figura 10. Fotografia della sorgente di Telesse Terme.



Figura 11. Fotografia delle sorgenti di Caposele (sinistra) e Cassano Irpino (destra).

SORGENTE	LATITUDINE	LONGITUDINE	TIPOLOGIA
Capo Volturno	41°38'12.60"N	14° 4'17.02"E	Sorgente
Bojano	41°28'45.59"N	14°28'40.95"E	Captazione
Grassano	41°13'29.08"N	14°30'52.86"E	Sorgente
Telese Terme	41°13'17.96"N	14°31'40.45"E	Sorgente
Caposele	40°49'5.43"N	15°13'20.32"E	Sorgente
Cassano	40°52'20.00"N	15° 1'51.42"E	Sorgente

Tabella 3. Elenco ed ubicazione delle sei sorgenti selezionate per il progetto HydroQuakes (area Matese-Beneventana).

4. Metodi

4.1. Razionale

A valle della selezione delle sorgenti da monitorare, il monitoraggio è proseguito contemporaneamente in tre direzioni:

- un monitoraggio in continuo delle sorgenti tramite sonde in situ controllate da remoto;
- un campionamento circa mensile delle sorgenti per le analisi chimico-fisiche ed isotopiche delle acque in laboratorio;
- un monitoraggio in continuo della sismicità dell'area e delle sequenze temporali dei terremoti per definire il ciclo sismico (dati da INGV).

4.2. Caratterizzazione Idrogeochimica Preliminare

Le sorgenti scelte sono sorgenti profonde il cui percorso sotterraneo è regionale, stabile e risente al minimo degli effetti stagionali e locali. In particolare, sono state selezionate le seguenti sei sorgenti ([Tab. 3](#)):

- la sorgente di Rocchetta a Volturno in quanto è la sorgente di recapito del sistema di circolazione nel Volturno ([Fig. 8](#));
- le sorgenti di Bojano e Grassano perché sono due sorgenti di recapito a Nord e a Sud dell'acquifero regionale del Matese ([Fig. 9](#));
- la sorgente di Telesse Terme poiché è una sorgente mineralizzata a solfati ([Fig. 10](#));

-e le sorgenti di Caposele e Cassano Irpino in quanto sono due sorgenti rappresentative dell'acquifero regionale dei Monti Picentini (Fig. 11).

Una volta identificate le sorgenti da monitorare, è stato eseguito un primo set di campionamenti al fine di analizzare le caratteristiche principali fisico-chimiche dell'acqua e l'interazione fluido-roccia, per verificare la fattibilità idrogeochimica del progetto.

4.3. Monitoraggio Idrogeochimico

La procedura utilizzata per il campionamento consiste nella misurazione in situ dei valori di pH, temperatura (°C), conducibilità elettrica ($\mu\text{S}/\text{cm}$) e potenziale redox Eh (mV) per mezzo di pH-metro e conducimetro portatili. Poi si effettua il prelievo di diversi campioni d'acqua per le analisi da svolgere in laboratorio e per la titolazione dei bicarbonati contenuti nell'acqua. Per ogni sorgente vengono prelevati 5 campioni d'acqua: 1 campione filtrato per l'analisi degli elementi maggiori tramite cromatografia ionica, 1 campione filtrato e acidificato per l'analisi degli elementi in tracce tramite spettrometria di massa, 1 campione tal quale per l'analisi degli isotopi della molecola d'acqua e 2 campioni per l'analisi del $\delta^{13}\text{C}$. I campioni per le analisi degli elementi maggiori e in tracce vengono filtrati con un filtro da 0,45 micron.

Le analisi degli elementi maggiori e in tracce vengono eseguite dal gruppo di lavoro nei laboratori di idrogeochimica del dipartimento di Scienze della Terra della Sapienza Università di Roma (Fig. 12-14), mentre i campioni per gli isotopi dell'acqua e del $\delta^{13}\text{C}$ vengono mandati ai laboratori di geochimica isotopica dell'Università di Parma. Per quanto riguarda la procedura di campionamento del $\delta^{13}\text{C}$, si utilizza una tabella di calcolo per i volumi di campione da iniettare in apposite fiale preparate con elio all'interno. Si deve inserire il contenuto di HCO_3 calcolato e leggere il contenuto in ml da prelevare. A questo punto, con una siringa e un filtro da 0.2 micron si inietta il campione nella fiala forando il setto di chiusura con l'ago, iniettando con precisione il volume di campione calcolato. Per ogni sorgente si considerano due campioni. Per questi

campioni è necessario mantenere la temperatura di stoccaggio tra 1 e 4 °C per evitare che si sviluppino processi batterici e che si verifichi la precipitazione del CaCO_3 .

Il campionamento delle sorgenti viene fatto con cadenza mensile, così da sviluppare un database per ogni sorgente, costruendo delle serie temporali. L'obiettivo è quello di cercare il valore di fondo tipico di ogni sorgente per poter mettere in relazione eventuali variazioni di questi valori con il tempo e con la sismicità.

4.4. Analisi di Laboratorio

Per le analisi degli elementi maggiori si utilizza la cromatografia ionica. Per cromatografia si intende un metodo fisico di separazione nel quale i componenti da separare sono distribuiti tra due fasi di cui una è fissa, o stazionaria, e l'altra è mobile e scorre in maniera continua sulla fase stazionaria. La cromatografia nasce come tecnica di separazione e solo successivamente inizia ad essere utilizzata anche come tecnica analitica. La tecnica si basa sul fatto che i diversi componenti di una miscela tendono ad avere affinità diverse tra le due fasi. Oggi la tecnica della cromatografia è diventata una delle tecniche maggiormente utilizzate nella ricerca scientifica idrogeochimica e non solo.

La cromatografia ionica è una tecnica utilizzata per la determinazione dei costituenti maggiori (cationi e anioni) in campioni acquosi. Il metodo si basa sullo scambio ionico tra una fase mobile costituita dall'eluente, che contiene il campione, e una fase stazionaria allo stato solido (resine a scambio ionico), che si trova all'interno della colonna. Questa tecnica si basa sulla separazione degli analiti, mediante colonna a scambio ionico, in base alla loro affinità per la fase stazionaria; cioè, i singoli analiti fuoriescono dalla colonna con differenti tempi di ritenzione. L'eluente, che contiene gli analiti, passa attraverso un dispositivo elettrochimico post-colonna chiamato soppressore che, generando ioni H^+ per elettrolisi, neutralizza l'eluente e abbassa la sua conducibilità di fondo, in modo tale da consentire di risolvere meglio il segnale

dell'analita, che viene rilevato mediante un conduttimetro in linea. Il riconoscimento degli analiti avviene tramite il confronto dei tempi di ritenzione dei picchi del campione con quelli di una soluzione di riferimento. Dall'integrazione delle aree dei singoli picchi cromatografici si ricavano le concentrazioni degli analiti, mediante confronto con curve di taratura ottenute iniettando, nelle stesse condizioni sperimentali adottate per i campioni, soluzioni a concentrazione note, comprese nel campo di indagine analitica. Per costruire le curve di calibrazione vengono analizzate tre soluzioni standard per gli anioni e due per i cationi con differenti concentrazioni.

Il cromatografo è in grado di effettuare analisi chimiche di cationi e anioni quali: litio, sodio, potassio, calcio, magnesio, ammonio, fluoruri, cloruri, nitrati, nitriti, solfati e fosfati in mg/L. Il tempo di analisi di ciascuna corsa analitica è di 20 minuti per i cationi e di 25 minuti per gli anioni. I cromatografi utilizzati per questo progetto sono il cromatografo Dionex ICS-1100 per i cationi ed il cromatografo Dionex ICS-5000 per gli anioni ([Fig. 12](#)).



Figura 12. Fotografia del cromatografo del laboratorio di idrogeochimica della Sapienza Università di Roma.

Una quantità di eluente deve circolare attraverso i componenti del cromatografo con lo scopo di trasportare il campione ed il flusso è mantenuto costante da una pompa (Fig. 13). Il campione viene iniettato all'interno dello strumento tramite una siringa in modo che la valvola Loop venga lavata dal campione precedente e, successivamente, il campione viene messo in serie con il carrier e viene portato alla colonna. Attraverso la colonna, gli ioni si muovono con velocità diverse in base alla loro affinità per la fase solida, uscendo quindi in tempi diversi. In

genere fuoriescono prima gli elementi più piccoli. Il rivelatore di conducibilità si divide in soppressore e detector. Il soppressore ha la funzione di eliminare la conducibilità di fondo dell'eluente in modo tale da migliorare il segnale da rivelare (Fig. 13). Il detector ha la funzione di produrre un segnale elettrico che poi viene amplificato e digitalizzato tramite un apposito convertitore analogico–digitale. Il segnale viene poi inviato ad un calcolatore che lo elabora realizzando un cromatogramma costituito da una serie di picchi che si innalzano da un fondo. Ogni picco corrisponde ad una deflessione del segnale legata ad una specie ionica presente nel campione. L'identificazione delle specie chimiche avviene misurando il tempo di comparsa del picco e la sua concentrazione è calcolata dall'elaboratore integrando l'area del picco stesso. La calibrazione dello strumento fatta prima dell'inizio delle analisi dei campioni permette proprio di associare ad ogni area un valore di concentrazione.

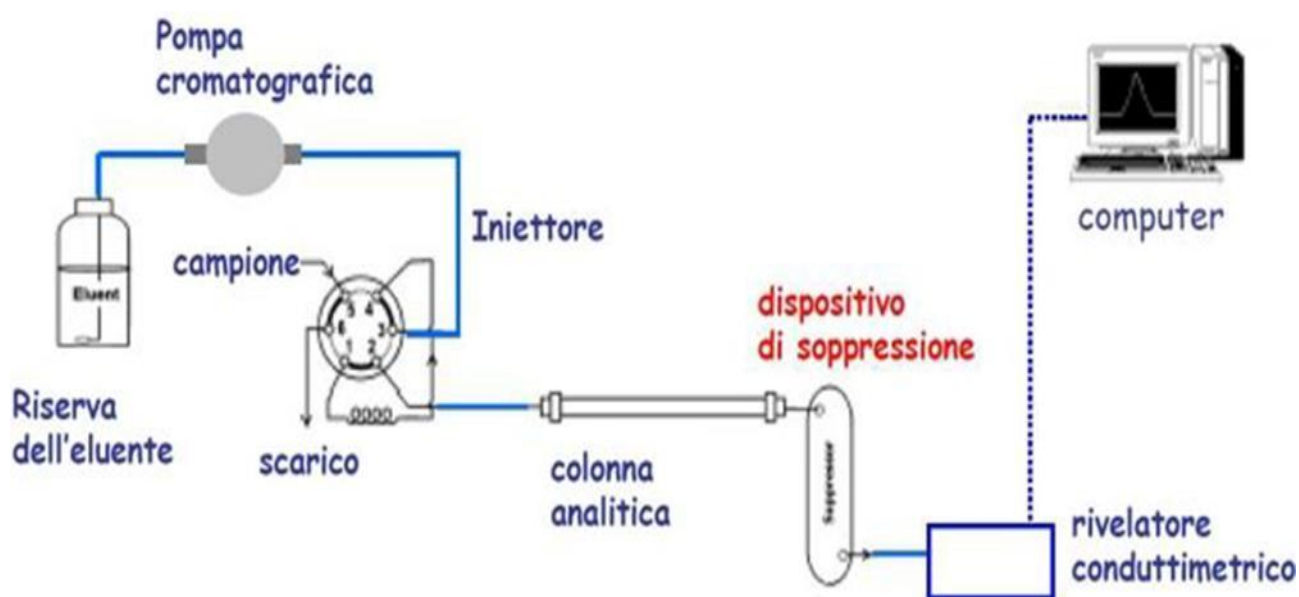


Figura 13. Schema di analisi chimica tramite cromatografia (da www.soschimica.it).

Per le analisi degli elementi in traccia presso il laboratorio di idrogeochimica della Sapienza Università di Roma si utilizza la spettroscopia di massa (Fig. 14). L'ICP-MS (inductively coupled plasma mass spectrometry) è una tecnica analitica basata sull'utilizzo della spettrometria di massa abbinata al plasma accoppiato induttivamente in grado di determinare elementi metallici, non-metallici ed isotopi in concentrazioni inferiori ad un ppb (parte per miliardo). Questa tecnica sfrutta l'utilizzo di una torcia al plasma ICP per indurre la ionizzazione e di uno spettrometro di massa per la separazione e la rivelazione degli ioni prodotti sulla base del rapporto massa/carica. La retta di calibrazione viene costruita usando 5 soluzioni standard a concentrazione crescente. L'analisi di ogni campione viene fatta 3 volte ai fini di avere un dato il più rappresentativo possibile. Le concentrazioni degli elementi in traccia vengono espresse in ppb.

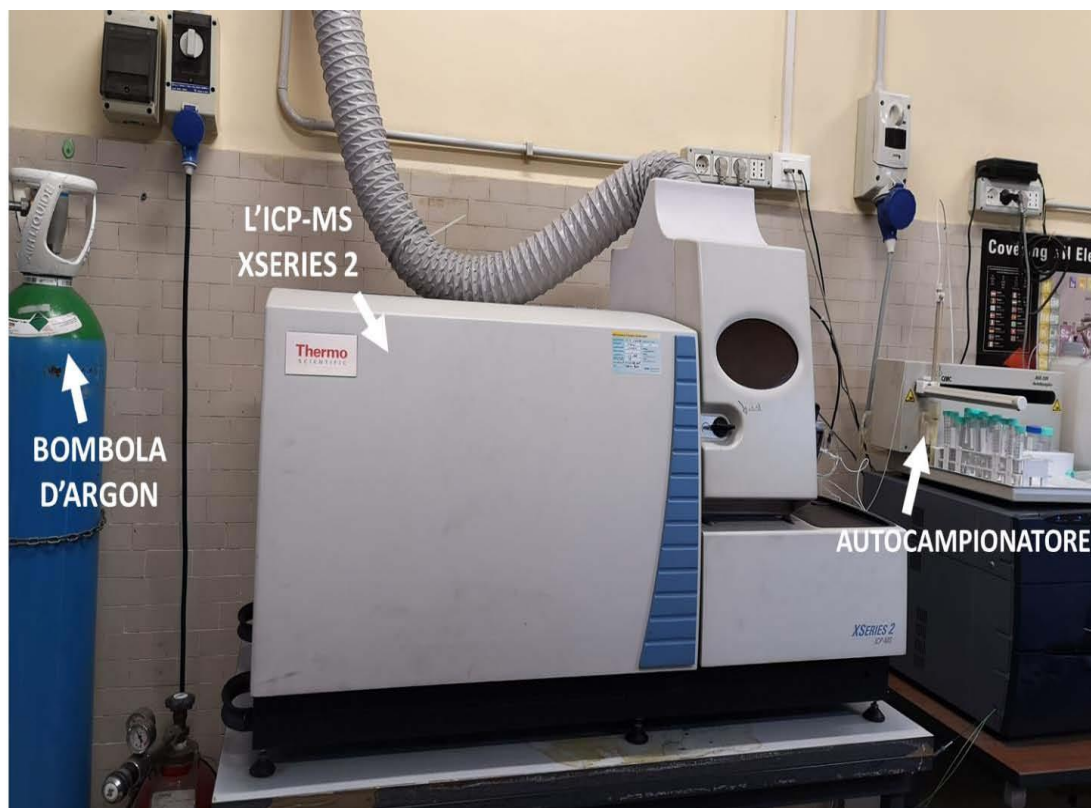


Figura 14. Fotografia dello spettrometro del laboratorio di idrogeochimica della Sapienza Università di Roma.

4.5. Installazione Sonde in Situ e Controllo da Remoto

Nel corso dei mesi, la rete di monitoraggio è stata rafforzata con l'installazione in situ di alcune sonde. In particolare, nel sito di Bojano è stata installata una sonda per la misura in continuo della concentrazione di Radon disciolto in soluzione (Alphaguard-Radon Monitor, [Fig. 15](#)), mentre nel sito di Grassano è stata installata sia la sonda radonometrica Alphaguard-Radon Monitor sia una sonda multiparametrica per la misura in continuo di parametri come pH, conducibilità elettrica e temperatura (Hydrolab HL4, [Fig. 16](#)) e sia una sonda per la misura della CO₂ disciolta in acqua (sonda Mini CO₂). Inoltre, la sonda radonometrica Alphaguard-Radon Monitor è stata installata anche presso la stazione Giardino nei pressi di Sulmona ([Barberio et al., 2018](#)) ed una sonda multiparametrica (OttEcolog 800) è stata installata nel pozzo Pf60.3 sempre nei pressi di Sulmona per la misura del livello piezometrico, della temperatura e della conducibilità elettrica.

Con la sonda Alphaguard, monitoriamo e registriamo in continuo, con una misura ogni 10 minuti, la concentrazione di Radon disciolto in acqua. Contemporaneamente al Radon, la sonda misura e registra anche la temperatura, l'umidità relativa e la pressione atmosferica. Combinando il monitoraggio del Radon con questi parametri ambientali associati è possibile trarre conclusioni valide sulla distribuzione temporale e spaziale del gas Radon.

Con la sonda Hydrolab HL4 monitoriamo e registriamo in continuo, con una misura ogni 15 minuti, le condizioni del bacino idrografico. Si tratta infatti di una sonda multiparametrica per mezzo della quale misuriamo in continuo, pH, conducibilità elettrica, e temperatura. La sonda OttEcolog 800 è simile alla sonda Hydrolab HL4 e si adatta alle condizioni di pozzo ed è in grado di misurare anche il livello piezometrico della falda in pozzo.



Figura 15. Fotografia della sonda Alphaguard-Radon presso la sorgente di Bojano.



Figura 16. Fotografia della sonda Hydrolab HL4 presso la sorgente di Grassano.

La sonda “Mini CO₂ analog model”, prodotta dalla “Pro-Oceanus”, è un sensore sommergibile compatto progettato per il monitoraggio in situ e per un uso continuo. Il sensore può essere utilizzato sia in acqua dolce che marina. Lo strumento Mini CO₂ può essere utilizzato per il monitoraggio a lungo termine in aree remote, per l’analisi di punti specifici e in applicazioni industriali. Il Mini CO₂ opera eseguendo lo strippaggio del gas disciolto in soluzione attraverso una membrana semipermeabile al gas per veicolarlo al rivelatore a infrarossi non dispersivo (NDIR). Il sensore NDIR viene calibrato in fabbrica usando gli standard tracciabili WMO (<http://www.esrl.noaa.gov/gmd/ccl/>). Il range di misurazione viene scelto prima di effettuare la

calibrazione per cui ogni strumento può essere calibrato per diversi intervalli di misura (accuratezza $\pm 2\%$ dell'intervallo massimo di misura).

Di recente è stato installato presso la sorgente di Bojano uno spettrometro di massa Hiden HPR-40 con ingresso a membrana (Continuous Flow-Membrane Inlet Mass Spectrometer, CF-MIMS). Si tratta di un sistema di analisi compatto per l'analisi quantitativa e in tempo reale dei gas disciolti. La cella d'ingresso utilizza una membrana permeabile che consente il passaggio dalla soluzione di piccole concentrazioni di specie gassose verso l'analizzatore. Una valvola di isolamento manuale consente il controllo del campionamento e una valvola di sicurezza a solenoide fornisce la protezione allo spettrometro di massa e del sistema di vuoto in caso di rottura della membrana. Il dispositivo offre la possibilità di analisi a livelli sub-ppm ed è adatto alle applicazioni di analisi dei gas soprattutto laddove il volume del campione è molto piccolo, per le applicazioni ambientali e quando è richiesta la possibilità di rilevare piccolissime concentrazioni di analiti. La semplicità di utilizzo e le diverse caratteristiche personalizzabili della membrana permeabile ai gas rendono questo strumento utilizzabile per una vasta gamma di applicazioni tra cui:

Analisi dei gas nel suolo;

Analisi del processo di fermentazione;

Analisi delle acque fluviali, lacustri e marine;

Studi sulla contaminazione delle acque sotterranee;

Controllo della produzione di metano;

Studi di attività microbiologica/enzimatica; Monitoraggio ambientale.

Lo strumento, opportunamente calibrato ed escluse le possibili interferenze spettrali, è in grado di determinare le concentrazioni di gran parte dei gas disciolti in soluzione fino a massa atomica 200 amu.

Dal 2019 le sonde per gas (ad es. AlphaGUARD, Mini CO2 e CF-MIMS) sono collegate a un sistema di acquisizione online sviluppato da Digimatic s.r.l. (<http://www.digimatic.it/Home.html>) che consente agli operatori di visualizzare e scaricare tutti i dati acquisiti in tempo reale. La piattaforma digitale consente inoltre agli utenti autorizzati di visualizzare la posizione georeferenziata dei siti, consultare i manuali degli strumenti collegati e verificarne il corretto funzionamento. Il trasferimento in remoto dei dati avviene tramite un collegamento delle sonde via GPRS, grazie all'utilizzo di una SIM telefonica, a un server stabilito presso il dipartimento di Scienze della Terra (Sapienza Università di Roma) al quale si può accedere tramite computer o dispositivi mobili in qualsiasi momento e da ogni luogo. Visti gli obiettivi della ricerca, è stato impostato un intervallo di campionamento di 5 minuti e una trasmissione dei dati in remoto ogni 8 ore. Nelle tre figure seguenti, mostriamo tutte le sonde installate in situ nei pressi delle sorgenti monitorate (Fig. 17) e le relative schermate del controllo da remoto (Figg. 18 e 19).

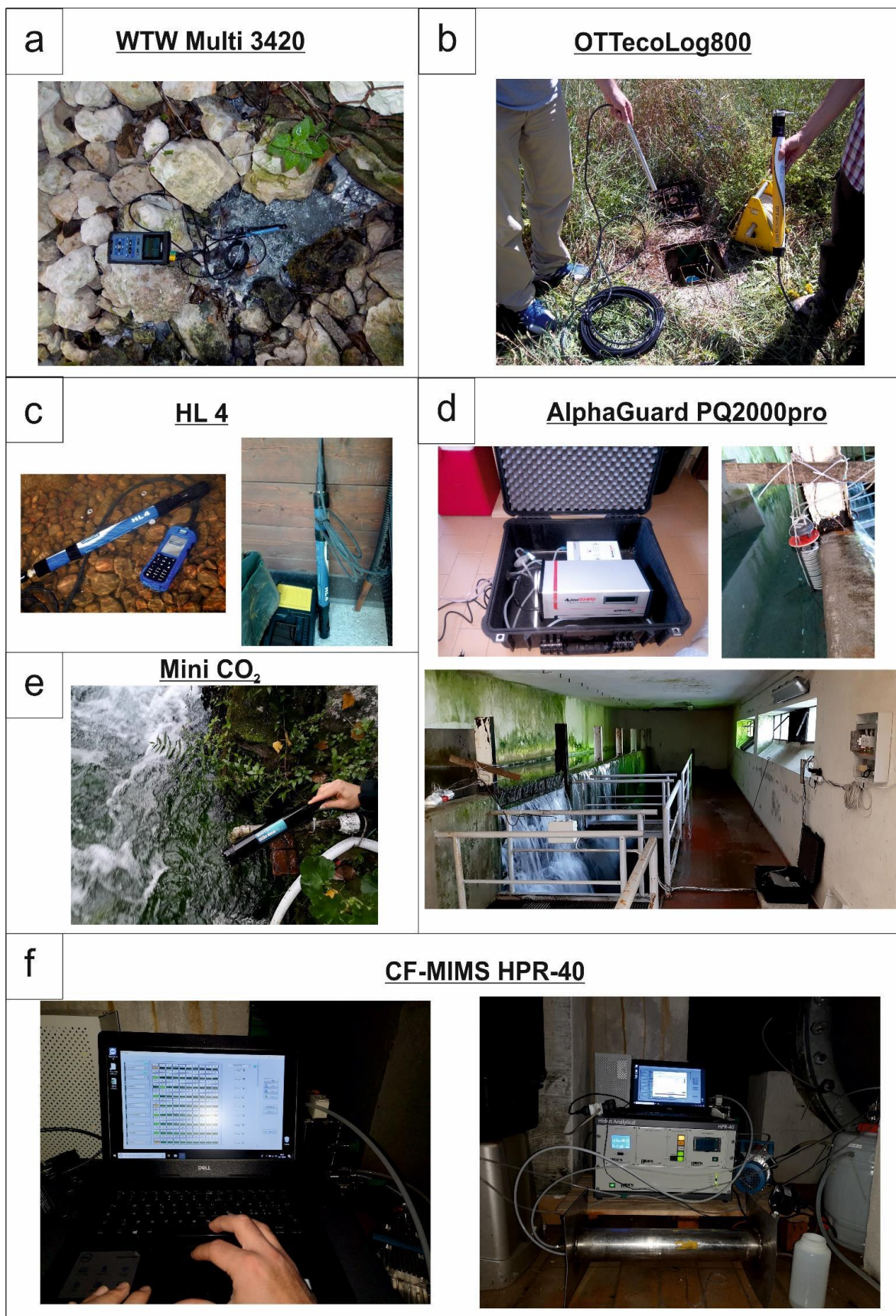


Figura 17. Fotografie delle sonde e strumenti installati nei pressi delle sorgenti Appenniniche per il loro monitoraggio idrogeochimico continuo.

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SISTEMI INFORMATIVI PER IL CONTROLLO IDROSFERA INGEGNERIA

ISI CON

IAG Ania FONDAZIONE

DIPARTIMENTO DI SCIENZE DELLA TERRA SAPIENZA UNIVERSITÀ DI ROMA

HYDROQUAKES Monitoring and fo earthquakes in ce hydrogeochemic

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Mostra filtro

Pos	Identificativo	Descrizione	Tipo	Matricola	Ultimo contatto	Servizi
1	giardino_alphaguard	Popoli (CH)	Acquisizione dati		20-12-2019 17:14:44	
2	giardino_minico2	Popoli (CH)	Acquisizione dati		20-12-2019 17:16:40	
3	grassano_alphaguard	San Salvatore Telesino (BN)	Acquisizione dati		20-12-2019 17:16:25	
4	grassano_minico2	San Salvatore Telesino (BN)	Acquisizione dati		20-12-2019 17:16:02	
5	rio_freddo_alphaguard	San Polo Matese (CB)	Acquisizione dati		20-12-2019 17:16:25	

5 righe totali

Pagina 1 di 1

Scrivi qui per eseguire la ricerca

Collegamenti

17:25 20/12/2019

Figura 18. Schermata dell'interfaccia digitale per il controllo e monitoraggio da remoto di alcune sonde e strumenti installati nei pressi delle sorgenti Appenniniche per il loro monitoraggio idrogeochimico continuo.



Figura 19. Schermata dell'interfaccia digitale che mostra il monitoraggio del radon nella sorgente di Rio Freddo, Appennino centrale.

4.6. Monitoraggio Sismico

Per il monitoraggio sismico abbiamo utilizzato i dati forniti dall'INGV tramite il sito <http://cnt.rm.ingv.it/search>. In particolare, abbiamo impostato come criterio di ricerca un cerchio dal diametro di 85 km centrato a Telese Terme, e scarichiamo con frequenza settimanale i dati di tutti gli eventi sismici registrati nell'area di studio (Fig. 20). In particolare, per lo studio preliminare dei siti da monitorare, abbiamo scaricato i dati a partire dal 01/01/1990. Per quanto

riguarda invece le serie temporali del progetto, abbiamo scaricato i dati a partire da qualche giorno prima del nostro campionamento iniziale (21/12/2017).

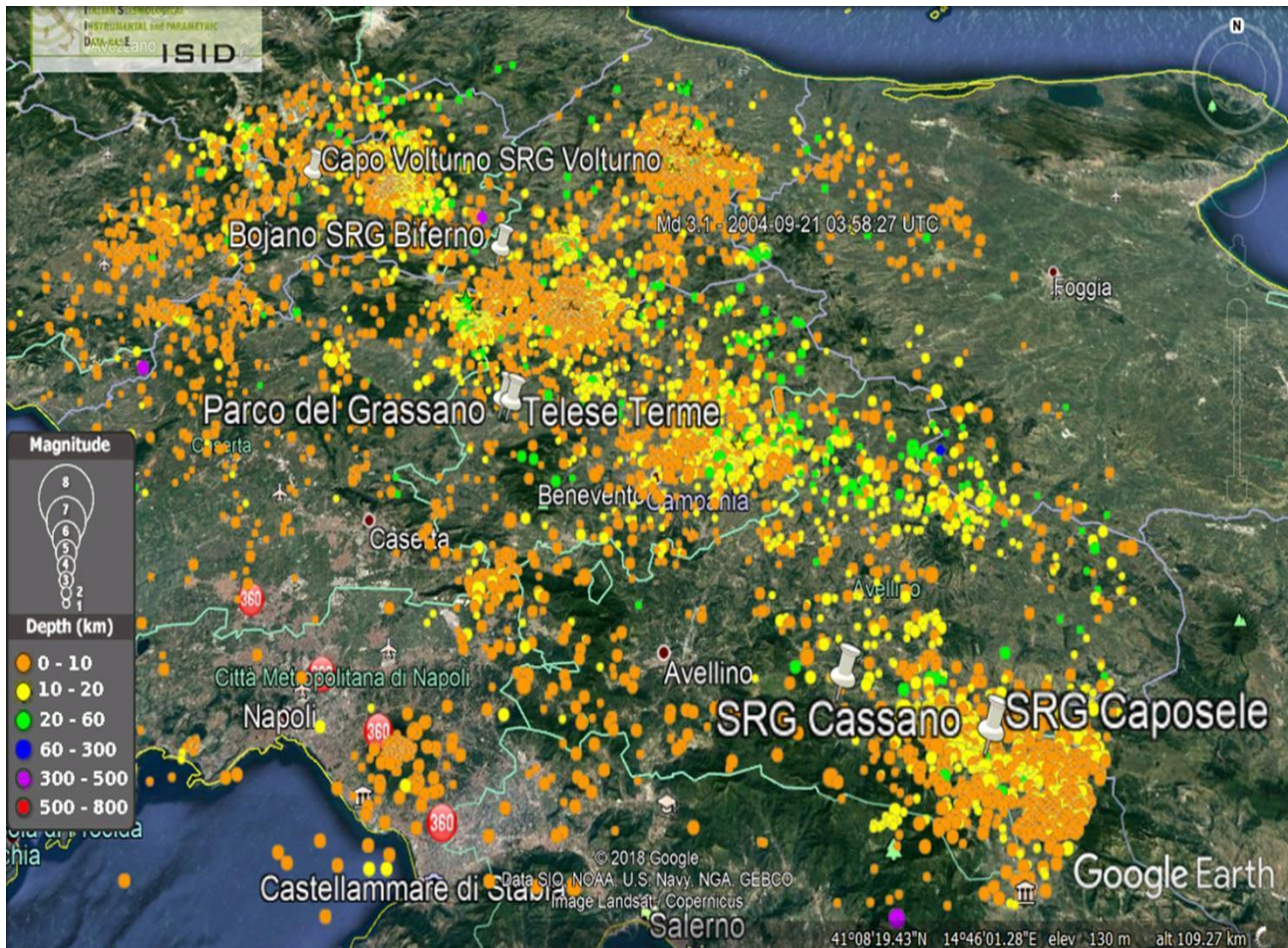


Figura 20. Appennino Campano-Molisano e relativi epicentri dei terremoti ($M_w > 2$) per il periodo 1990-2018 (da www.ingv.it).

5. Risultati: Appennino Centrale

5.1. Caratterizzazione Preliminare delle Sorgenti

Dai risultati ottenuti dalle analisi del primo set di campionamento si è costruito il diagramma di [Piper \(1944\)](#), che permette di visualizzare la composizione di un'acqua e di conseguenza consente di definirne la facies idrochimica sulla base delle concentrazioni degli ioni principali (in meq/L). In sintesi, dal diagramma ([Fig. 21](#)) si evince che le sei sorgenti sotto monitoraggio nell'area Matese-Beneventana sono sostanzialmente bicarbonato-calciche. Inoltre, le acque di Telese Terme sono più mineralizzate rispetto alle altre sorgenti.

Dal primo set di campionamento si è costruito anche il diagramma di [Schoeller \(1935\)](#) per le sei sorgenti monitorate. Tale diagramma permette di visualizzare i rapporti quantitativi tra ioni e offre la possibilità di un confronto immediato tra composizioni diverse, sia in relazione ai singoli ioni, sia in termini di concentrazioni totali ([Fig. 22](#)). In particolare, abbiamo riconosciuto tre sistemi: uno di acque più profonde, che è rappresentato dalle acque di Telese Terme (linea blu), un sistema di acque più superficiali, che è rappresentato dalle acque di Bojano (linea celeste), e le restanti sorgenti fanno parte di un sistema intermedio.

EXPLANATION

- Capo Volturno
- Grassano
- ▲ Telese Terme
- Bojano
- ★ Caposele
- ☆ Cassano Irpino

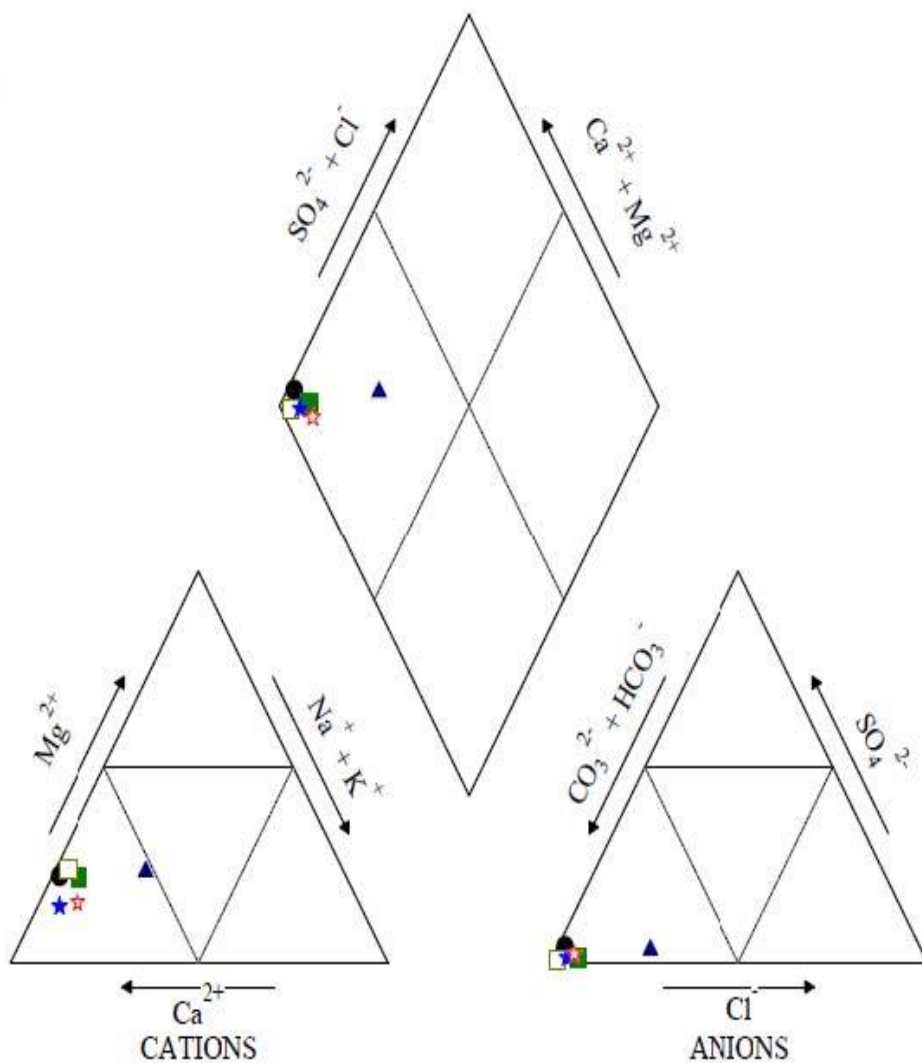


Figura 21. Diagramma di Piper per le acque delle sei sorgenti monitorate nell'Appennino Matese-Beneventano.

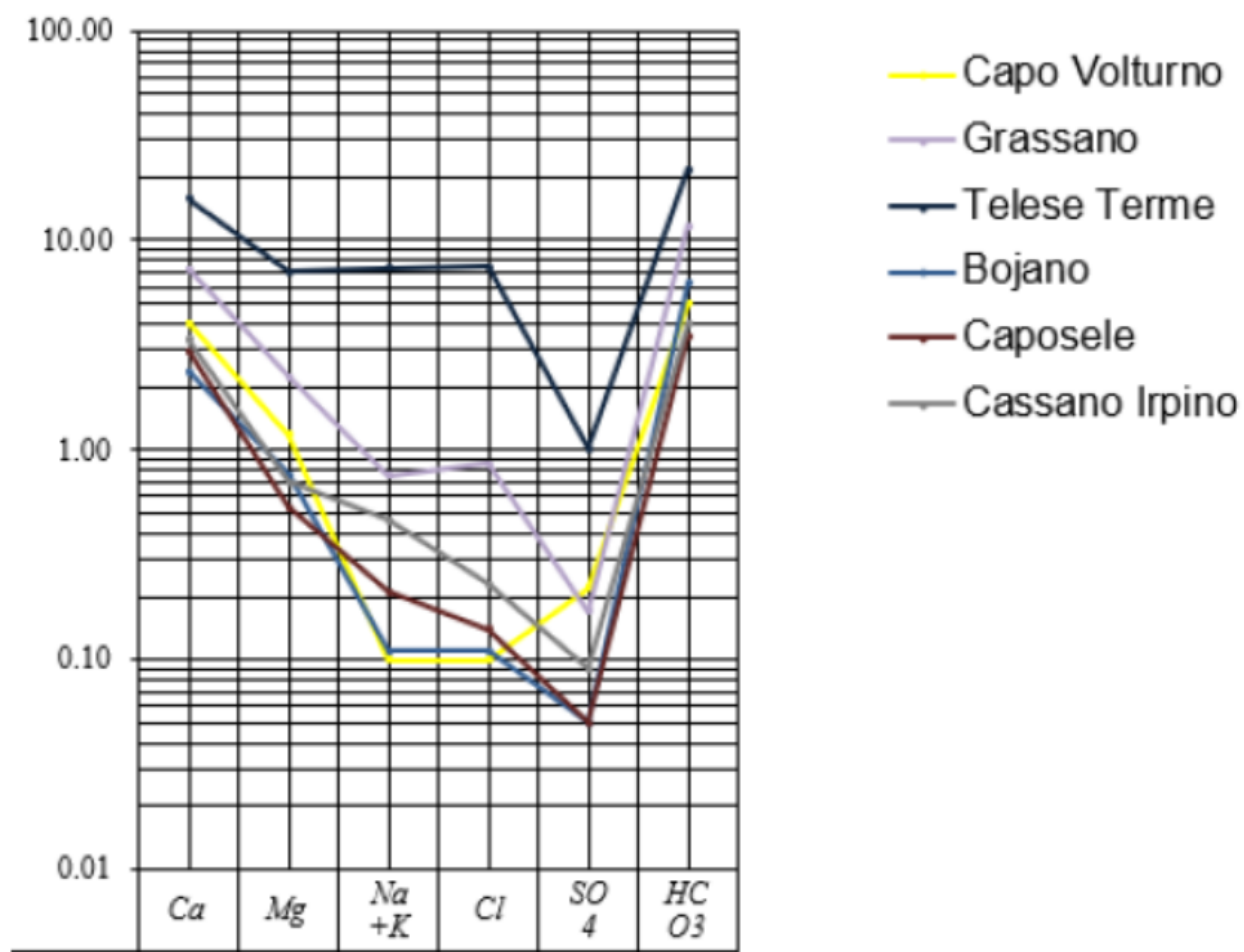


Figura 22. Diagramma di Schoeller per le acque delle sei sorgenti monitorate nell'Appennino Matese-Beneventano.

5.2. Serie Temporalì (2018-2020)

Dal punto di vista idrogeochimico, le acque di tutte le sorgenti hanno dimostrato di avere una sostanziale invariabilità nel tempo degli elementi analizzati durante gli anni di monitoraggio (dicembre 2017 – dicembre 2020; [Tabb. 4 e 5](#)). Le sorgenti dell'area Matese-Beneventana sono caratterizzate da temperature dell'acqua che vanno da 7,7 a 20,6 °C, pH compreso tra 6,15 e 8,68 e da conducibilità elettrica compresa tra 249 e 3170 $\mu\text{S}/\text{cm}$. I valori del $\delta\text{D}-\text{H}_2\text{O}$ e $\delta^{18}\text{O}-\text{H}_2\text{O}$ ottenuti vanno rispettivamente da -46,2 a -62,4 ‰ e da -7,75 a -9,5 ‰ VSMOW ([Tab. 6](#)). Le sorgenti analizzate nell'area di Sulmona sono caratterizzate da temperature dell'acqua che vanno da 9,8 a 14,2 °C, pH compreso tra 7 e 8,06 e da conducibilità elettrica compresa tra 296 e 851 $\mu\text{S}/\text{cm}$. I valori del $\delta\text{D}-\text{H}_2\text{O}$ e $\delta^{18}\text{O}-\text{H}_2\text{O}$ ottenuti vanno rispettivamente da -63,3 a -73,7 ‰ e da -10,06 a -11,13 ‰ VSMOW ([Tab. 6](#)).

Durante il corso di questi anni di monitoraggio non si sono verificati terremoti di magnitudo elevata nei pressi dei siti monitorati. Gli eventi sismici con magnitudo più elevata sono stati il terremoto di Collelongo (Mw 4.1; 1 Gennaio 2019) e il terremoto di Balsorano (Mw 4.4; 7 Novembre 2019). Nel mese di Novembre 2018, due mesi prima del terremoto di Collelongo, si sono registrati piccoli incrementi nelle concentrazioni di Li, B e Sr in tutte le sorgenti tranne Caposele e Cassano Irpino. Nella sorgente Le Fonti si è registrato un incremento solo nella concentrazione dello Sr ([Tab. 5](#)). Per questo motivo, si è scelto di svolgere le analisi degli isotopi del B e dello Sr per le acque delle sorgenti Grassano e Decontra. I valori del $\delta^{11}\text{B}$ ottenuti vanno da 4,82 a 5,42 ‰ per la sorgente Grassano e da 5,86 a 5,96 ‰ per la sorgente Decontra, mentre i valori del δSr ($^{87}\text{Sr}/^{86}\text{Sr}$) ottenuti vanno da 0,707748 a 0,707765 per la sorgente Grassano e da 0,707922 a 0,707940 per la sorgente Decontra.

L'analisi delle serie temporalì di tutte le sorgenti monitorate dimostra che le concentrazioni degli elementi, sia maggiori sia in tracce, non risentono (se non forse minimamente nel caso del terremoto di Collelongo dell' 1 Gennaio 2019) della sismicità di fondo

dell'area investigata, bensì presentano solo variazioni stagionali (Figg. 23, 24 e 25).

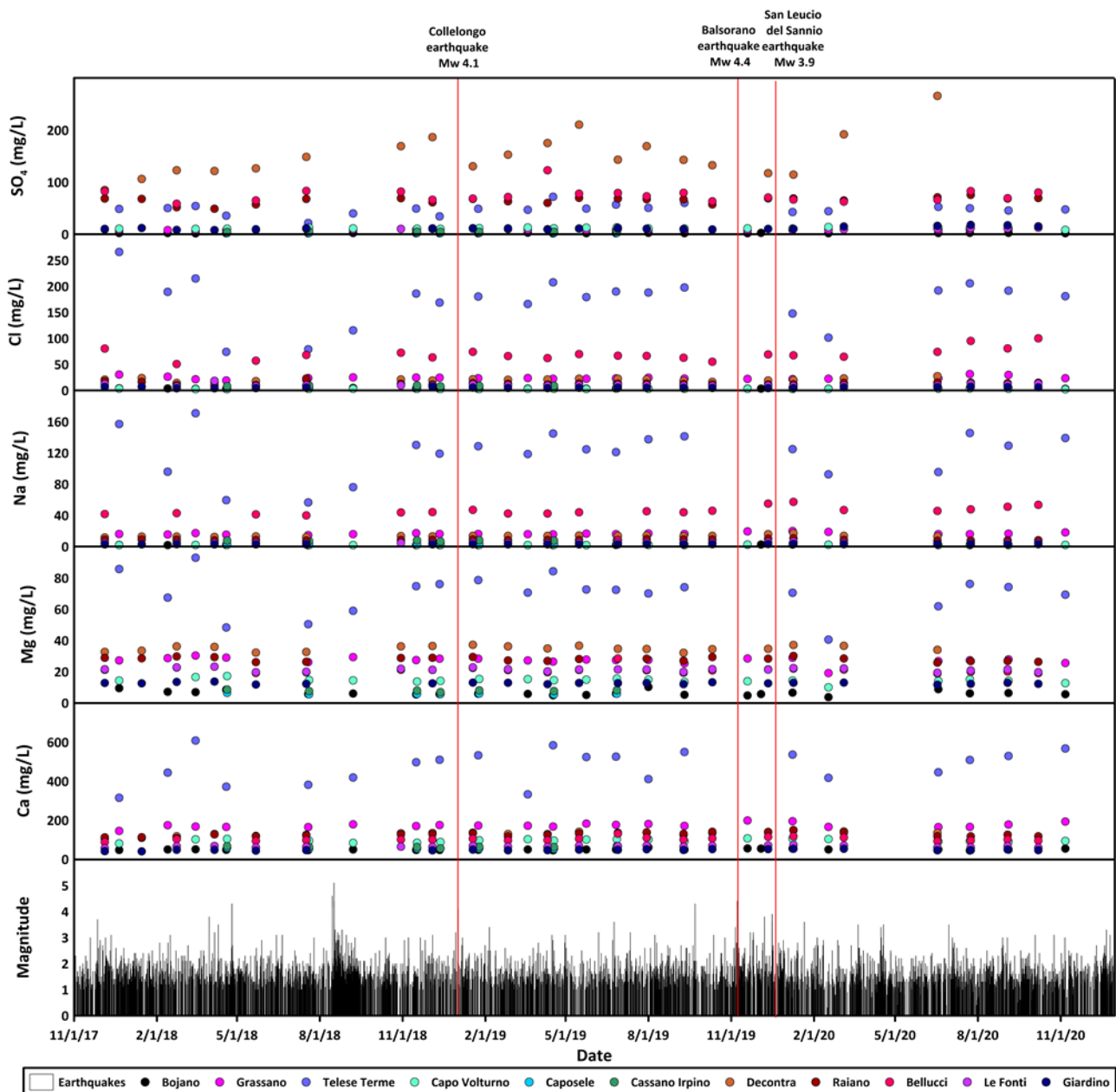


Figura 23. Grafico con le concentrazioni degli elementi maggiori delle sorgenti monitorate in relazione alla sismicità di fondo dell'area di studio.

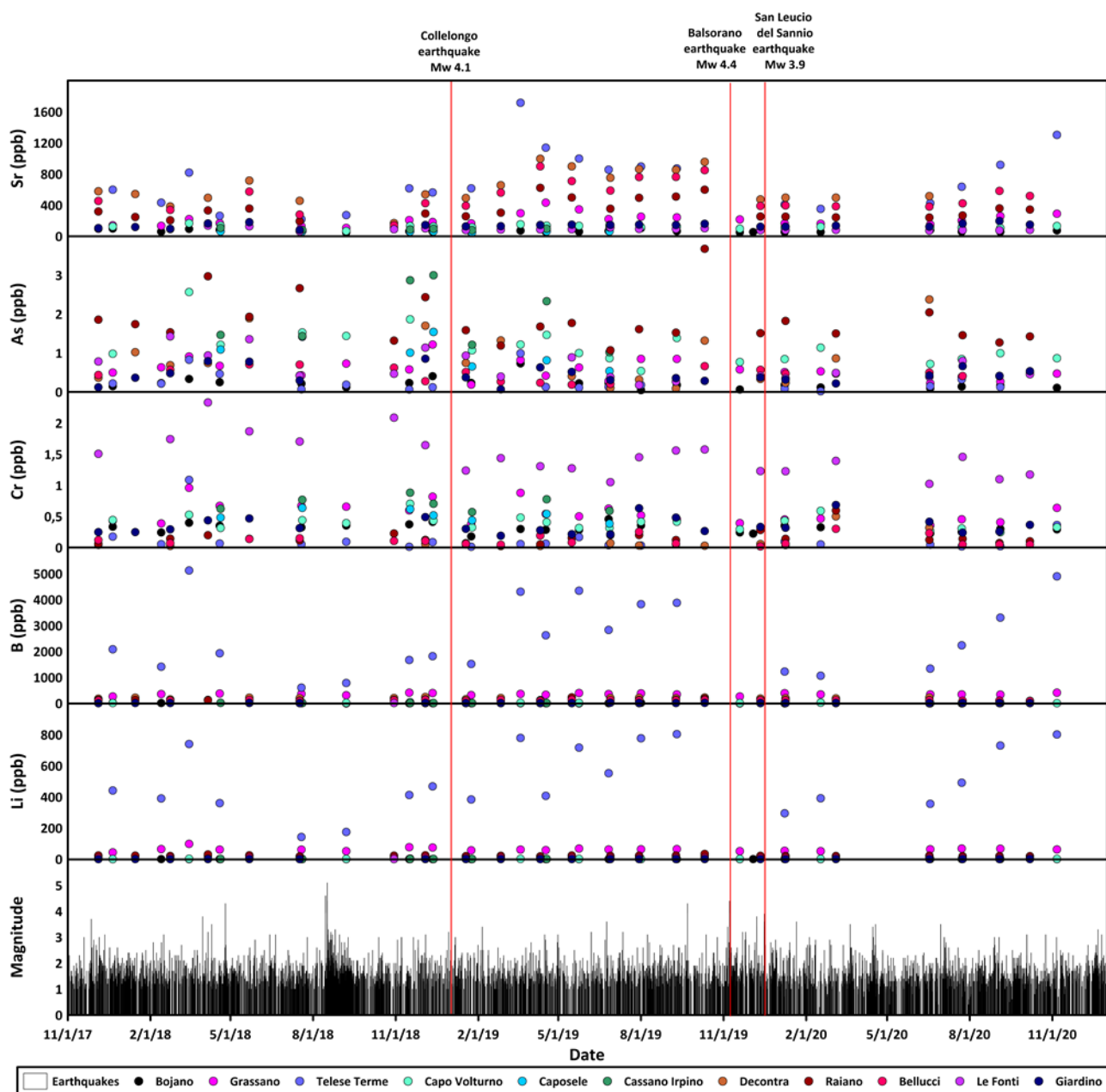


Figura 24. Grafico con le concentrazioni degli elementi in tracce delle sorgenti monitorate in relazione alla sismicit  di fondo dell'area di studio.

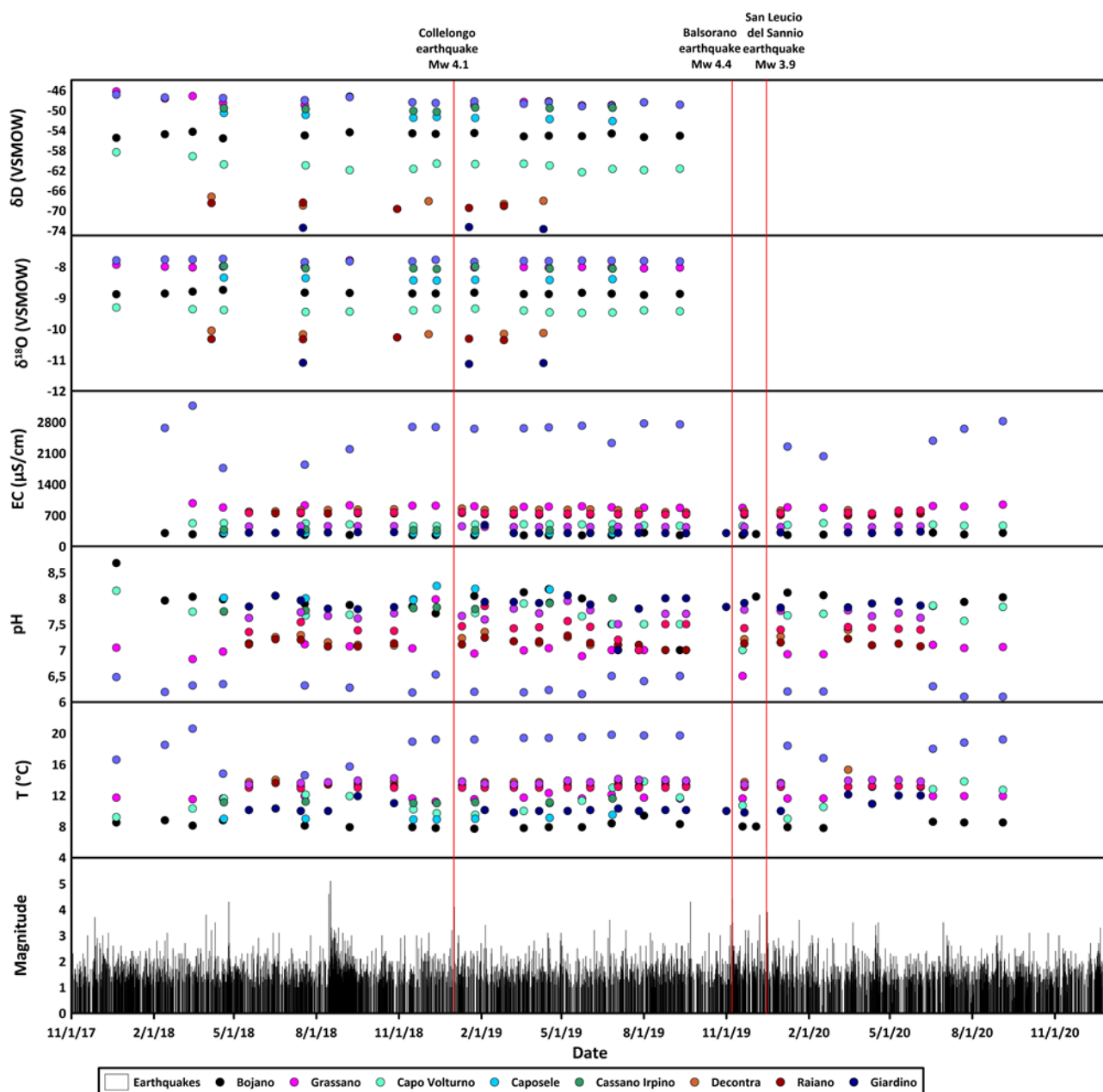


Figura 25. Grafico con i parametri chimici e gli isotopi della molecola d'acqua in relazione alla sismicit  di fondo dell'area di studio.

Nel mese di Novembre 2018, due mesi prima del terremoto di Collelongo (1 Gennaio 2019), abbiamo registrato un incremento nella concentrazione del Boro e una corrispondente diminuzione dell'isotopo $\delta^{11}B$. Il mese successivo, la concentrazione del Boro ha ricominciato a

diminuire tornando ai soliti valori di concentrazione dopo il terremoto di Collelongo, mentre il valore del $\delta^{11}\text{B}$ ha avuto un aumento dopo il terremoto. Questi risultati dimostrano che l'aumento della concentrazione del Boro è legato ad un abbassamento simultaneo dell'isotopo del Boro prima degli eventi sismici e questo può essere correlato al desorbimento dalle superfici dei minerali. Questo stesso andamento è stato registrato anche nel sito di Sulmona prima della sequenza sismica di Amatrice-Norcia 2016-2017, come riportato in [Boschetti et al. \(2019\)](#). Questo andamento è più evidente nel caso della sorgente di Grassano piuttosto che nella sorgente di Decontra in quanto nella prima si è registrato un aumento più netto della concentrazione del Boro ([Fig. 26](#)).

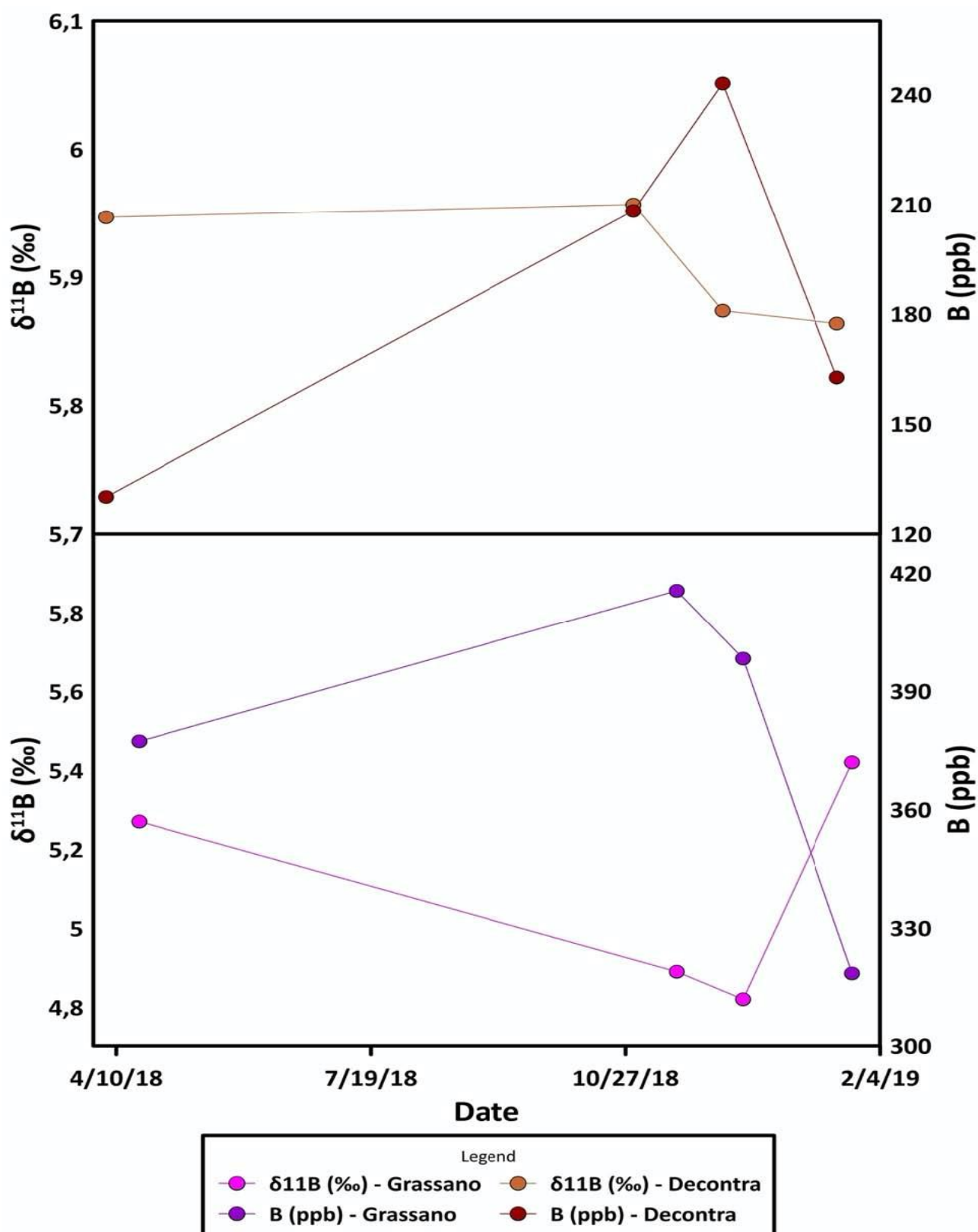


Figura 26. Grafico in cui sono stati messi in relazione i valori delle concentrazioni del Boro nelle sorgenti Grassano e Decontra con i rispettivi valori dell'isotopo $\delta^{11}\text{B}$ prima e dopo il terremoto di Collelongo dell' 1 gennaio 2019.

I risultati ottenuti dagli isotopi dello Stronzio mostrano delle differenze minime, al limite dell'errore di misura; questo indica che la firma isotopica dello Stronzio è sempre la stessa e che quindi il circuito non è cambiato ma che possono esserci stati degli scambi acqua-roccia differenti, che potrebbero essere più intensi quando aumenta la concentrazione dello stronzio e più rapidi quando diminuisce la medesima concentrazione (Fig. 27).

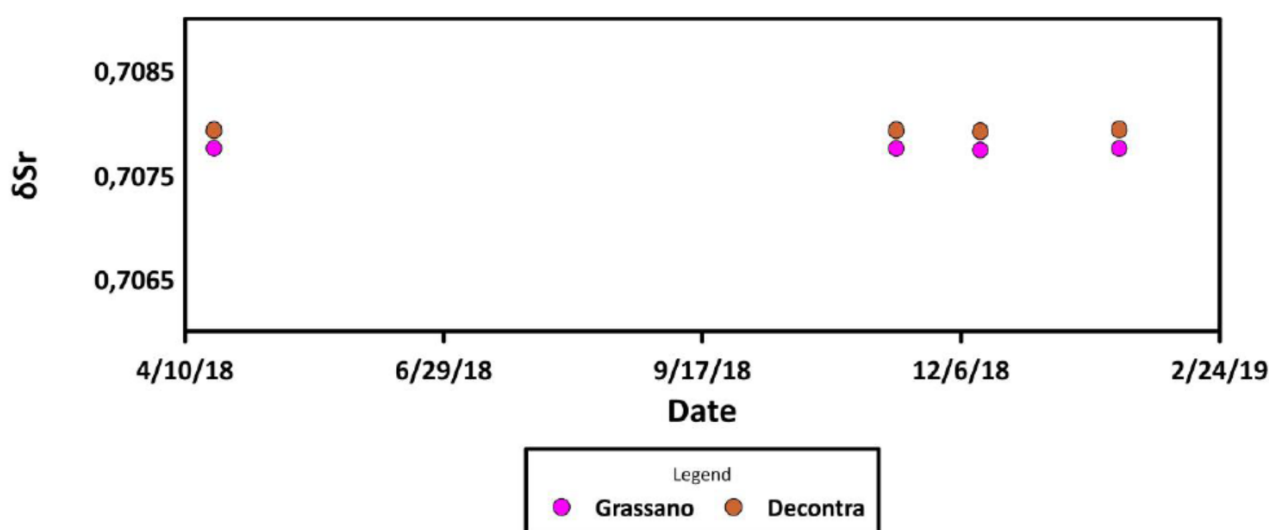


Figura 27. Grafico con i risultati delle analisi degli isotopi dello Stronzio nel tempo, sorgenti di Grassano e Decontra, prima e dopo il terremoto di Collelongo dell' 1 gennaio 2019.

Questi risultati ci permettono di capire che nel caso di acquiferi carbonatici, come quelli considerati in questo progetto, lo studio dell'isotopo del boro dà un riscontro migliore rispetto allo studio dell'isotopo dello stronzio.

In questi due anni di monitoraggio abbiamo quindi registrato qualche piccolo segnale che non è abbastanza definito in quanto all'interno delle tipiche variazioni stagionali delle sorgenti monitorate. Questo risultato ci permette quindi di affermare che non si riescono a registrare

precursori sismici di tipo idrogeochimico per terremoti di magnitudo inferiore a circa 5. Questo progetto, oltre allo studio di potenziali precursori sismici di tipo idrogeochimico, ha lo scopo di istituire una futura rete idrogeochimica italiana, e le piccole variazioni registrate nei due nodi di monitoraggio di questo progetto prima del terremoto di Collelongo ci indicano che stiamo andando nella direzione giusta, in quanto avere più stazioni di monitoraggio ci permette di registrare meglio le variazioni e di conseguenza di triangolarle meglio. Avere un database idrogeochimico di ogni sorgente permette di costruire delle serie temporali nelle quali si può individuare il valore di fondo tipico di ogni sorgente, il quale è fondamentale per definire eventuali variazioni e anomalie nel tempo. Quindi oltre ad avere una valenza nello studio dei precursori sismici di tipo idrogeochimico ha anche altre implicazioni sociali, come ad esempio per il controllo della qualità delle acque e degli inquinamenti delle falde.

Data	Nome	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	F ⁻	NO ₃ ⁻
19/11/2019	Bojano	55,3	4,7	2,5	0,3	164,8	3,4	1,9	0,1	1,7
04/12/2019	Bojano	54,6	5,6	2,7	0,7		3,3	2,5	0,1	3,2
08/01/2020	Bojano	54,5	6,6	2,7	1,8	170,0	4,5	10,2	0,1	1,6
17/02/2020	Bojano	50,14	3,68	2,37	0,21		3,16	1,85	0,11	1,69
18/06/2020	Bojano	50,39	8,80	1,95	0,54	204,42	3,29	2,38	0,23	1,85
23/07/2020	Bojano	45,01	6,08	2,06	0,69	170,86	4,29	2,55	0,10	2,48
04/09/2020	Bojano	49,73	6,38	1,97	0,46	173,91	4,02	2,60	0,18	2,17
06/11/2020	Bojano	54,37	5,52	2,27	0,50	176,96	3,19	2,07	0,13	2,08
19/11/2019	Grassano	198,30	28,40	19,46	2,28	576,64	22,09	7,35	0,08	2,89
08/01/2020	Grassano	195,17	28,86	19,99	2,75	650,00	21,83	8,33	0,20	2,39
17/02/2020	Grassano	165,77	19,12	18,81	1,34		22,28	8,19	0,15	2,51
18/06/2020	Grassano	164,72	26,79	16,06	2,99	604,10	23,10	7,58	0,11	2,39
23/07/2020	Grassano	165,65	27,33	16,03	2,64	610,20	31,46	9,11	0,10	3,34
04/09/2020	Grassano	177,82	27,94	16,57	2,62	604,10	29,72	10,16	0,27	3,40
06/11/2020	Grassano	193,19	25,52	18,27	1,98	625,46	23,39	7,86	0,23	2,73
08/01/2020	Telese Terme	536,87	70,57	124,77	14,64	1650,00	147,72	42,53	0,45	
17/02/2020	Telese Terme	416,99	40,57	92,71	10,86		101,55	44,37	0,50	
18/06/2020	Telese Terme	445,71	61,91	95,54	12,97	1510,25	192,05	52,74	0,46	
23/07/2020	Telese Terme	508,96	76,23	145,62	15,95	1723,82	205,92	49,87	0,24	
04/09/2020	Telese Terme	529,76	74,18	129,38	15,20	1751,27	191,61	45,76	0,76	1,24
06/11/2020	Telese Terme	567,37	69,31	139,16	15,45	1790,94	180,96	47,54	1,28	
19/11/2019	Capo Volturno	107,26	13,90	2,55	0,26	299,00	2,96	11,21	0,12	1,03
08/01/2020	Capo Volturno	106,25	14,30	3,22	0,73	350,00	2,61	10,98	0,15	1,05
17/02/2020	Capo Volturno	103,86	9,99	2,42	0,16		2,80	13,90	0,19	1,06
18/06/2020	Capo Volturno	91,09	14,06	2,08	0,57	317,30	3,67	12,97	0,18	1,33
23/07/2020	Capo Volturno	93,20	15,08	2,39	1,14	314,25	3,84	12,41	0,19	1,14
04/09/2020	Capo Volturno	89,44	14,13	2,02	0,49	299,00	3,18	11,57	0,19	1,33
06/11/2020	Capo Volturno	94,15	12,71	2,29	0,59	317,30	2,19	8,10	0,07	1,04
12/12/2019	Deontra	140,10	34,68	15,90	3,32	414,94	19,09	117,25	0,35	
09/01/2020	Deontra	148,87	37,14	16,98	4,57	450,00	19,70	114,58	0,39	
05/03/2020	Deontra	142,58	36,58	13,70	4,36	445,45	23,05	192,11	0,43	
17/06/2020	Deontra	135,14	33,99	13,02	4,91	390,53	27,52	265,90	0,37	
12/12/2019	Raiano	139,15	28,38	10,27	2,28	451,55	11,54	69,00	0,30	
09/01/2020	Raiano	149,42	30,10	10,70	2,51	460,00	11,69	68,86	0,23	
05/03/2020	Raiano	136,62	28,49	8,54	2,45	434,43	14,36	65,01	0,30	
17/06/2020	Raiano	117,71	25,78	7,48	2,03	424,09	15,02	70,91	0,29	
24/07/2020	Raiano	117,89	26,80	7,68	2,39	411,89	15,21	75,72	0,18	
03/09/2020	Raiano	125,45	26,92	7,96	2,44	408,83	13,67	68,71	0,31	0,35
07/10/2020	Raiano	117,63	26,33	8,18	1,84	433,00	14,87	69,71	0,19	0,49
12/12/2019	Bellucci	115,37	21,42	55,04	4,12	350,87	69,22	70,64	0,24	
09/01/2020	Bellucci	117,61	22,03	57,22	3,69	365,00	67,48	66,76	0,35	
05/03/2020	Bellucci	111,56	21,39	46,83	3,17	325,30	64,80	62,55	0,31	
17/06/2020	Bellucci	93,07	18,87	45,65	2,60	320,36	73,99	66,32	0,04	
24/07/2020	Bellucci	96,69	19,88	47,82	3,19	320,36	95,18	82,90	0,36	
03/09/2020	Bellucci	101,40	20,09	51,20	3,09	323,41	80,71	69,32	0,35	
07/10/2020	Bellucci	95,12	19,15	53,63	2,45	305,00	100,12	80,43	0,22	
12/12/2019	Le Fonti	70,56	21,39	5,73	1,05	268,49	9,22	10,25	0,14	13,35
09/01/2020	Le Fonti	73,12	22,33	6,45	1,65	280,00	8,48	10,17	0,08	12,12
05/03/2020	Le Fonti	71,01	22,06	4,86	1,14	272,34	9,50	9,29	0,15	12,51
17/06/2020	Le Fonti	59,95	19,33	3,88	0,84	256,28	9,52	10,99	0,16	12,98
24/07/2020	Le Fonti	60,89	20,78	4,52	1,23	283,74	12,84	12,23	0,11	17,32
03/09/2020	Le Fonti	66,79	21,43	4,70	1,11	268,49	11,24	11,20	0,16	15,33
07/10/2020	Le Fonti	59,18	19,71	4,67	0,80	255,00	12,94	12,64	0,11	17,61
12/12/2019	Giardino	51,71	12,59	3,34	0,49	198,32	4,49	10,31	0,11	1,56
09/01/2020	Giardino	53,82	12,87	3,50	0,67	200,00	4,52	10,20	0,09	1,58
05/03/2020	Giardino	53,61	13,04	3,03	0,65	189,16	5,60	14,78	0,17	1,30
17/06/2020	Giardino	46,15	11,71	2,88	0,63	189,16	5,94	16,24	0,09	1,55
24/07/2020	Giardino	46,85	12,25	3,11	0,89	195,26	7,09	17,81	0,07	1,68

Tabella 4. Valori degli ioni maggiori delle sorgenti monitorate nel progetto HydroQuakes.

Data	Nome	Li	B	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Rb	Sr	Mo	Cd	Cs	Ba	Pb	U
19/11/2019	Bojano	0,160	2,870		0,385	0,245				0,604			0,064	1,07	50,940	0,182			4,583		
04/12/2019	Bojano	0,194		1,196	0,509	0,223			0,019			15,42		1,198	55,400	0,183			5,160		0,032
08/01/2020	Bojano	0,241	1,111	25,19	0,425	0,352	0,333	8,016	0,039	0,339	1,304	9,723	0,177	1,529	54,45	0,159	0,057	0,01		1,502	0,178
17/02/2020	Bojano	0,267	27,3	25,19	0,411	0,327	0,373	18,24	0,031		1,056		0,118	1,264	54,25	0,109	0,081	0,008		1,851	0,168
18/06/2020	Bojano	0,661	0,371	1,34	0,3	0,231	0,006	0,266	0,038		0,174		0,092	1,136	84,16	0,126	0,007	0,011		0,091	0,179
23/07/2020	Bojano	0,278	1,489	15,14	0,497	0,253	0,149	5,609	0,055	0,991	2,845	14,98	0,137	1,495	58,22	0,155	0,016	0,009		0,271	0,157
04/09/2020	Bojano	0,276	4,627	14,69	0,494	0,3	0,233	18,63	0,032	0,699	2,33	6,374	0,168	1,139	56,47	0,194		0,007		0,25	0,133
06/11/2020	Bojano	0,298		16,14	0,4	0,293	0,07	7,132	0,039	1,006	1,748	10,58	0,106	0,961	74,84	0,19	0,012	0,007	6,42		0,106
19/11/2019	Grassano	51,630	268,000		1,448	0,393				0,614				4,665	217,600	0,333			1,009		0,404
08/01/2020	Grassano	54,020	393,400	17,130	1,462	0,453	0,625	7,044	0,148	0,161	0,534		0,510	5,780	165,200	0,285	0,038	1,627		0,954	0,951
17/02/2020	Grassano	51,480	347,800	22,160	1,714	0,466	0,230	5,623	0,133		0,372		0,530	5,637	162,100	0,247	0,052	1,556		1,077	0,948
18/06/2020	Grassano	63,920	346,900	1,429	1,230	0,357	0,066	1,373	0,156	0,040	0,991		0,221	5,392	151,700	0,129	0,011	1,494		0,134	0,689
23/07/2020	Grassano	68,020	348,400	10,090	1,821	0,454	0,261	13,430	0,165	0,814	1,046	1,742	0,388	5,845	200,400	0,339	0,012	1,614		0,165	0,710
04/09/2020	Grassano	67,450	340,500	7,486	2,173	0,409	0,199	12,970	0,116	0,581	0,578		0,265	5,707	259,200	0,292		1,593		0,085	0,661
06/11/2020	Grassano	62,190	414,900	19,270	1,630	0,637	0,129	13,850	0,108	0,725	0,378	0,805	0,471	4,409	290,000	0,364	0,015	1,122	17,440		0,508
08/01/2020	Telese Terme	295,300	1224,000	22,160	0,640	0,097	9,618	15,640	0,406		0,377		0,079	30,160	407,800	0,014	0,034	15,550		0,867	0,068
17/02/2020	Telese Terme	391,300	1065,000	10,070	0,590	0,052	8,694	7,689	0,338		0,281		0,020	23,640	352,400		0,049	11,610		1,219	0,086
18/06/2020	Telese Terme	355,800	1342,000	0,536	0,524	0,046	2,229	1,742	0,452		0,737		0,147	31,220	424,900	0,147		15,340			
23/07/2020	Telese Terme	491,400	2240,000	10,090	0,630	0,020	9,607	0,867	0,464	0,024	0,372		0,319	38,870	636,900	0,207	0,001	19,360			0,038
04/09/2020	Telese Terme	730,500	3306,000	10,540	4,025	0,022	7,705	1,121	0,389	0,093			0,126	37,810	919,500	0,075		19,330			0,058
06/11/2020	Telese Terme	801,700	4901,000	220,300	1,044	0,362	7,558	389,100	0,305	1,266	1,607	5,302		27,850	1303,000	0,025	0,004	13,030	51,710		0,038
19/11/2019	Capo Volturno	1,155	10,960		0,466	0,293				0,594			0,771		97,880	0,435			12,74		
08/01/2020	Capo Volturno	1,229	18,680	8,060	0,526	0,434	0,310	17,630	0,091	0,161	1,254	1,796	0,844	0,976	109,300	0,586	0,058	0,041		0,712	0,416
17/02/2020	Capo Volturno	1,616	24,310	17,130	0,786	0,592	0,455	9,703	0,214	0,267	1,849	2,285	1,139	1,190	123,900	0,958	0,214	0,164		1,641	0,583
18/06/2020	Capo Volturno	1,511	10,710	0,447	0,383	0,262	0,030	1,519	0,085		0,949		0,719	0,912	107,500	0,374	0,019	0,035		0,105	0,307
23/07/2020	Capo Volturno	1,486	11,150	11,100	0,513	0,308	0,362	4,482	0,076	0,324	1,446	2,601	0,844	1,102	111,500	0,451	0,016	0,028		0,156	0,340
04/09/2020	Capo Volturno	1,474	19,500	11,640	0,734	0,247	0,409	6,498	0,051	0,191	1,090		0,998	0,977	105,600	0,404		0,029		0,111	0,313
06/11/2020	Capo Volturno	1,309	5,061	18,350	0,467	0,327	0,171	6,808	0,050	0,662	2,212	4,321	0,869	1,092	133,500	0,481	0,024	0,020	16,840		0,238
12/12/2019	Deontra	15,59	187,5	11,08	0,119	0,059	7,232	4,774	0,081		0,023		0,334	5,533	474		0,015	0,29		0,281	
09/01/2020	Deontra	16,55	200,6	22,67	0,148	0,04	7,763	7,952	0,089		0,084		0,236	5,84	497,2		0,042	0,312		0,97	
05/03/2020	Deontra	16,03	195,7	125,9	0,443	0,503	8,31	60,91	0,102	0,773	0,263	5,843	0,864	5,916	496,6		0,163	0,307		3,65	0,016
17/06/2020	Deontra	19,79	229,1	7,504	0,617	0,32	3,13	7,616	0,254	0,606	0,6		2,379	6,622	516,6	0,852	0,08	0,323		0,465	0,108
12/12/2019	Raiano	21,27	128,7	6,045	0,64	0,282	1,913	16,22	0,202		0,528		1,512	4,421	255,4	1,188	0,098	1,538		0,33	0,626
09/01/2020	Raiano	20,78	123,3	19,14	0,512	0,141	1,809	27,68	0,121		0,402		1,826	4,337	253,1	0,626	0,034	1,425		0,805	0,514
05/03/2020	Raiano	20,03	121	120,9	0,718	0,597	2,427	89,95	0,138	0,722	0,803	4,967	1,502	4,195	243,6	0,837	0,125	1,372		2,352	0,555
17/06/2020	Raiano	22,98	127	0,804	0,454	0,124	0,602	4,399	0,178		0,254		2,047	4,266	240,5	0,821	0,012	1,418		0,255	0,474

24/07/2020	Raiano	19,27	100,3	15,14	0,427	0,141	1,887	31,57	0,15	0,435	1,074	1,46	3,682	267,8	0,706	0,045	1,197	31,68	0,237	0,423
03/09/2020	Raiano	20,16	103	7,763	0,812	0,075	1,458	19,63	0,099	0,186		1,27	3,42	359,3	0,638		1,146	31,37	0,044	0,337
07/10/2020	Raiano	19,15	99,54	10,21	0,476	0,102	1,51	24,56	0,2	0,76	0,843	1,425	3,758	342,5	0,693		1,259	33,55	1,366	0,452
12/12/2019	Bellucci	9,558	118,3	10,07	0,165	0,02	3,551	5,59	0,076			0,569	4,913	389,4	0,56	0,006	0,303	0,162	0,716	
09/01/2020	Bellucci	9,614	121,6	21,16	0,169	0,062	3,711	10,12	0,109			30,56	4,987	395,8	0,583	0,046	0,307	0,715	0,75	
05/03/2020	Bellucci	9,153	117,5	103,8	0,343	0,302	3,906	39,44	0,087		0,129	1,6	4,947	384,9	0,528	0,074	0,306	1,75	0,773	
17/06/2020	Bellucci	10,47	122,4	1,429	0,159	0,233	0,879	2,062	0,106		0,201	0,498	5,075	380,8	1,048	0,009	0,337	0,131	0,685	
24/07/2020	Bellucci	8,888	102,5	11,1	0,155	0,049	2,955	8,732	0,076	0,349	1,301	0,411	4,427	422,5	0,978	0,007	0,289	63,46	0,155	0,595
03/09/2020	Bellucci	8,872	101,3	12,48	0,434	0,048	2,585	6,323	0,057	0,151		0,405	4,129	583,4	0,92		0,275	61,98	0,101	0,549
07/10/2020	Bellucci	8,102	86,93	33,76	0,19	0,048	2,881	10,56	0,147	0,883	1,335	12,62	4,403	519,6	0,544	0,298	0,275	61,98	0,101	0,549
12/12/2019	Le Fonti	0,461	3,147	10,07	1,339	1,231	0,15	3,051	0,028		0,585	0,412	2,838	77,01	0,414	0,017	0,07	0,506	1,356	
09/01/2020	Le Fonti	0,476	4,333	8,06	1,526	1,226	0,138	3,663	0,036		0,369	0,353	2,935	80,08	0,476	0,034	0,071	0,521	1,409	
05/03/2020	Le Fonti	0,554	6,011	94,7	1,737	1,395	0,689	40,01	0,08	0,232	0,902	4,781	3,006	81,62	0,531	0,122	0,077	2,939	1,428	
17/06/2020	Le Fonti	0,503	1,324	1,697	1,265	1,024	0,035	0,504	0,041		0,271	0,387	2,642	71,61	0,375	0,007	0,064	0,204	1,021	
24/07/2020	Le Fonti	0,676	6,76	14,13	1,597	1,458	0,161	3,643	0,115	0,49	0,932	2,816	3,177	79,36	0,865	0,071	0,138	16,81	0,17	1,121
03/09/2020	Le Fonti	0,605	5,983	6,377	1,664	1,098	0,072	1,4	0,03	0,292	0,765	0,412	2,903	77,08	0,485		0,071	16,32	0,052	0,869
07/10/2020	Le Fonti	0,572	3,557	8,637	1,387	1,174	0,127	6,654	0,102	0,146	0,776	2,801	2,962	80,46	0,525	0,074	0,074	16,99	0,7	1,157
12/12/2019	Giardino	0,919	11,770	9,067	0,740	0,334	0,313	7,387	0,025	0,683	0,820	0,373	0,995	122,600	0,592	0,024		0,881	0,544	
09/01/2020	Giardino	0,969	15,280	19,140	0,626	0,320	0,246	6,535	0,028		0,195	0,314	1,006	124,100	144,500	0,030		0,884	0,549	
05/03/2020	Giardino	1,453	19,450	130,000	0,987	0,686	1,160	66,270	0,047	1,200	1,413	0,216	1,279	136,900	0,664		0,043	4,421	0,574	
17/06/2020	Giardino	1,572	13,120	1,787	0,758	0,417	0,102	1,041	0,107	1,245	1,524	0,424	1,217	123,500	293,400		0,101	0,977	0,460	
24/07/2020	Giardino	1,523	22,670	10,090	1,196	0,242	0,694	7,859	0,055	0,612	3,046	55,730	0,662	1,331	164,200	533,800	0,047	8,117	0,675	0,398
03/09/2020	Giardino	1,429	17,860	14,690	0,709	0,258	0,304	13,280	0,025	0,538	5,129	28,560	0,412	1,154	196,000	0,498	0,035	6,482	1,074	0,383
07/10/2020	Giardino	1,372	13,210	18,060	0,620	0,367	0,373	20,600	0,092	1,187	2,041	14,630	0,534	1,181	149,500	1,078	0,044	6,688	1,186	0,458

Tabella 5. Valori degli ioni minori delle sorgenti monitorate nel progetto HydroQuakes

Data	Nome	T°	pH	EC
19/11/2019	Bojano	8	7,00	256
04/12/2019	Bojano	8	8,04	278
08/01/2020	Bojano	7,9	8,11	259
17/02/2020	Bojano	7,8	8,06	266
18/06/2020	Bojano	8,6	7,85	307
23/07/2020	Bojano	8,5	7,93	270
04/09/2020	Bojano	8,5	8,02	304
06/11/2020	Bojano	8,3	8,01	276
19/11/2019	Grassano	11,6	6,50	869
08/01/2020	Grassano	11,6	6,92	879
17/02/2020	Grassano	11,6	6,92	869
18/06/2020	Grassano	11,9	7,10	912
23/07/2020	Grassano	11,9	7,04	900
04/09/2020	Grassano	11,9	7,06	940
06/11/2020	Grassano	11,7	7,17	939
08/01/2020	Telese Terme	18,40	6,20	2250
17/02/2020	Telese Terme	16,80	6,20	2030
18/06/2020	Telese Terme	18,00	6,30	2380
23/07/2020	Telese Terme	18,80	6,10	2650
04/09/2020	Telese Terme	19,20	6,10	2820
06/11/2020	Telese Terme	19,40	6,05	2740
19/11/2019	Capo Volturno	10,7	7,00	459
08/01/2020	Capo Volturno	9,0	7,67	481
17/02/2020	Capo Volturno	10,5	7,70	524
18/06/2020	Capo Volturno	12,8	7,86	491
23/07/2020	Capo Volturno	13,8	7,57	469
04/09/2020	Capo Volturno	12,7	7,84	469
06/11/2020	Capo Volturno	10,7	7,83	469
12/12/2019	Decontra			
09/01/2020	Decontra	13,7	7,21	787
05/03/2020	Decontra	13,60	7,27	805,00
17/06/2020	Decontra	15,30	7,39	817,00
12/12/2019	Raiano			
09/01/2020	Raiano	13,1	7,13	714
05/03/2020	Raiano	13,1	7,147	708
17/06/2020	Raiano	13,1	7,221	701
24/07/2020	Raiano	13,1	7,094	702
03/09/2020	Raiano	13,2	7,123	736
07/10/2020	Raiano	13,1	7,076	738
12/12/2019	Bellucci			
09/01/2020	Bellucci	13,1	7,42	742
05/03/2020	Bellucci	13,1	7,394	746
17/06/2020	Bellucci	13,1	7,448	754
24/07/2020	Bellucci	13,2	7,432	746
03/09/2020	Bellucci	13,2	7,411	805
07/10/2020	Bellucci	13,2	7,394	808
12/12/2019	Le Fonti			

09/01/2020	Le Fonti	13,4	7,78	436
05/03/2020	Le Fonti	13,5	7,761	436
17/06/2020	Le Fonti	13,9	7,767	436
24/07/2020	Le Fonti	14	7,659	434
03/09/2020	Le Fonti	14	7,713	456
07/10/2020	Le Fonti	13,8	7,623	452
12/12/2019	Giardino	10,0	7,84	299
09/01/2020	Giardino	9,8	7,91	297
05/03/2020	Giardino	10	7,822	312
17/06/2020	Giardino	12,1	7,827	312
24/07/2020	Giardino	10,9	7,903	299
03/09/2020	Giardino	12	7,943	314

Tabella 6. Parametri chimico fisici delle sorgenti monitorate

6. Risultati: Precursori Fossili in Appennino Centrale

6.1. Razionale e Stato dell'Arte

I fluidi svolgono un ruolo fondamentale in molte fasi del ciclo sismico e possono essere coinvolti attivamente o passivamente nella dinamica dei terremoti ([Sibson et al., 1975](#); [Chiodini et al., 2020](#)). Comprendere l'interazione fluido-roccia durante il ciclo sismico è, quindi, di fondamentale importanza per comprendere la sorgente sismica e i relativi meccanismi. Poiché le sorgenti sismiche attive sono comunemente inaccessibili a profondità ipocentrali, lo studio delle sorgenti esumate (fossili) può essere utile per comprendere quelle caratteristiche tessiturali, mineralogiche e geochimiche che sono state testimoni della circolazione del fluido a profondità ipocentrali o minori lungo rotture cosismiche ([Smeraglia et al., 2018](#); [Ohl et al., 2020](#)).

Studi su istanze fossili di faglia assistita da fluidi contribuiscono ad affrontare la questione fondamentale se i fluidi possano essere considerati potenziali precursori di terremoti ([Skelton et al., 2014](#)). Vi è infatti evidenza della variazione delle velocità delle onde sismiche (rapporto V_p/V_s) dovuta a fluidi che drenano verso le rocce pre-sismicamente dilatate ([Scholz et al., 1973](#)). Per una serie di recenti terremoti estensivi con $M_w > 5,5$ in Appennino (Italia), sono stati documentati grandi volumi di fluidi pressurizzati in entrata alla base della crosta sismogenica e relative anomalie V_p/V_s prima delle scosse principali ([Chiarabba et al., 2020](#); vedere anche [De Luca et al., 2018](#)), inducendo successivamente un drammatico scarico di acque sotterranee post-sismiche ([Petitta et al., 2018](#)). Tale dilatanza crostale profonda pre-sismica e i relativi fluidi erano anche all'origine di anomalie geochimiche pre-sismiche (da 4-5 mesi prima della scossa principale) nelle acque sorgive prima del terremoto di Amatrice del 2016 $M_w 6.0$ ([Barberio et al., 2017](#); [Boschetti et al., 2019](#)) e probabilmente all'origine di picchi nel flusso profondo di CO_2 osservati in periodi di alta sismicità e successivi decadimenti in periodi post-sismici negli ultimi dieci anni in Appennino ([Barbieri et al., 2020](#); [Chiodini et al., 2020](#)).

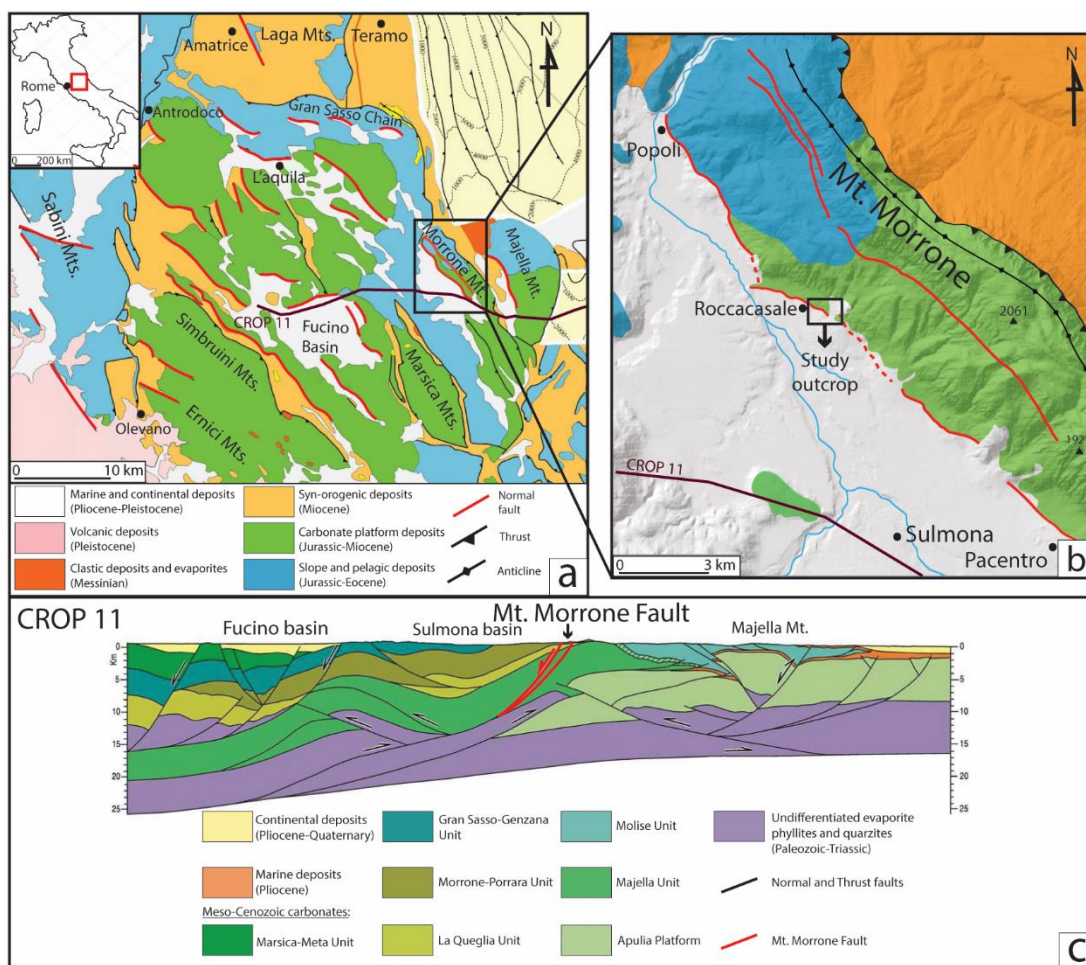


Figura 28. (a) Mappa geologica e strutturale semplificata dell'Appennino centrale (modificata da Cosentino et al., 2010) e traccia del profilo a riflessione sismica profonda CROP 11. (b) Mappa strutturale semplificata della zona della Faglia del Monte Morrone (Lat. $42^{\circ}07'14.63''N$, Long. $13^{\circ}53'35.49''E$) (c) Interpretazione del profilo a riflessione sismica profonda CROP 11 (modificato da [Patacca et al., 2008](#)). Due segmenti principali del sistema di faglia normale del Monte Morrone sono in rosso. Questi segmenti sono esposti lungo il Monte Morrone e tagliano la crosta fino a circa 12 km.

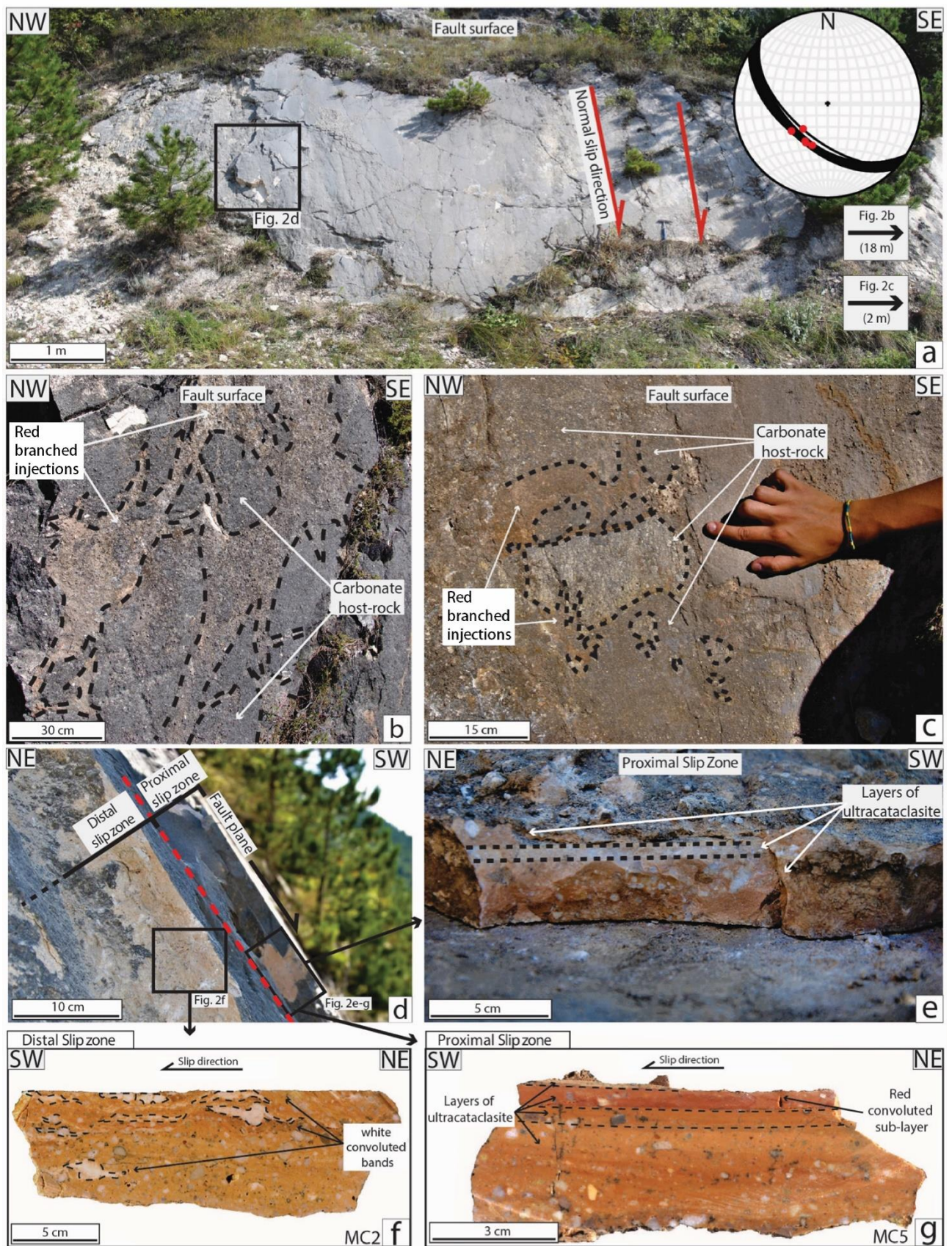


Figura 29. (a) Affioramento della Faglia del Monte. (b) Le iniezioni rosse permeano ampiamente la superficie di scorrimento principale della faglia vista dall'alto. (c) Vista della

superficie di scivolamento principale che mostra le iniezioni rosse. (d) Vista in sezione trasversale del nucleo di faglia che giace al di sotto della superficie di scorrimento principale della Faglia del Monte Morrone. Il nucleo della faglia comprende una zona di scorrimento prossimale e una distale. Prossimale e distale si riferiscono alla distanza dalla superficie di scivolamento principale. (e) Zona di scorrimento prossimale costituita da sottili strati di ultracataclasite separati da superfici di scorrimento. (f) Campione della zona di scorrimento distale costituito da una cataclasite parzialmente sovrainpressa da bande bianche allungate e deformate in modo coerente con il senso di scorrimento. (g) Campione della zona di scorrimento prossimale che mostra alcuni strati di ultracataclasite. Notare uno strato con strutture fossili fluide rosse all'interno dell'ultracataclasite.

Qui presentiamo i risultati di uno studio di una faglia normale sismicamente attiva ospitata in rocce carbonatiche esumate (Faglia del Monte Morrone; [Figg. 28 e 29](#)) nell'Appennino centrale, Italia. Abbiamo adottato un approccio multidisciplinare per caratterizzare le strutture alla meso e nanoscala osservate all'interno della zona di scivolamento principale (7-8 cm di spessore) della Faglia del Monte Morrone, risultante in dati unici sui processi da macro a nanoscala di fagliazione normale assistita da fluido su finestre temporali co- o quasi sismiche. Poiché la Faglia del Monte Morrone si trova accanto alle sorgenti che hanno registrato le suddette anomalie idrogeochimiche pre-sismiche ([Barberio et al., 2017](#); [Chiodini et al., 2020](#)), i nostri risultati contribuiscono a far luce su potenziali precursori di terremoti come fatto precedentemente in Islanda ([Skelton et al., 2014](#); [Andrén et al., 2016](#)).

6.2. Inquadramento Geologico, Metodi e Risultati

L'Appennino centrale ([Fig. 28a](#)) è una catena montuosa NW-SE, che si è sviluppata a partire dal tardo Oligocene a seguito della subduzione verso ovest della micropiastra di Adria al di sotto della placca eurasiatica. La cintura di montagne è costituita principalmente da strati

imbricati che si estendono verso nord-est dominati da successioni di carbonato meso-cenozoico che prevalgono su sedimenti ricchi di argilla clastica sintettonica (flysch) del Miocene-Pliocene depositati in bacini di avampaese o piggy-back (Patacca et al., 2008; Cosentino et al., 2010). La fascia appenninica ha subito un'estensione migratoria post-orogena verso est che ha avuto inizio nel settore interno (ovest) dell'Appennino dal Messiniano circa, associata all'apertura del bacino di retroarco tirrenico (Cosentino et al., 2010). Il recente regime estensionale è testimoniato da un sistema di faglie normali orientate NW-SE che hanno sezionato la fascia appenninica, formando ampi bacini intermontani dove si sono depositati sedimenti clastici marini e continentali pliocenici (Fig 28a).

La faglia del Monte Morrone è una faglia normale post-orogena sismicamente attiva nell'Appennino centrale. La faglia ha una struttura en-échelon segmentata NW-SE che è complessivamente lunga ~ 23 km. Tale faglia confina, ad est, con il bacino di Sulmona, che è una delle strutture estensive intermontane più recenti ed esterne (orientale) dell'Appennino centrale (Figg. 28a, 28b). La faglia del Monte Morrone si estende per circa 12 km nella crosta (Patacca et al., 2008) e comprende due principali rami paralleli (Fig. 28c), caratterizzati da un offset verticale stratigrafico totale ≥ 400 m, probabilmente fino a 1000 m o anche più (Ghisetti e Vezzani, 2000; Patacca et al., 2008; Ferraro et al., 2018).

Questo studio si concentra su un segmento lungo ~ 25 m della superficie di scivolamento principale (Faglia del Monte Morrone), che è ospitata nel Calcari a *Palaeodasycladus* del Giurassico ed è esposta nei pressi dell'abitato di Roccacasale (Figg. 28b e 29a). Questo segmento di faglia, precedentemente studiato (Ferraro et al., 2018, 2019), è stato esumato geologicamente da una profondità < 3 km (Ghisetti e Vezzani, 2000).

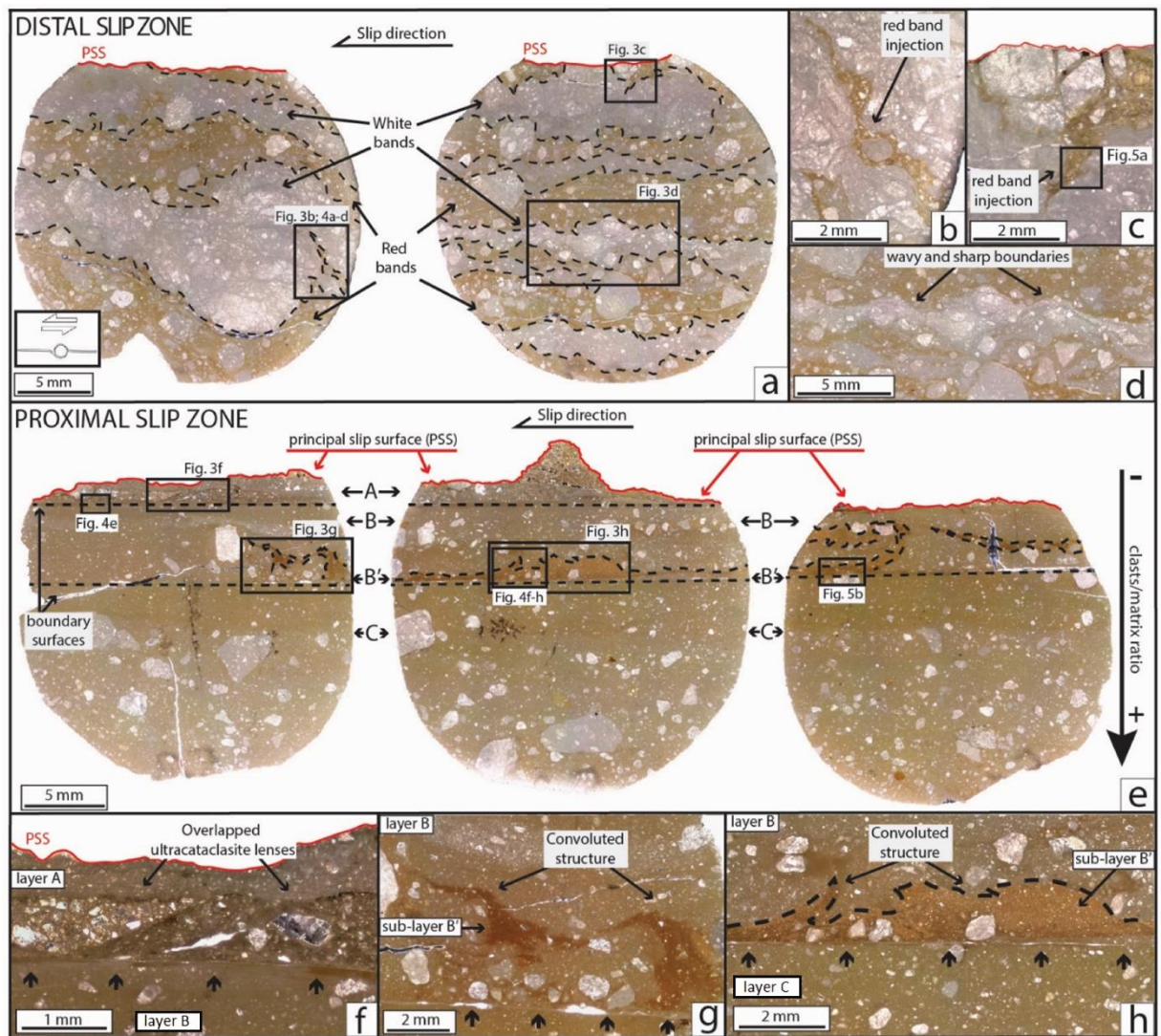
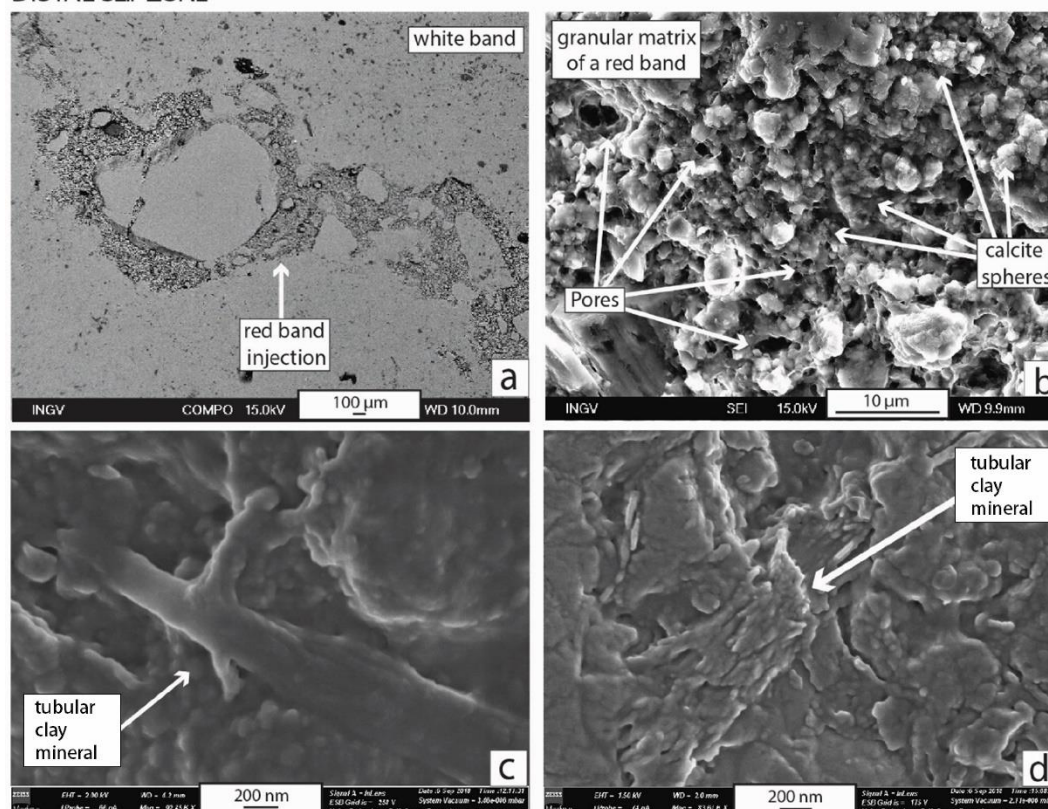


Figura 30. (a) Viste di scansione ad alta risoluzione e relativo disegno al tratto di due sezioni sottili (2.1, 2.2) dalla zona di scorrimento distale. Le immagini mostrano l'alternanza di bande bianche e rosse. Le bande bianche sovrainprimono la zona di scivolamento e appaiono allungate parallelamente alla superficie di faglia principale e deformate coerentemente con la direzione di scorrimento. (b, c) Iniezioni delle bande rosse nelle bande bianche. (d) Confini ondulati tra bande bianche e rosse. (e) Viste di scansione ad alta risoluzione e relativo disegno di linea di tre sezioni sottili (5.3, 5.2, 5.1) dalla zona di scorrimento prossimale della Faglia del Monte Morrone. Le immagini mostrano la stratificazione della zona di scorrimento prossimale. Strato A: strato di ultracataclasite grigio; Strato B: strato di ultracataclasite rosso; sottostrato B': sottostrato fluidale; Strato C: strato di cataclasite. (f) Lenti di ultracataclasite impilate e sovrapposte dello strato A. (g) Struttura simile alla fiamma dal sottostrato fluida B'. (h) Il sottostrato fluido B' penetra nello strato B con strutture fluido-plastiche. Le frecce nere indicano la superficie di confine tra i due strati.

DISTAL SLIP ZONE



PROXIMAL SLIP ZONE

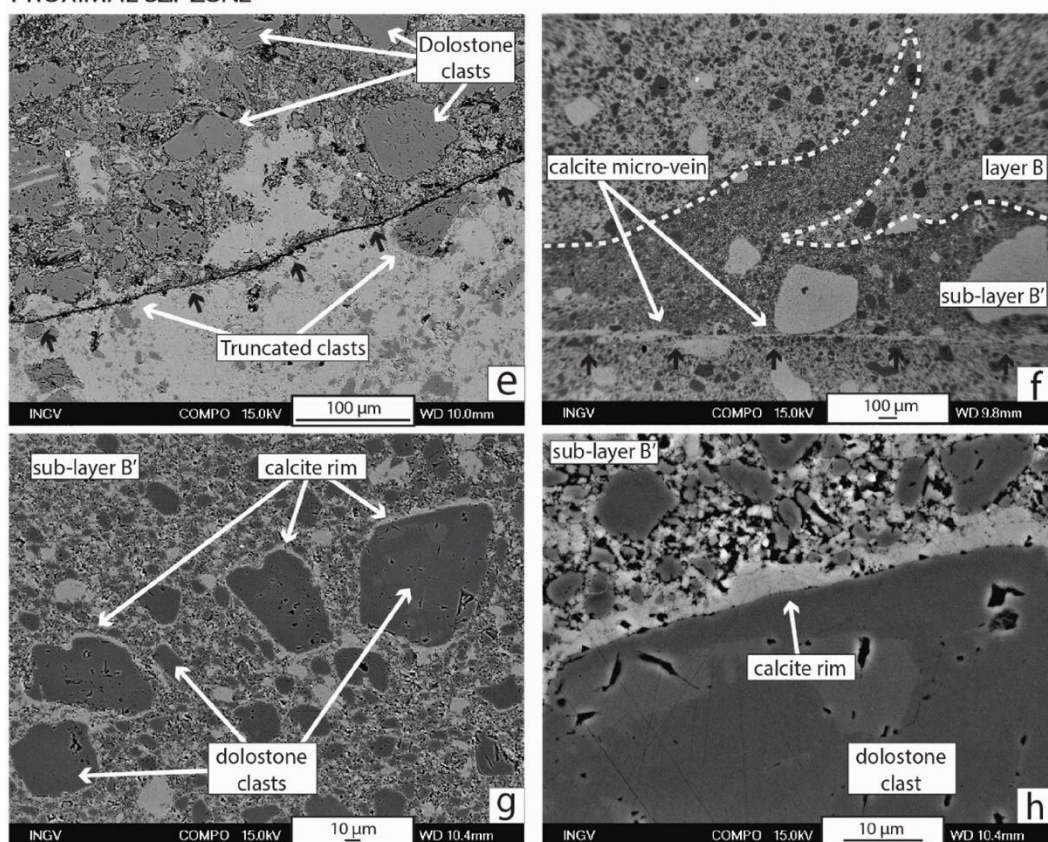


Figura 31. Immagini SEM ad alta risoluzione dalle zone di scivolamento distale e prossimale (aree quadrate come indicato in Fig. 30). (a) Iniezione della banda rossa nella banda bianca

della zona di scorrimento distale. (b) Consistenza granulare porosa della matrice della banda rossa. Questa matrice è composta da sfere di calcite di $\sim 4 \mu\text{m}$ di diametro. (c, d) Immagini SEM ad alta risoluzione di minerali argillosi con un abito fibroso simile a un filamento composto da nanosfere e nanocilindri allineati. (e) Clasto dolomitico troncato da una superficie di scivolamento che divide gli strati della zona di scivolamento prossimale. (f) Struttura simile alla fiamma del sottostrato fluida B' che si estende nello strato B. Una piccola vena di micro-calcite separa il sottostrato B' dallo strato sottostante C. (g, h) I micro-clasti che formano la matrice del sottostrato B' mostrano un piccolo bordo di calcite intorno a loro.

Abbiamo studiato la principale zona di slittamento della Faglia del Monte Morrone, spostandoci dalla superficie di scivolamento principale (Figg. 29a-29c) verso il basso di 7-8 cm (Fig. 29d, 29e). Per raggiungere i nostri obiettivi, abbiamo eseguito indagini strutturali in situ e campionamento di rocce seguite da analisi tessiturali e geochimiche alla micro e nanoscala: microscopia ottica a luce trasmessa (OM) e catodoluminescenza ottica (CL); microscopia elettronica a scansione di emissione di campo (FE-SEM) con spettroscopia a dispersione di energia (EDS); microscopia elettronica a trasmissione (TEM) con EDS e analisi di diffrazione elettronica ad area selezionata (SAED); spettrometria di massa al plasma accoppiato induttivamente (ICPMS); microanalizzatore a sonda elettronica (EPMA); ICPMS di ablazione laser (LA-ICPMS); e spettroscopia Raman.

La superficie di scivolamento principale della Faglia del Monte Morrone (Fig. 29a) si estende in direzione NW-SE, è inclinata di $50-55^\circ$ verso SW e separa i calcari del Giurassico inferiore, i calcari dolomitici e le dolomie (Calcari a *Palaeodasycladus*) in basso dai depositi ghiaino-argillosi alluvionali e lacustri del bacino Pleistocenico di Sulmona (unità di Catignano) verso l'alto (Fig. 28b). Sotto i depositi del Pleistocene, sono presenti spessi depositi di flysch Miocenico ricco di argilla. Gli indicatori cinematici sulla superficie di scorrimento principale mostrano una cinematica di scivolamento estensionale (Fig. 29a). Oltre agli indicatori cinematici,

la superficie di scivolamento principale esposta è caratterizzata da iniezioni ramificate rosse diffuse di materiale ultracataclastico (Figg. 29b e 29c).

Immediatamente sotto la superficie di scivolamento principale e approssimativamente parallela ad essa, abbiamo identificato due zone di scivolamento strutturalmente distinte:

- La zona di scorrimento distale ha uno spessore massimo di 3-4 cm e si trova al di sotto della zona di scorrimento prossimale (Fig. 29d). È costituita da cataclasiti con clasti carbonatici arrotondati e angolari, dispersi in una matrice a grana fine rossa o disposti in bande bianche simili a fluidi deformate coerentemente con la direzione di scorrimento e che producono una foliazione dinamica incipiente (Figg. 29f e 30a-30d) comparabile con quelli descritti da Smith et al. (2017).
- La zona di scorrimento prossimale ha uno spessore fino a 3-4 cm ed è delimitata superiormente dalla superficie di scorrimento principale (Fig. 29d, 29e, 29g e 30e). La zona di scorrimento prossimale include strati di ultracataclasite da rosa a bianco (strati A – C nella Fig. 30e), incorporando localmente un sottile sottostrato convoluto rosso opaco di ultracataclasite (sottostrato B 'nelle Figg. 30g e 30h). A causa dell'erosione o dello scivolamento tettonico, la zona di scorrimento prossimale è assente in alcuni punti.

La zona di scorrimento distale è costituita da clasti di calcite e dolomite da arrotondati ad angolari di dimensioni fino a pochi centimetri, dispersi all'interno di una matrice rossa (Figg. 29d-29f e 30a-30d). Sotto la luce ottica CL, la zona di scorrimento distale mostra una luminescenza da opaca a rosso vivo della matrice rossastra a grana fine che incorpora i clasti di carbonato. I clasti di carbonato mostrano una luminescenza non luminescente (nera) o rossa opaca, dove i clasti luminescenti sono frammenti rielaborati di matrice granulare cementata.

A livello locale, la matrice rossa è parzialmente sovrainpressa da bande cementizie bianche meno porose a formare bande rosse e bianche alternate (Fig. 30a). La microscopia elettronica a scansione (SEM) accoppiata con EDS e analisi chimiche puntuali EPMA mostrano che le bande bianche sono dominate da calcite cementizia e dolomiti minori, (rapporto molare Ca / (Ca

+ Mg) misurato da EPMA di $0,53 \pm 0,03$), mentre nelle bande più porose, la matrice della banda rossa è dominata dalle argille (rapporto molare EPMA Si / Al compreso tra 2,13 e 3,51 e quantità minori di K, Na, Sr, Fe, Ni), sebbene nei micropori sia presente anche calcite cementizia. Le bande rosse e bianche mostrano contorni da convoluti a ondulati con forme asimmetriche tendenti in modo coerente con la direzione e il senso di scorrimento, e le pieghe reciproche cuspatolobate a geometrie intrusive (Figg. 30a-30d e 31a).

A differenza delle bande bianche, le bande rosse sono caratterizzate da una matrice microgranulare porosa (Figg. 31a e 31b). Entrambe le immagini FE-SEM e TEM (vedere le sezioni successive) delle intrusioni rosse hanno rivelato la presenza di <1 μm di dimensioni, particelle di calcite arrotondate e nanoclasti di dolomite deformati plasticamente (200-500 nm di dimensione) avvolti da fillosilicati nanocilindrici con tipica tessitura tabulare e forma allungata (Figg. 31b-31c). Le analisi con microsonda elettronica mostrano contenuti significativi di Si e Al nei dati dell'area di massa (Fig. 33) che suggeriscono la presenza pervasiva di silicati di strato all'interno della matrice porosa a grana fine. L'acquisizione di immagini ad alta risoluzione da FE-SEM supporta la presenza di minerali ricchi di Al e Si all'interno della matrice delle bande rosse. Questi minerali sono caratterizzati da una morfologia cilindrica allungata (Figg. 31c e 31d) e da una composizione chimica tipica dei fillosilicati. È importante sottolineare che abbiamo notato la presenza di micropori con diametri di 1-3 μm spesso distribuiti tra i clasti sferici di calcite (Figg. 31b).

I clasti dolomitici frammentati fino alla microscala, circondati da una matrice di calcite o sigillati e pervasi da un cemento di calcite, sono localmente osservati nella zona di scorrimento distale. Questi clasti frammentati sono caratterizzati da strutture di brecce polverizzate o craquelé, finemente sminuzzate con la forma originaria sostanzialmente conservata.

La zona di scivolamento prossimale è costituita da ultracataclasiti con clasti angolari e subarrotondati di calcite e dolomite di dimensioni fino a 3 mm, dispersi all'interno di una matrice rossa a grana fine (Figg. 30e-30h). Sotto la luce ottica CL, la zona di scorrimento prossimale

mostra un colore rosso opaco luminescente della matrice a grana fine tra i clasti di carbonato. I clasti carbonatici mostrano una non luminescenza (nera) o una luminescenza rossa più brillante di quella della matrice.

La zona di scorrimento è disposta in più strati ultracataclastici distinguibili macroscopicamente, in base al colore, alla granulometria e all'abbondanza della matrice (Fig. 30e). Abbiamo riconosciuto almeno tre diversi strati principali (strati A – C) strettamente al di sotto della superficie di scorrimento principale, separati da superfici di scorrimento secondarie (Fig. 30e). A causa dell'erosione e/o dello scivolamento della faglia, non tutti e tre gli strati sono sempre presenti nella zona di scorrimento prossimale. Spostandosi verso il basso dalla superficie di scivolamento principale, i tre strati principali sono:

- Lo strato A è un'ultracataclasite grigia fino a pochi millimetri di spessore con una matrice a grana ultrafine. A livello locale, lo strato include lenti contenenti clasti impaccati di grandi dimensioni (fino a 1 mm di dimensione) e una matrice, probabilmente derivata dalla rottura delle ex zone di scivolamento litificate. Queste lenti si sovrappongono e sono intrise dalla matrice a grana ultrafine dello strato A (Fig. 30e e 30f).

- Lo strato B è un'ultracataclasite rossa spessa ~ 5 mm costituita da una matrice di carbonato a grana ultrafine, in cui sono dispersi clasti di carbonato con un diametro di ~ 1 mm (Fig. 30e). Lo strato B è caratterizzato alla sua base dalla presenza di un particolare sottostrato convoluto rosso opaco (sottostrato B 'nelle Figg. 30e, 30g e 30h). Il Sottostrato B 'è probabilmente la microstruttura più significativa di questo studio, che ricorda i potenziali precursori dei terremoti recentemente identificati attraverso il monitoraggio idrogeochimico nell'Italia centrale (Barberio et al., 2017), come verrà ulteriormente discusso di seguito. Il sottostrato è di spessore variabile (fino a circa 1 mm) e mostra un bordo superiore ondulato e molto irregolare, simile a una fiamma, simile a una fiamma, con le lingue di fiamma solitamente deviate in modo coerente con il senso di scivolamento (Figg. 30g e 30h). Il fondo dello strato B è rappresentato da una superficie di scivolamento minore acuta che tronca gli ultracataclasi sottostanti (Fig. 30h).

- Lo strato C è uno strato cataclastico di ~ 1,5 cm di spessore che presenta un numero di clasti grossolani maggiore del numero di clasti grossolani negli strati A e B. Lo strato C è composto da clasti carbonatici da angolari a subarrotondati che vanno da 0,5 a 3 mm di diametro (Fig. 30e). La parte inferiore dello strato C è rappresentata da una superficie di scorrimento che delimita la parte superiore della zona di scorrimento distale.

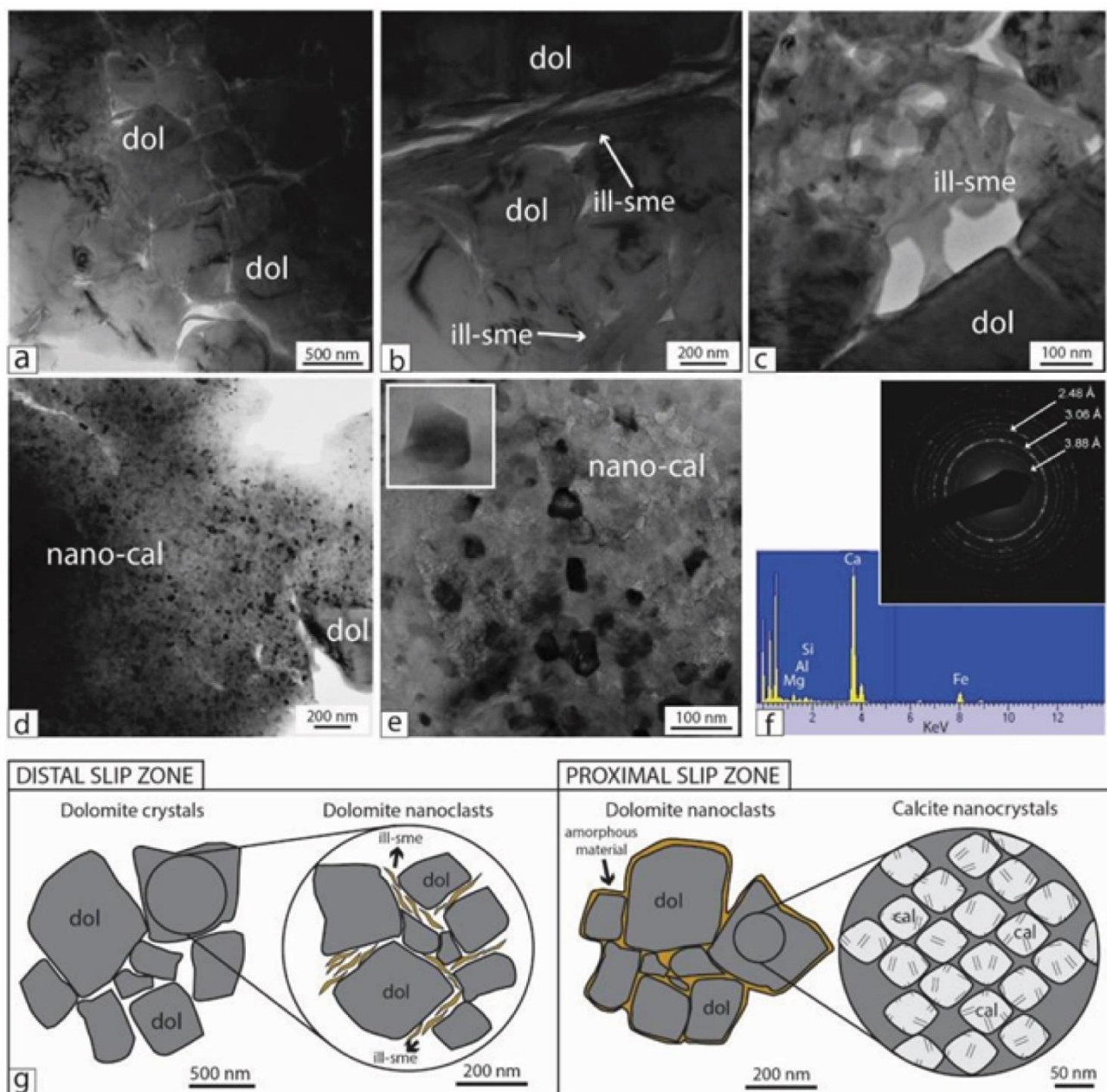


Figura 32. Osservazioni TEM sulla Faglia del Monte Morrone. (a) Cristallo dolomitico delle dimensioni di un micron dalla zona di scorrimento distale, che mostra una deformazione

fragile, riduzione della dimensione dei grani e formazione di nanoclasti (lato destro). (b) Particolare dei nanoclasti di dolomite (qui di circa 500 nm di dimensione), avvolti da una sottile pellicola interstiziale di smectite (silicati stratificati, Illite-Smectite, nella zona di scorrimento distale). (c) nanoclasti dolomitici dal sottostrato B '(zona di scorrimento prossimale), che mostrano bordi di grano lobati e materiale interstiziale amorfo, spesso formando una sorta di "ponte" tra i nanoclasti vicini. (d) Nella matrice ultrafine del sottostrato B '(zona di scorrimento prossimale), i nanoclasti di dolomite possono essere sostituiti da nanoclasti di calcite, di diametro 10-50 nm, con orientamenti casuali. (e) Particolare delle nanografie di calcite (zona di scorrimento prossimale), in luoghi associati a materiale ricco di vescicole e pori da poco cristallino ad amorfo. L'inserito mostra un nanocristallo di calcite con bordi di grano poligonali e frange reticolari non deformate regolarmente distanziate. (f) Spettro EDS Mg-calcite e pattern SAED con riflessioni a forma di anello dovute all'orientamento casuale delle nanografie di calcite nella zona di scorrimento prossimale. (g) Disegni che mostrano zone di scivolamento distale (sinistra) e prossimale (destra) con caratteristiche osservate attraverso analisi TEM e SAED nelle Figg. 32a-32f.

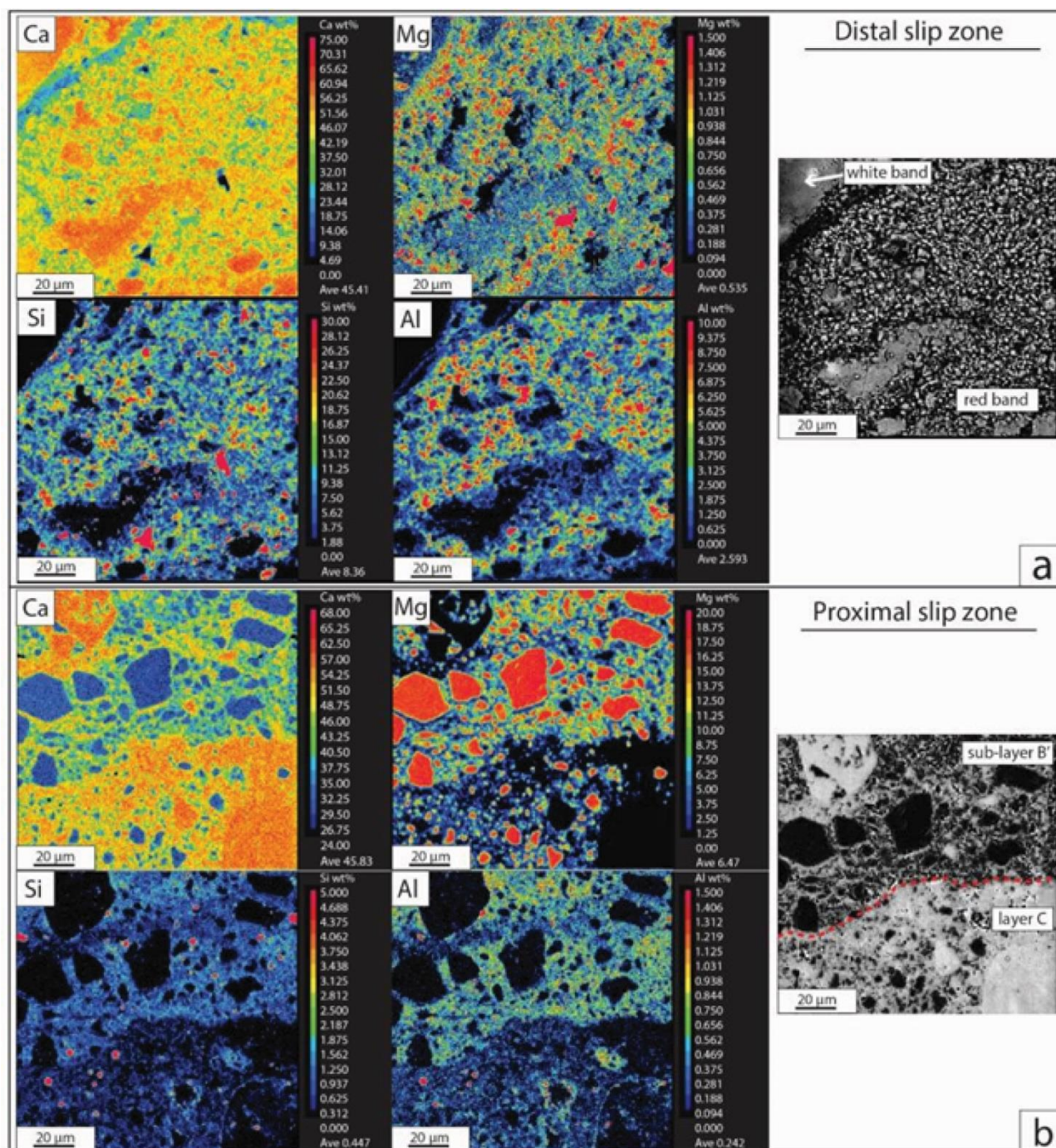


Figura 33. Mappe EDS (mappe a sinistra) dalle zone di scivolamento distale e prossimale (la posizione delle mappe è indicata nella Fig. 30). A destra, immagini SEM corrispondenti alle mappe a sinistra. (a) Zona di scivolamento distale. Iniezione di una fascia rossa in una fascia bianca. La banda rossa ha una consistenza granulare e contiene non solo Ca e Mg ma anche Si e Al. (b) Zona di scivolamento prossimale. Porzione del contatto tra il sottostrato B' e lo strato sottostante C. Il sottostrato B' è composto da un alto contenuto di Mg nei clasti che sono incorporati in un bordo ricco di Ca. La matrice ha un alto contenuto

di Ca e un considerevole contenuto di Mg, Si e Al. Lo strato C ha un contenuto più elevato in Ca e Mg e un contenuto più scarso in Si e Al rispetto al sottostrato B ''.

Alla microscala, i tre strati A – C mostrano strutture simili con calcite scarsamente arrotondata e clasti di dolomite con $Ca \#$ (calcolato come rapporto molare $Ca / (Ca + Mg)$) compreso tra 0,43 e 0,59 circondato da una dolomite (Fig. 31f) o matrici di calcite (Fig. 31g e 31h). Sono presenti anche cemento calcitico intergranulare e micro vene di calcite. I confini degli strati sono solitamente contrassegnati da superfici scivolose e clasti troncati, spesso accompagnati da sottili vene di calcite (Fig. 31e e 31f). Al contrario, il sottostrato convoluto B ' appare strutturalmente distinto alla microscala, con grossi clasti subangolari di calcite ($> 1 \mu m$ di dimensione) intrappolati all'interno di un'ultracataclasite a grana molto fine (granulometria media $50 \mu m$) (Fig. 31f). Particolari clasti dolomitici (dimensioni 20–50 μm) sono caratterizzati da bordi arrotondati e incastonati e sono circondati da un sottile bordo di calcite (Fig. 31g e 31h).

Abbiamo eseguito analisi TEM su granuli di carbonato dalla zona di scorrimento distale e nella zona di scorrimento prossimale, sulla matrice ultrafine che si trova vicino alla superficie di scorrimento principale, in particolare sul sottostrato B '(Fig. 32).

Nella zona di scorrimento distale, i cristalli (fino a $1 \mu m$ di dimensione) di dolomite appaiono spesso caratterizzati da un'intensa deformazione e relativa riduzione della granulometria (Fig. 32a). Ciò si traduce nella formazione di nanoclasti a grana ultrafine, 200–800 nm o anche meno di diametro, con bordi dei grani angolari. Nella zona di scorrimento distale, i cristalli di calcite sono notevolmente meno abbondanti della dolomite. Gli spazi interstiziali tra i nanoclasti di dolomite sono riempiti da silicati di strato simile a smectite (Fig. 32b). I silicati a strati formano un involucro sottile attorno ai nano clasti di dolomite e sono spessi

pochi (001) frange di reticolo. Inoltre, sono deformati, scarsamente cristallini e includono alcune porzioni amorse.

Nella zona di scorrimento prossimale, in particolare nella matrice del sottostrato B', i grani di dolomite e i nano clasti presentano bordi più arrotondati e lobati, mentre le argille smectitiche interstiziali sembrano essere parzialmente o completamente decomposte, producendo un materiale amorfo privo di contrasto che forma tipicamente una sorta di involucro che collega i grani vicini e i nano clasti (Fig. 32c). Questa caratteristica è coerente con le precedenti osservazioni SEM (Fig. 32g). In alcuni casi, i nano clasti di dolomite dal sottostrato B' sembrano essere cristalli singoli omogenei mentre, in altri casi, mostrano un peculiare contrasto eterogeneo, suggerendo che siano stati sostituiti da nanograins di 10-20 nm di diametro con orientamenti variabili (Fig. 32d). I risultati EDS e SAED indicano che le nanografie corrispondono alla calcite (Fig. 32f) associata a materiale ricco di vescicole amorse (Figg. 32c e 32d). La Fig. 32(f) mostra un modello SAED a forma di anello rappresentativo di nanografi di calcite, caratterizzato da riflessi nitidi e intensi. Questa evidenza è coerente con la presenza di calcite non deformata altamente cristallina con orientamento casuale. A livello locale, le nanografie di calcite mostrano bordi di grano poligonali taglienti, ad esempio, inseriti nella Fig. 32e (confrontare con Smith et al., 2013).

Attraverso uno spettrometro ICP-MS, abbiamo misurato la chimica di massa (28 elementi) su un campione della zona di scorrimento distale (MC2) e due campioni della zona di scorrimento prossimale (MC5 e MC7). I risultati mostrano l'abbondanza (in ppm) di elementi come Al e Fe (> 1500 e 1900 ppm, rispettivamente) e B, Mn, Sr, As e V (> 60, 70, 50, 20, e 10 ppm, rispettivamente).

Abbiamo anche eseguito analisi chimiche puntuali tramite EDS ed EPMA. La mappa EDS della Fig. 33a mostra un'iniezione di banda rossa granulare in una banda bianca della zona di scorrimento distale. La mappa rivela una matrice granulare (diametro <20 µm) per la banda rossa contenente non solo Ca e Mg ma anche grandi quantità di Si e Al. Questa iniezione

granulare è incorporata da una banda bianca (in alto a sinistra delle mappe in [Fig. 33a](#)) dominata da Ca, accompagnata da un po' di Mg, ma priva di Si e Al.

La mappa EDS della [Fig. 33b](#) si riferisce al contatto tra il sottostrato fluidale B' e lo strato sottostante C dalla zona di scorrimento prossimale. Il sottostrato B' è costituito da clasti dolomitici con Ca fino a ~ 38wt.% e ~ 18wt.% di Mg che galleggia all'interno di una matrice ricca di Ca e Mg ma anche di Si e Al. Al contrario, lo strato C (sotto) è costituito da porzioni compatte ricche di Ca (in basso a destra delle mappe in [Fig. 33b](#)) con clasti ricchi di Ca e Mg incorporati in una matrice calcitica granulare. Occasionalmente si verificano macchie ricche di Al e Si (parte inferiore delle mappe in [Fig. 33b](#)). Le mappe EDS rivelano, quindi, un sottostrato B' fluidale e granulare composto prevalentemente da clasti dolomitici dispersi in una matrice di alluminosilicato, che contrasta con la prevalente composizione calcitica dello Strato C che è, almeno in parte, molto compatto e solo raramente mescolato anche con matrice di alluminosilicato.

Caratteristiche chimiche e tessiturali molto simili a quelle osservate in [Fig. 33](#) per le zone di scivolamento distale e prossimale si osservano anche in altri campioni. In questi ultimi casi, una matrice granulare fluida contenente Al e Si (oltre a Ca e Mg) che ingloba clasti ricchi di Mg e Ca viene iniettata o tagliata da una o più vene ricche di Ca e/o mineralizzazioni.

Abbiamo eseguito analisi spot di oligoelementi su clasti, vene e matrici di tre sezioni sottili dalle zone di scivolamento prossimale (sezioni 5.1 e 5.2) e distale (sezione 2.1,) della Faglia del Monte Morrone utilizzando LA-ICPMS. In dettaglio, abbiamo studiato la distribuzione e l'abbondanza degli oligoelementi nello strato B e nel sottostrato B', dove quest'ultimo si intromette nello strato B con una tipica tessitura fluida ([Figg. 30e, 30g e 30h](#)).

In generale, l'abbondanza della maggior parte degli oligoelementi, inclusi gli elementi delle terre rare (REE) dal sottostrato B', è in media superiore a quella degli oligoelementi dallo strato B, che al contrario presenta concentrazioni elementari assolute paragonabili a quelle del carbonato clasti e vene dalle zone di scivolamento investigate ([Fig. 34](#)). Ad esempio, un

arricchimento in Ba e Sr nel sottostrato B' rispetto allo strato B è mostrato nei transetti LA-ICPMS di Fig. 34b. Inoltre, le concentrazioni REE misurate dei carbonati sono molto bassi, compresi tra 0,002 e 15 ppm (Fig. 43a). I pattern normalizzati post-Archean Australian Shale (PAAS) dello strato B, sottostrato B', i clasti di carbonato e le vene sono tutti comparabili, esibendo, in media, profili piatti (cioè, $(La / Yb)_N$ varia tra 0,2 e 2; Fig. 34a). Le anomalie negative al cerio caratterizzano la maggior parte dei campioni (Ce / Ce^* varia tra 0,3-1,4; Fig. 34a) e riflettono le condizioni ossiche dell'ambiente marino, dove queste rocce carbonatiche sono state depositate (Elderfield e Greaves, 1982). I diagrammi spider normalizzati-PAAS degli interi campioni analizzati sono tutti confrontabili, mostrando marcate anomalie positive di K e Ti.

Abbiamo confrontato i dati dei nostri campioni con quelli di alcuni frammenti calcarei dei carbonati di Polino nell'Appennino centrale, Italia (Rosatelli et al., 2010), come rappresentativi di un esempio locale di rocce carbonatiche indisturbate, cioè i carbonati di Polino appartengono al Massiccio Fm. che è equivalente alla formazione dei Calcari a *Palaeodasycladus* che ospita l'affioramento della faglia in studio. I carbonati di Polino presentano concentrazioni REE intermedie tra quelle dello strato B e del sottostrato B' e un pattern REE simile (Fig. 34a). Inoltre, per indagare sulle possibili relazioni tra il sistema di faglie studiato e una sorgente magmatica profonda, abbiamo confrontato la composizione degli oligoelementi dalla Faglia del Monte Morrone con alcune rocce vulcaniche affioranti nell'Appennino centrale, vale a dire le province magmatiche romane e intra-appenniniche in Fig. 34a. I risultati mostrano che il contenuto di REE è uno o più ordini di grandezza più alto nelle rocce vulcaniche che nei carbonati, con modelli piatti simili e nessuna anomalia di Ce (Fig. 34a).

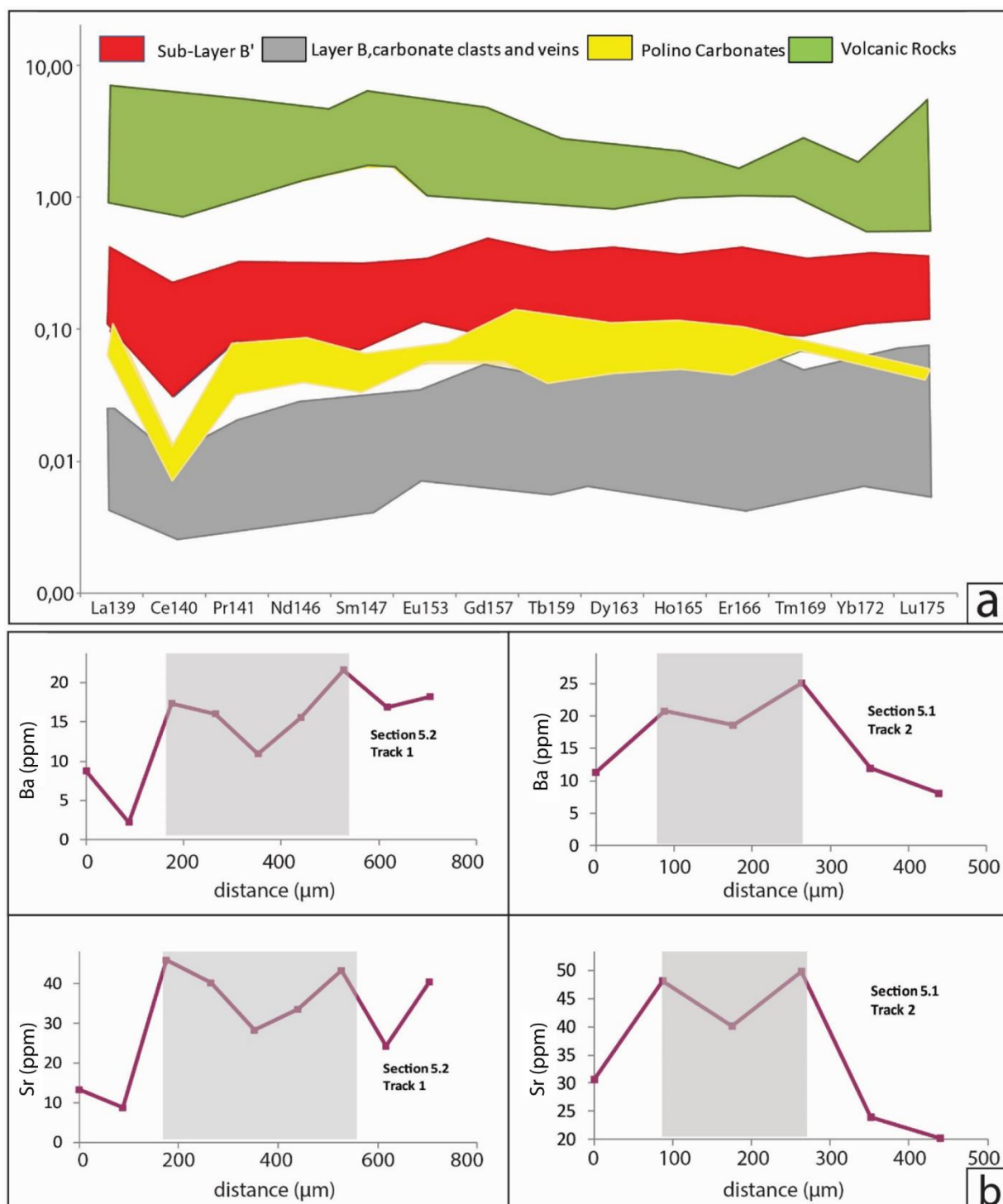


Figura 34. Diagramma REE dello strato B e sottostrato B '. Per confronto, si riporta la composizione REE dei carbonati del Polino (Calcare Massiccio Fm. Dall'Appennino centrale) e di alcune rocce vulcaniche dell'Appennino centrale (le province intra-appenniniche e magmatiche romane). I dati del prodotto vulcanoclastico provengono da Peccerillo (2005) e sono per le province magmatiche intra-appenniniche e romane (ad esempio, Vico, Colli Albani e Monte Sabatini nell'intra-appennino centrale). I dati sulle rocce carbonatiche provengono da Rosatelli et al. (2010) e sono per i carbonati di Polino

dell'Appennino centrale. (b) Traccia elemento (Ba e Sr) tracce dello strato B e sottostrato B ' dove quest'ultimo si intromette, con la sua tipica trama di tipo fluido, nello strato B. La porzione grigia è per il sottostrato B' mentre le parti bianche sono per lo strato B.

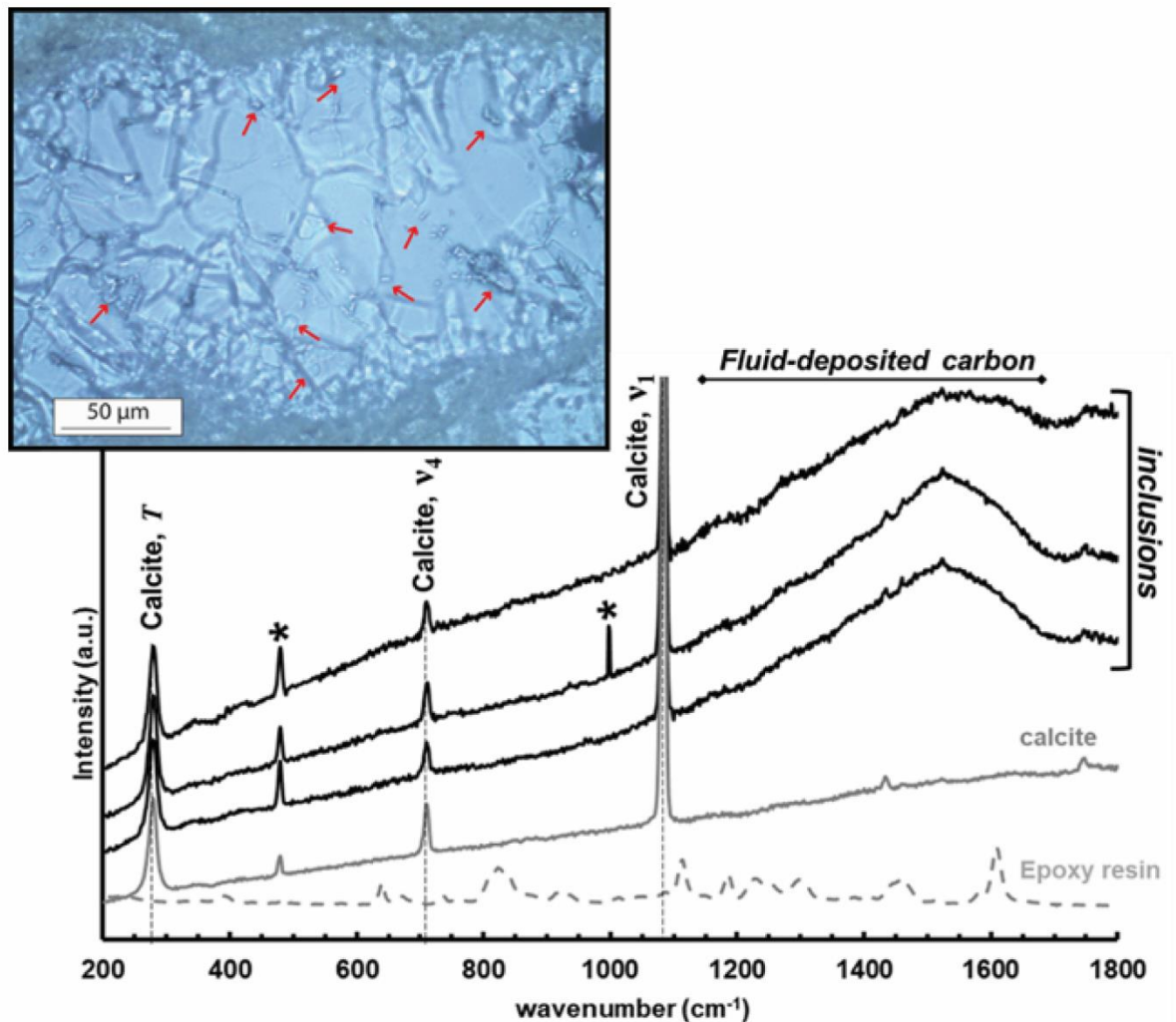


Figura 35. Spettri Raman di tre inclusioni osservate all'interno di mineralizzazioni di calcite dalla zona di scorrimento prossimale. Ogni spettro mostra l'intervallo di frequenza del carbonio disordinato (vedi testo). I picchi acuti sono relativi alla calcite cristallina dalla matrice, il cui spettro è anche mostrato in grigio. Viene mostrato anche lo spettro della resina epossidica per confronto. L'inserito (in alto a sinistra) mostra la posizione dell'inclusione di fluido all'interno della calcite sparitica osservata sotto luce trasmessa. Gli asterischi sono relativi a picchi non identificati.

Abbiamo eseguito misurazioni di spettri confocali micro-Raman su piccole inclusioni (diametro $\leq \sim 30 \mu\text{m}$) osservate nelle vene di calcite e mineralizzazioni sotto luce trasmessa polarizzata (Fig. 35) dalla zona di scorrimento prossimale (Strato A e Strato B) e dalle relative superfici di scivolamento. Gli spettri raccolti (Fig. 35) sono caratterizzati da picchi acuti relativi alla matrice di calcite cristallina a 280, 710 e 1085 cm^{-1} associati alla vibrazione di stiramento simmetrico (ν_1) in-plane bending mode (ν_4) del gruppo carbonato. Inoltre, sono visibili larghe bande sovrapposte che vanno da 1200 a 1700 cm^{-1} e possono essere indicate come vibrazioni di carbonio strutturalmente disordinato; tuttavia, queste caratteristiche sono difficili da deconvolgere con le tipiche bande D e G (Frezzotti et al. 2012), probabilmente a causa della presenza di vibrazioni di flessione CH intermedie (Orange et al. 1996), che sono state spesso indicate come carbonio (amorfo o con struttura cristallina disordinata) da bitume solido, precipitato da fluidi ricchi di idrocarburi (Schito et al. 2017).

Le zone di scorrimento distale e prossimale della Faglia del Monte Morrone suggeriscono che i singoli strati ultracataclasitici e sottostrati si sono comportati come materiali granulari fluidizzati durante la deformazione assistita da fluido. Le relazioni di sovrastampa tra questi strati così come le relazioni di incrocio e iniezione reciproci (Figg. 30 e 31) indicano, in alcuni punti, la contemporaneità di formazione degli strati (cioè iniezione reciproca) e, in altri luoghi, la molteplicità degli eventi di scivolamento (es. relazioni di taglio o sovrastampa). In particolare, gli strati di iniezione (bande rosse all'interno della zona di scorrimento distale e sottostrato B 'all'interno della zona di scorrimento prossimale) sono caratterizzati da una maggiore porosità rispetto ai materiali circostanti (Figg. 30e, 30g, 30h, e 31f). Strutture simili sono state precedentemente descritte in carote di faglia naturale e in esperimenti di deformazione delle rocce eseguiti a velocità di scorrimento sismiche e sono state frequentemente associate alla pressurizzazione co-sismica di fluidi intrappolati o iniettati all'interno delle zone di scorrimento (Brodsky et al., 2009; Smith et al., 2011; Fondriest et al., 2012; Smeraglia et al., 2017a; Ferraro et al., 2019). Nel caso di origine sismica, l'aumento della pressione del fluido può essere

generato da un flusso mirato e rapido di fluidi esterni profondi (pompaggio sismico; [Sibson et al., 1975](#)), e/o pressurizzazione termochimica dei fluidi interstiziali (es. H_2O e CO_2) associati al riscaldamento per attrito ([De Paola et al., 2011](#); [Collettini et al., 2013](#)). La pressurizzazione meccanica può anche verificarsi all'interno di strati a compattazione attiva, in particolare all'interno di quelli a bassa permeabilità, deformati sia a velocità di scorrimento sub-sismiche che co-sismiche ([Faulkner et al., 2018](#)). Recentemente, [Demurtas et al. \(2020\)](#) hanno mostrato lo sviluppo di caratteristiche fluide all'interno di zone sperimentali miste di calcite e dolomite bagnate anche a velocità di scorrimento sub-sismiche, probabilmente a causa dell'aumento della pressione locale all'interno di volumi isolati saturi di fluido.

Inoltre, la zona di scorrimento prossimale è caratterizzata da micro-strati ultracataclasitici con bordi che si trancano l'un l'altro e che suggeriscono la localizzazione ciclica di deformazione di taglio possibilmente durante singoli eventi di scivolamento sismico ([Figg. 31e e 31f](#); [Smith et al., 2011, 2017](#)). Inoltre, i clasti dolomitici esplosi (polverizzati), che sono altamente sminuzzati ma con una forma del grano originale riconoscibile, sono immersi nella matrice di calcite e potrebbero derivare da un carico dinamico impulsivo associato a rotture sismiche ([Dor et al., 2006](#)). Ulteriori prove alla micro e nanoscala sono compatibili con l'attivazione della decomposizione minerale possibilmente associata al riscaldamento per attrito co-sismico (cioè a scorrimento $\sim 1 \text{ m/s}$). In particolare, la presenza di nanoclasti di dolomite ([Figg. 32d e 32e](#)) e soprattutto nanograins di Mg-calcite ([Fig. 32d-f](#)) potrebbe essere interpretati come il risultato di un'estrema frantumazione e decarbonatazione della dolomite in presenza di una soluzione acquosa ([Han et al., 2010](#); [De Paola et al., 2011](#)). Nanografie di Mg-calcite che mostrano bordi di grano poligonali taglienti, ad esempio, inserti nella [Fig. 32e](#), potrebbe essere interpretate come il risultato della ricristallizzazione dinamica co-sismica termicamente guidata in modo simile alle trame di calcite riportate in [Smith et al. \(2013\)](#). Questa interpretazione implicherebbe la decomposizione termica della dolomite per riscaldamento per attrito ($T > 550^\circ \text{C}$, [De Paola et al., 2011](#)); in alternativa, un meccanismo di decarbonatazione e amorfizzazione meccanica a

bassa temperatura simile a quello proposto da Ohl et al. (2020) potrebbe essere invocato per spiegare queste microstrutture.

Allo stesso modo, i film ultrasottili di materiale di silicato amorfo trovati nella zona di scorrimento prossimale possono essere correlati alla deidrossilazione dell'argilla dovuta al riscaldamento per attrito co-sismico ($T > 400\text{ }^{\circ}\text{C}$) (Fig. 32c; Collettini et al., 2013; vedere anche Kuo et al., 2009), sebbene strutture simili siano state prodotte anche in esperimenti di laboratorio a tassi di scorrimento subsismici (Aretusini et al., 2019; Wu et al., 2020). In generale, la presenza di micropori sottosferici associati a materiale amorfo all'interno della zona di scivolamento studiata (Fig. 31b) potrebbe essere coerente con la decomposizione del carbonato o la deidrossilazione dell'argilla (Collettini et al., 2013) innescata dal riscaldamento per attrito cosismico (ad esempio Kuo et al., 2011).

La presenza di strutture nanocilindriche - carbonato o fillosilicato - (Figg. 31c e 31d) è dibattuta e interpretata dubitativamente come cosismica (Hirono et al., 2014; Verberne et al., 2014; Smeraglia et al., 2017b) (Figg. 31c e 31d). Ad esempio, Smeraglia et al. (2017a), con carbonati e argille molto simili a quelli trovati nella zona di scorrimento del Morrone e in condizioni al contorno molto simili ($< 3\text{ km}$ di profondità), ha prodotto strutture nanocilindriche simili a quelle mostrate nelle Figg. 31c e 31d in laboratorio solo a velocità sismiche (1 m/s).

In sintesi, le nostre evidenze suggeriscono fortemente il verificarsi di più episodi di fagliazione assistita da fluido e fluidificazione, probabilmente associati a rotture sismiche lungo la porzione investigata della Faglia del Monte Morrone.

Per comprendere l'origine dei fluidi che hanno contribuito a formare la zona di scorrimento studiata, confrontiamo i rapporti degli oligoelementi dal Monte Morrone con i carbonati di Polino (Appennino centrale) e da rocce vulcaniche delle Province Romana e Intra-Appenninica (Appennino Centrale) (Fig. 36 e 37a). Si considerano anche due depositi di flysch: uno prossimale (flysch di Popoli dalla parete pensile della Faglia del M. Morrone) e uno distale (Flysch Rosso dall'Appennino meridionale, a circa 200 km dalla Faglia del Morrone). Mostriamo

alcune coppie di oligoelementi caratterizzate da un'incompatibilità geochimica simile per ridurre al minimo l'effetto dei processi di differenziazione sui membri magmatici e per conservare le informazioni sulla fonte. Ci concentriamo sul sottostrato B 'che è lo strato più fluido tra quelli più vicini alla superficie di scorrimento principale, cioè all'interno della zona di scorrimento proximale (Figg. 30e, 30g e 30h).

La Fig.36 mostra i diagrammi Rb / Ba vs. Rb / Sr e Rb / Sr vs. La / Yb ed evidenzia una marcata differenza tra il sottostrato B 'e lo strato B. Il sottostrato fluida B', dove gli oligoelementi erano esclusivamente misurati sulla matrice (cioè, senza clasti o vene), è, in media, caratterizzato da rapporti Rb / Ba, Rb / Sr e La / Yb superiori a quelli dello Strato B, dove, viceversa, le analisi sono state condotte su entrambe le matrici, vene carbonatiche e clasti. I valori più bassi di Rb / Ba, Rb / Sr e La / Yb nello strato B sono mostrati dai clasti. I risultati evidenziano una zona intermedia in cui le due matrici si sovrappongono (Fig. 36). Inoltre, i valori Rb / Ba, Rb / Sr e La / Yb del sottostrato B 'sono compatibili con le rocce vulcaniche delle province magmatiche intra-appenniniche e romane, mentre la composizione dello strato B è simile ai carbonati indisturbati da Polino. È interessante notare che il fatto che i campioni più ricchi di oligoelementi del sottostrato B 'cadano nel campo dei depositi vulcanici suggerisce che il sottostrato B' è in qualche modo collegato all'interazione con fluidi aventi una firma magmatica e la cui natura e genesi sarà discusso in seguito. In questo contesto, i valori più ricchi di oligoelementi della matrice scura (sottostrato B ') traccerebbero il grado più avanzato di interazione con i fluidi magmatici, mentre i clasti carbonatici dello strato B sarebbero rappresentativi dei carbonati praticamente non modificati. La sovrapposizione compositiva dei due strati indicherebbe un intimo grado di miscelazione tra le due matrici.

La conferma che il fluido che scorreva nella zona di scorrimento originato dall'interazione tra sorgenti magmatiche e carbonatiche è data dalla variabilità chimica registrata su alcuni micro-profili che attraversano l'interfaccia B-B ', dove il sottostrato B' inietta la roccia carbonatica di Strato B (Fig. 35b). Si osserva un aumento della concentrazione di alcuni oligoelementi, cioè

Sr e Ba, spostandosi dalla porzione centrale dell'iniezione verso i due confini laterali, mostrando profili di composizione tipo "V" o "U". Al contrario, quando ci si sposta dall'interfaccia allo strato B, il contenuto degli oligoelementi diminuisce drasticamente. È stato suggerito che questo modello peculiare sia prodotto da processi di dissoluzione-ricristallizzazione all'interfaccia della zona di interazione tra un fluido circolante e la roccia campestre (Renard et al., 2019). Pertanto, una domanda chiave riguarda l'origine del fluido ricco di oligoelementi. Si possono ipotizzare due differenti processi principali:

(1) In un primo scenario, la zona di scivolamento studiata potrebbe essere stata interessata dalla percolazione delle acque superficiali che hanno interagito con i prodotti tefritici ricchi di oligoelementi presenti nel bacino di Sulmona come intercalazioni a profondità inferiori a circa 100 m (Giaccio et al., 2013). Tale ipotesi sembra altamente improbabile per diversi motivi. In primo luogo, è geochimicamente improbabile che gli oligoelementi, tra cui REE, siano stati semplicemente disciolti e trasportati da fluidi superficiali a bassa temperatura e scarsamente acidi, ad esempio le acque meteoriche. In effetti, la Fig. 34 mostra il contenuto di REE nel sottostrato B 'molto più alto che nello strato B e carbonati indisturbati. Inoltre, le acque meteoriche che percolano dovrebbero mostrare un pattern REE con un aumento monotono generale da REE leggero (LREE) a REE pesante (HREE) (Tostevin et al., 2016), poiché la solubilità HREE è superiore a quella di LREE (in particolare La) . Al contrario del comportamento atteso, il modello REE del sottostrato B 'è principalmente piatto, con un arricchimento quasi paragonabile di LREE, REE medio (MREE) e HREE nella Fig. 34a. Inoltre, i depositi di tefra del bacino di Sulmona sono molto sottili - solo pochi cm o meno - e la loro distribuzione è spazialmente discontinua a causa dell'erosione (Giaccio et al., 2013), rendendo improbabile un grado avanzato di interazione chimica con la meteorica acque che filtrano verso il basso lungo le zone di faglia.

(2) Una seconda ipotesi (Fig. 37b) suggerisce che la firma geochimica del sottostrato B 'è in parte la conseguenza dell'interazione tra i depositi di carbonato del Monte Morrone e/o

flysch e fluidi di derivazione magmatica che salgono da livelli crostali profondi lungo faglie profondamente radicate, in particolare durante le fasi di dilatazione pre-sismica (da 4-5 mesi prima della scossa principale secondo [Barberio et al., 2017](#)). È noto, infatti, che i fluidi di derivazione magmatica, caratterizzati da alte temperature e condizioni acide, possono trasportare grandi quantità di REE, sia LREE che HREE, per chilometri attraverso la crosta ([Michard e Albarede, 1986](#)). Pertanto, l'interazione di questi fluidi profondi con depositi di carbonato e flysch lungo una zona di faglia produrrebbe un arricchimento REE e un pattern REE piatto, come osservato per il sottostrato B ". La recente scoperta di picchi di CO₂ da sorgenti crostali profonde durante le fasi sismiche dell'Appennino centrale negli ultimi dieci anni supporta questa ipotesi ([Chiodini et al., 2020](#)). L'afflusso di fluidi esterni è anche coerente con alcuni diversi colori di CL del sottostrato B ', suggerendo iniezioni multiple di fluidi esterni, caratterizzati da composizioni chimiche leggermente diverse, cioè diversi colori di CL. Lo stesso vale per alcuni clasti dolomitici caratterizzati da imboccature del bordo ([Fig. 31e](#)), che suggeriscono l'interazione con fluidi aggressivi esterni (profondi).

La [Fig. 37a](#) confronta i rapporti Sr / V dei carbonati studiati con quelli di alcune acque sotterranee ossidate della provincia vulcanica laziale nell'Italia centrale, che hanno attraversato e parzialmente sciolto le unità vulcanoclastiche locali ([Sappa et al., 2014](#)). I rapporti Sr / V di queste acque fredde sono quasi coincidenti con quelli dei prodotti vulcanici delle province intra-appenniniche e romane. Al contrario, i rapporti Sr / V del sottostrato B ' cadono al di fuori del campo delle suddette acque sotterranee o depositi vulcanici, raggiungendo valori molto più bassi. Questa evidenza ci consente di escludere che una tipica acqua meteorica ossidata che ha interagito con depositi vulcanoclastici possa aver impresso geochimicamente la firma del sottostrato B '. Viceversa, i rapporti Sr / V inferiori evidenziati nel sottostrato B ' rispetto a quelli di un membro terminale vulcanico possono essere coerenti con la suddetta seconda ipotesi, supportando l'ascesa di un fluido crostale profondo lungo la Faglia del Monte Morrone. Infatti, V nei suoi stati ossidati (V + 4 e V + 5) è altamente insolubile, con solubilità che aumenta con le

condizioni riducenti tipiche dei fluidi di derivazione magmatica, risultando infine in una diminuzione dei rapporti Sr / V , come osservato in sub- Strato B '. È anche vero, tuttavia, che l'alto contenuto di V del sottostrato B 'è coerente con i depositi di flysch di argilla ricchi di V che si trovano sulla parte ribassata della Faglia del Monte Morrone (Fig. 37a) e ricorda i precursori idrogeochimici ricchi di V sorti nell'Italia centrale vicino al Monte Morrone 4-5 mesi prima del terremoto di Amatrice del 2016 Mw 6.0 (Barberio et al., 2017).

I potenziali precursori idrogeochimici dei terremoti del 2016 (Barberio et al., 2017) sono stati interpretati come collegati alla risalita di fluidi aggressivi profondi (ricchi di CO_2) pre-sismici (4-5 mesi prima della scossa principale) e alla conseguente interazione con rocce incassanti come il flysch argilloso (cioè desorbimento di ioni metallo e metalloidi da superfici minerali argillose; Boschetti et al., 2019, Barbieri et al., 2020). Simili strutture fluide ricche di V co-sismiche si riscontrano anche in altre faglie attive dell'Appennino centro-meridionale, come alcuni microstrati dalla zona di scivolamento della Faglia dei Tre Monti (Fig. 37a), situata in una delle zone più sismiche aree dell'Appennino (bacino del Fucino; Smith et al., 2011; Smeraglia et al., 2016). Di conseguenza, speculiamo sulla formazione del sottostrato fluidale B ', proponendo che la risalita pre-sismica di fluidi di derivazione magmatica lungo faglie in carbonati autentici e la loro interazione aggressiva (cioè desorbimento) con rocce ospiti meno profonde (es. Flysch ricco di argilla) ha modificato la chimica dei fluidi meno profondi (<3 km di profondità) che circondano o si infiltrano lungo la zona di faglia, che era soggetta e vicina alla rottura sismica. Nel caso del terremoto di Amatrice del 2016, ad esempio, le prove geologiche e geofisiche hanno mostrato un aumento della pressione del fluido subito prima della scossa principale (De Luca et al., 2018; Petitta et al., 2018; Chiarabba et al., 2020). Pertanto, ipotizziamo che, anche in eventi sismici passati, fluidi pressurizzati pre-sismici ricchi di sostanze chimiche possano essersi infiltrati nella zona di scorrimento della faglia (Fig. 37b) al momento della rottura del terremoto e aver contribuito a formare strutture fluidali co-sismiche ricche di sostanze chimiche esotiche (es. vanadio) come nel caso del sottostrato B ' (Figg. 30e-30h),

analogamente a strutture di faglia e fluidi cosismici precedentemente osservate altrove (Rowe e Griffith, 2015). Nel caso della Faglia del Monte Morrone, il verificarsi di inclusioni fluide che portano tracce di idrocarburi (Fig. 33), che sono comuni a livelli crostali intermedi sotto il Monte Morrone (Iadanza et al., 2016), corrobora ulteriormente il processo di risalita pre-/co-sismico di fluidi attraverso la crosta così come sopra descritto.

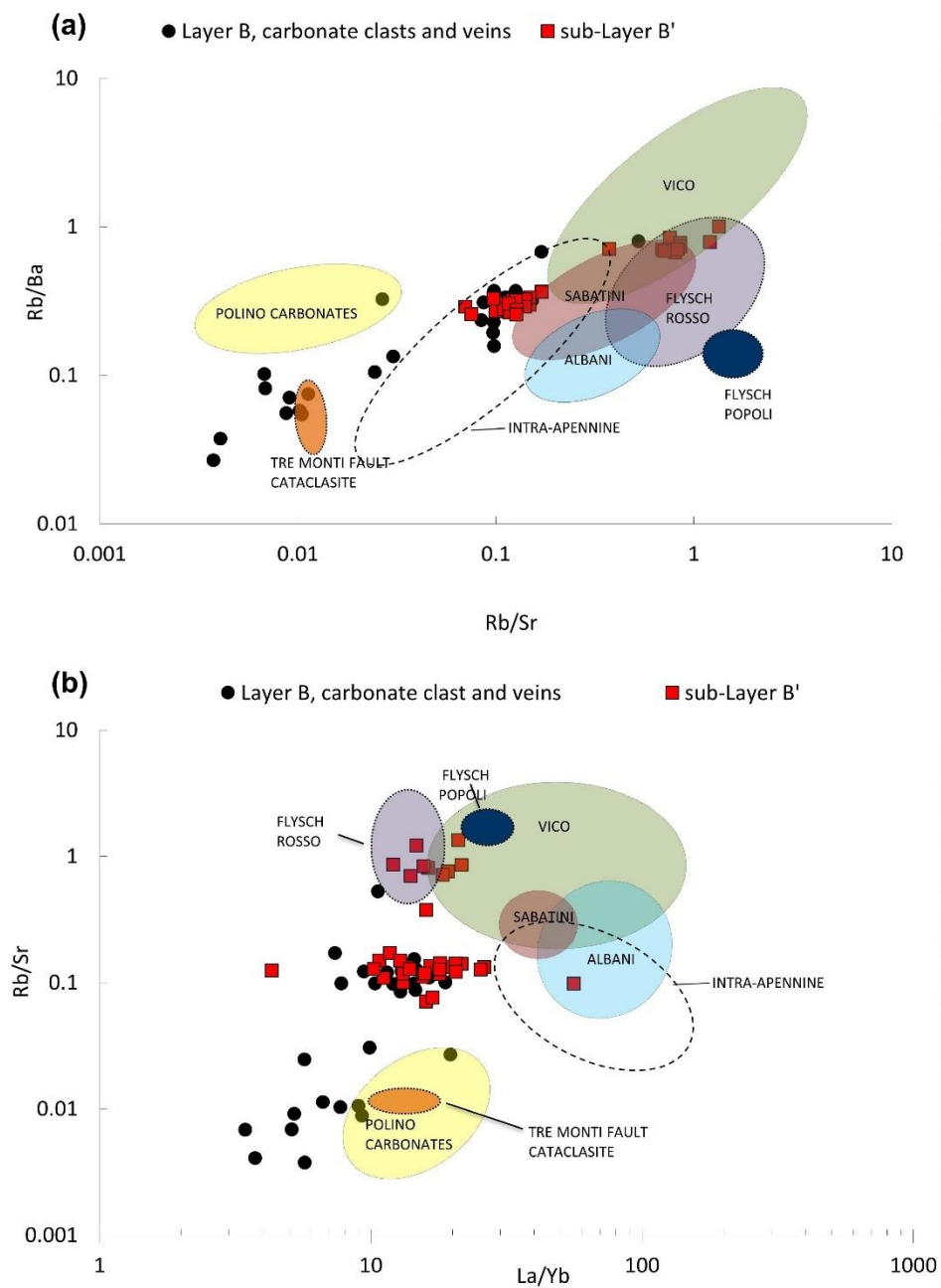


Figura 36. (a) rapporti La / Yb vs. Rb / Sr e (b) rapporti Rb / Sr vs. Rb / Ba per le zone di slittamento analizzate lungo la Faglia del Monte Morrone. I dati dei prodotti vulcanici provengono da Peccerillo (2005) e si riferiscono alle province magmatiche intra-appenniniche e romane dell'Appennino centrale (cioè Vico, Colli Albani e Monte Sabatini). I dati sulle rocce carbonatiche provengono da Rosatelli et al. (2010) e sono per i carbonati di Polino in Appennino centrale (Calcare Massiccio Fm.). I dati di Flysch provengono da Fiore et al. (2000) e da questo lavoro. I dati della Faglia di Tre Monti provengono da Smeraglia et al. (2016).

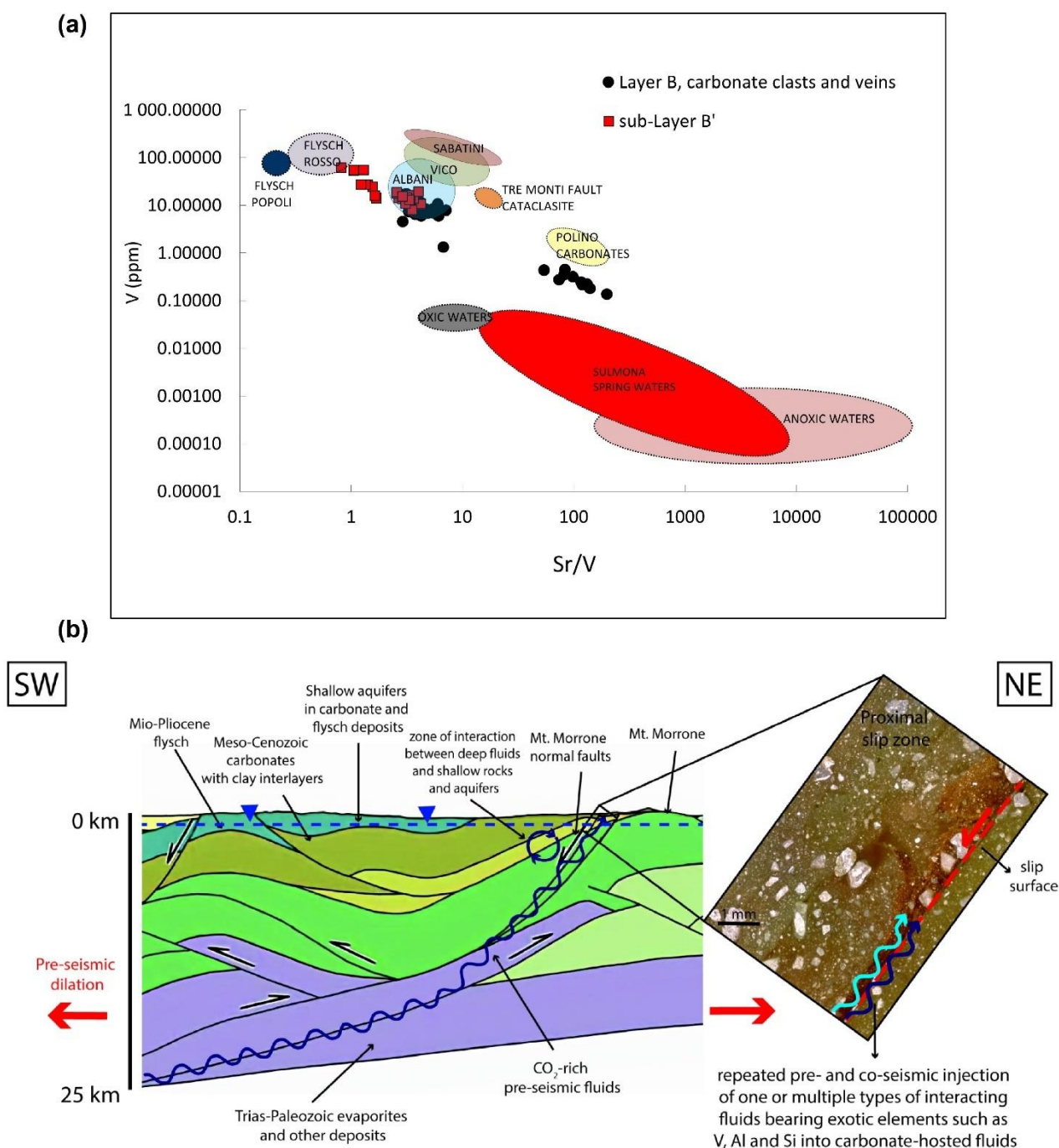


Figura 37. (a) Rapporto Sr / V rispetto al contenuto di Sr dei carbonati nella Faglia del Monte Morrone. I dati del prodotto vulcanoclastico provengono da Peccerillo (2005) e si riferiscono alle province magmatiche intra-appenniniche e romane dell'Appennino centrale (cioè Vico, Colli Albani e Monte Sabatini). I dati sulle rocce carbonatiche provengono da Rosatelli et al. (2010) e sono per i carbonati di Polino in Appennino centrale (Calcare Massiccio Fm.). I dati di Flysch provengono da Fiore et al. (2000) e da questo lavoro. I dati della Faglia di Tre Monti provengono da Smeraglia et al. (2016). I dati sui fluidi ossici e anossici provengono da Sappa et al. (2014) e Boschetti et al. (2005), rispettivamente. (b) Modello schematico

della risalita pre-sismica di fluidi ricchi di CO₂ in profondità lungo la Faglia del Monte Morrone e conseguente formazione di micro-strati fluidi ricchi di V nella zona di scorrimento (es. Sottostrato B '). La sezione geologica è dalla Fig. 1 (Patacca et al., 2008).

Con l'avanzare della conoscenza dei potenziali precursori idrogeochimici dei terremoti (ad esempio [Skelton et al., 2014](#); [Franchini et al., 2021](#)), diventa necessaria una conferma da strutture correlate ai paleofluidi riesumate per comprendere la frequenza e l'affidabilità di tali potenziali precursori. Questo studio e uno precedente in Islanda ([Andrén et al., 2016](#)) hanno questo merito, indicando la futura ricerca necessaria per validare, attraverso strutture fossili, potenziali precursori idrogeochimici dei terremoti. Allo stesso tempo, tale conferma o validazione è fattibile solo se i dati dei paleofluidi provengono da strutture pre-/co-sismiche chiaramente identificate (es. vene, micromineralizzazioni e relative inclusioni di fluidi). Questo studio e alcuni precedenti sopra citati contribuiscono all'identificazione di microstrutture pre-/co-sismiche legate ai paleofluidi lungo le faglie, dove tali microstrutture sono quindi fondamentali non solo per la comprensione dell'attrito di faglia ma anche per il progresso della conoscenza dei segnali precursori dei terremoti.

7. Modello Geochimico per i Precursori Idrogeochimici in Appennino Centrale

Il modello fisico che permette la risalita attraverso la crosta terrestre di fluidi profondi eventualmente ricchi di CO₂, metalli, metalloidi ed altri elementi chimici rari prima di un terremoto di magnitudo intermedia o elevata ($M_w > 5$) è noto e consiste sostanzialmente in una dilatazione pre-sismica del volume di roccia che sarà successivamente interessato dalla rottura sismica. Dunque, alcuni giorni, settimane o mesi prima del terremoto, il volume di roccia che successivamente ospiterà il terremoto stesso tende ad espandersi, fratturandosi e dunque richiamando geofluidi (soluzioni di acqua, metano, anidride carbonica ed altri fluidi) a riempire i vuoti creati dalle fratture. Tale modello è stato negli anni sviluppato soprattutto sulla base di dati provenienti dalla velocità delle onde sismiche (attraverso le rocce) che sono fortemente influenzate dalla presenza di vuoti e fratture nelle rocce. Un tale fenomeno è stato osservato e registrato prima del catastrofico terremoto de L'Aquila del 2009 ([Lucente et al., 2010](#)) e prima di numerosi altri forti terremoti ([Scholz et al., 1973](#); [Sibson, 1994, 2000](#)). Al contrario, un modello geochimico attendibile che spieghi i precursori geochimici di forti terremoti (ossia la risalita attraverso la crosta terrestre di fluidi profondi eventualmente ricchi di CO₂, metalli, metalloidi ed altri elementi chimici rari) non è stato ancora ben definito nella letteratura scientifica. Nell'ambito del Progetto HydroQuakes, un tale modello geochimico è stato sviluppato e pubblicato ([Boschetti et al., 2019](#); [Barbieri et al., 2020](#)) e viene di seguito illustrato.

A partire dalle anomalie pre-sismiche registrate da questo gruppo di ricerca, in relazione alla sequenza sismica di Amatrice-Norcia 2016-2017 (incrementi presismici delle concentrazioni di Arsenico, Vanadio e Ferro; [Barberio et al., 2017](#)) è stato sviluppato (in collaborazione con Tiziano Boschetti docente di geochimica all'università di Parma) un modello geochimico atto a descrivere i processi chimici in grado di provocare tali anomalie ([Boschetti et al., 2019](#)). La domanda a cui il modello si è trovato a rispondere è stata quella di verificare se un'eventuale risalita di gas profondi (CO₂ nel caso in questione), potesse o meno provocare incrementi di concentrazione di Arsenico e Vanadio nella soluzione acquosa. Per fare questo è stato prima

verificato l'eventuale ingresso di CO₂ profonda nel sistema carbonatico. Attraverso le relazioni note in letteratura (Chiodini et al., 2004) sono stati quindi calcolati i diversi contributi di CO₂ disciolta in soluzione (Fig. 38). Questo ha permesso di verificare che le anomalie sono state precedute da un aumento del contributo di CO₂ profonda (pallini blu in Fig. 38).

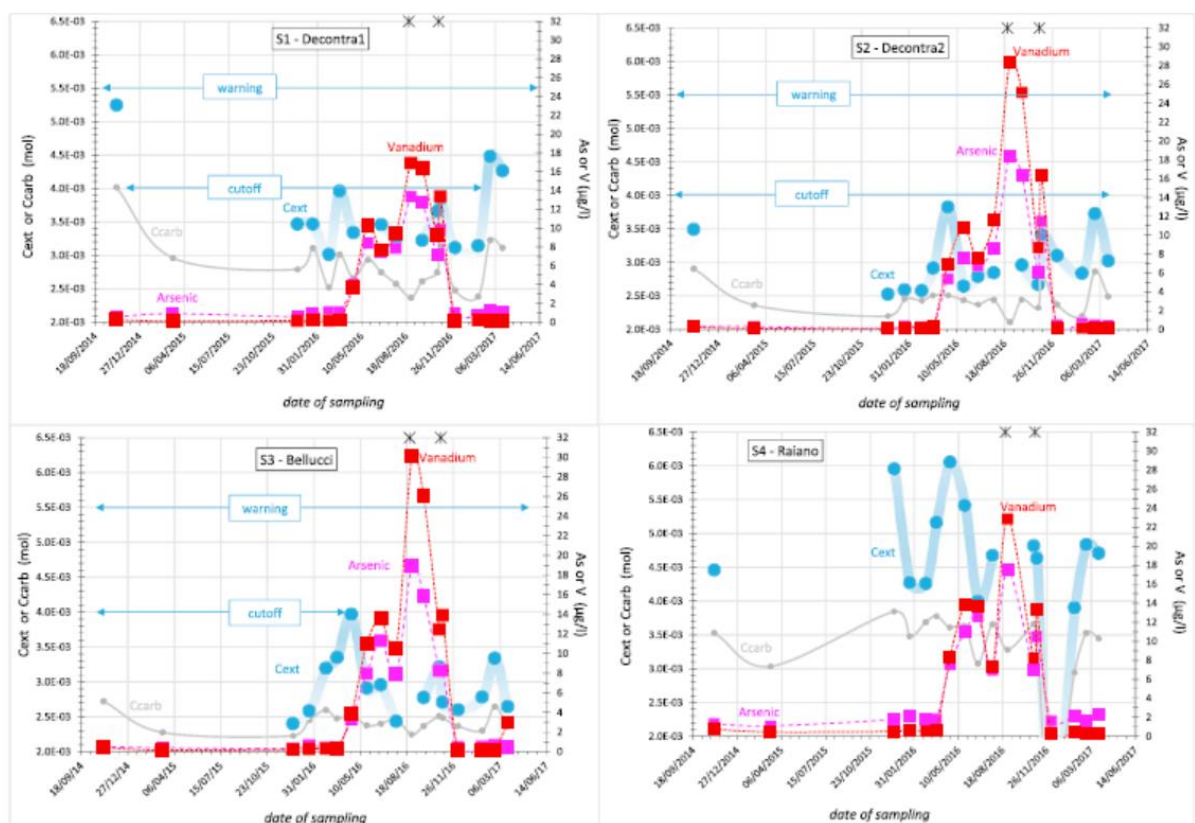


Figura 38. Serie temporali di 4 sorgenti di As, V, CO₂ profonda (Cext) e CO₂ superficiale (Ccarb).

Una volta verificata la prima ipotesi, abbiamo ipotizzato quale possibile sorgente dei metalli e metalloidi in soluzione, gli ossidi e idrossidi di Ferro che naturalmente agiscono da trappole geochimiche per questi elementi. Ciò ha permesso di passare alla fase di modellazione vera e propria. In questa fase, è stato scelto di partire da un campione d'acqua rappresentativo

di una situazione “normale” priva di anomalie (fase non sismica) e di simulare l’aumento della concentrazione di CO₂ in presenza di concentrazioni variabili di idrossidi di ferro attraverso l’aumento della fugacità di CO₂ (Fig. 39). Il risultato ottenuto da questa simulazione (curva rossa e blu in Fig. 39) è estremamente interessante poiché conferma le ipotesi di lavoro fatta restituendo un *fit* perfetto con i risultati ottenuti sui campioni reali (simboli in bianco e nero in Fig. 39).

Il modello idrogeochimico realizzato sulle acque delle sorgenti sottoposte a monitoraggio idrogeochimico in questo progetto ha offerto diversi spunti per approfondire le questioni legate alle migrazioni dei fluidi profondi (da circa 10 km) verso la superficie. In particolare, è stato scelto di studiare la relazione tra i rapporti isotopici del ¹³C/¹²C della CO₂, per meglio vincolarne l’origine e la genesi, e la geotermometria dei campioni selezionati. Per fare questo, sono state condotte delle specifiche campagne di campionamento mirate alla determinazione del contenuto isotopico della CO₂, sia sui siti sottoposti a monitoraggio che su altri siti nell’area del Reatino (Fig. 40).

I risultati isotopici ottenuti hanno permesso di identificare l’origine della CO₂ disciolta nelle acque delle sorgenti campionate e di verificare l’esistenza di processi di mixing tra acque superficiali e profonde nonché di caratterizzare il flusso di CO₂ prodotta dal metamorfismo e dal termo-metamorfismo in atto nel mantello e nella crosta terrestre (Barbieri et al., 2020). La comprensione di questi processi risulta essere di fondamentale importanza per la comprensione, nelle fasi di preparazioni di un potenziale evento sismico, dell’innesco delle anomalie geochimiche pre-sismiche.

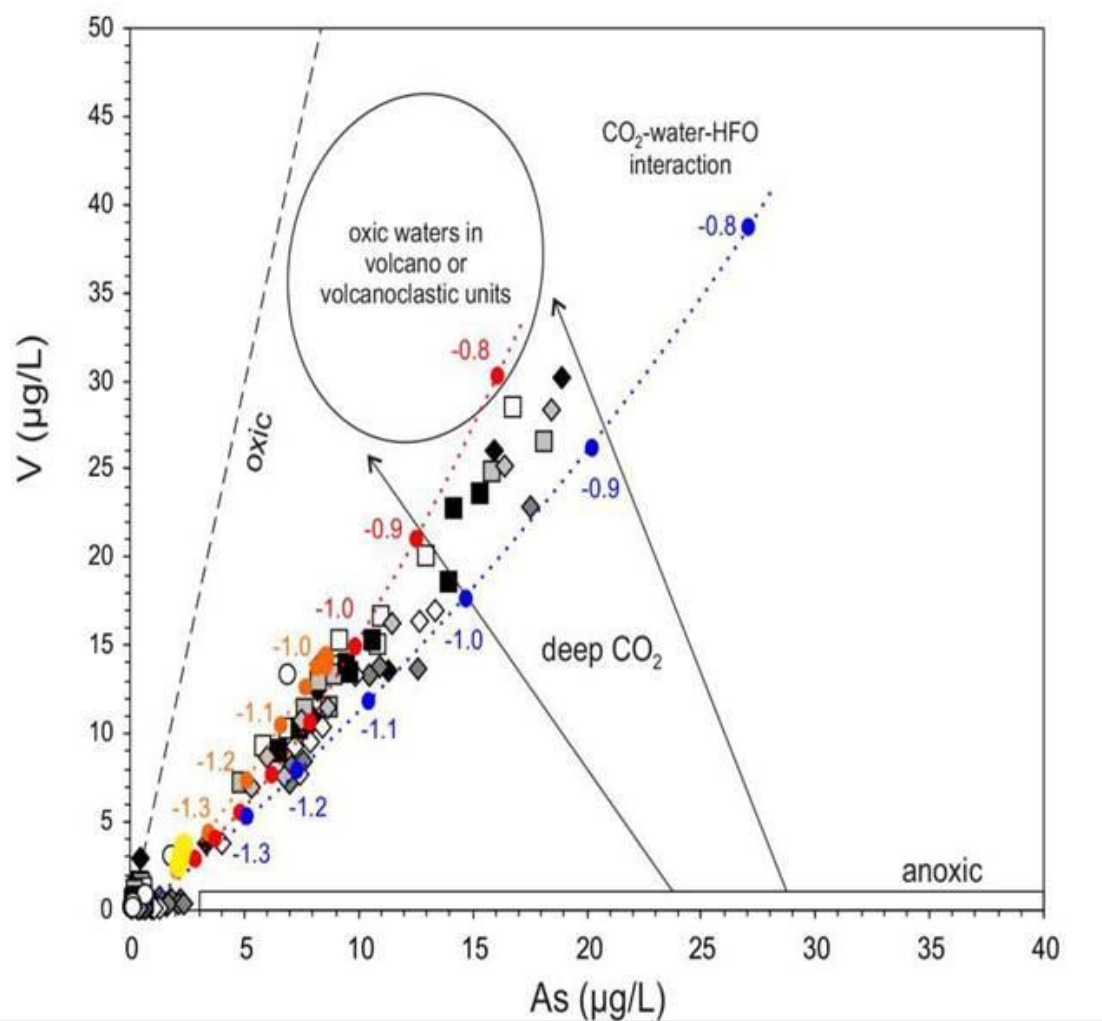


Figura 39. Vanadio e Arsenico in campioni reali (in bianco e nero) e dai risultati del modello geochimico (pallini colorati).

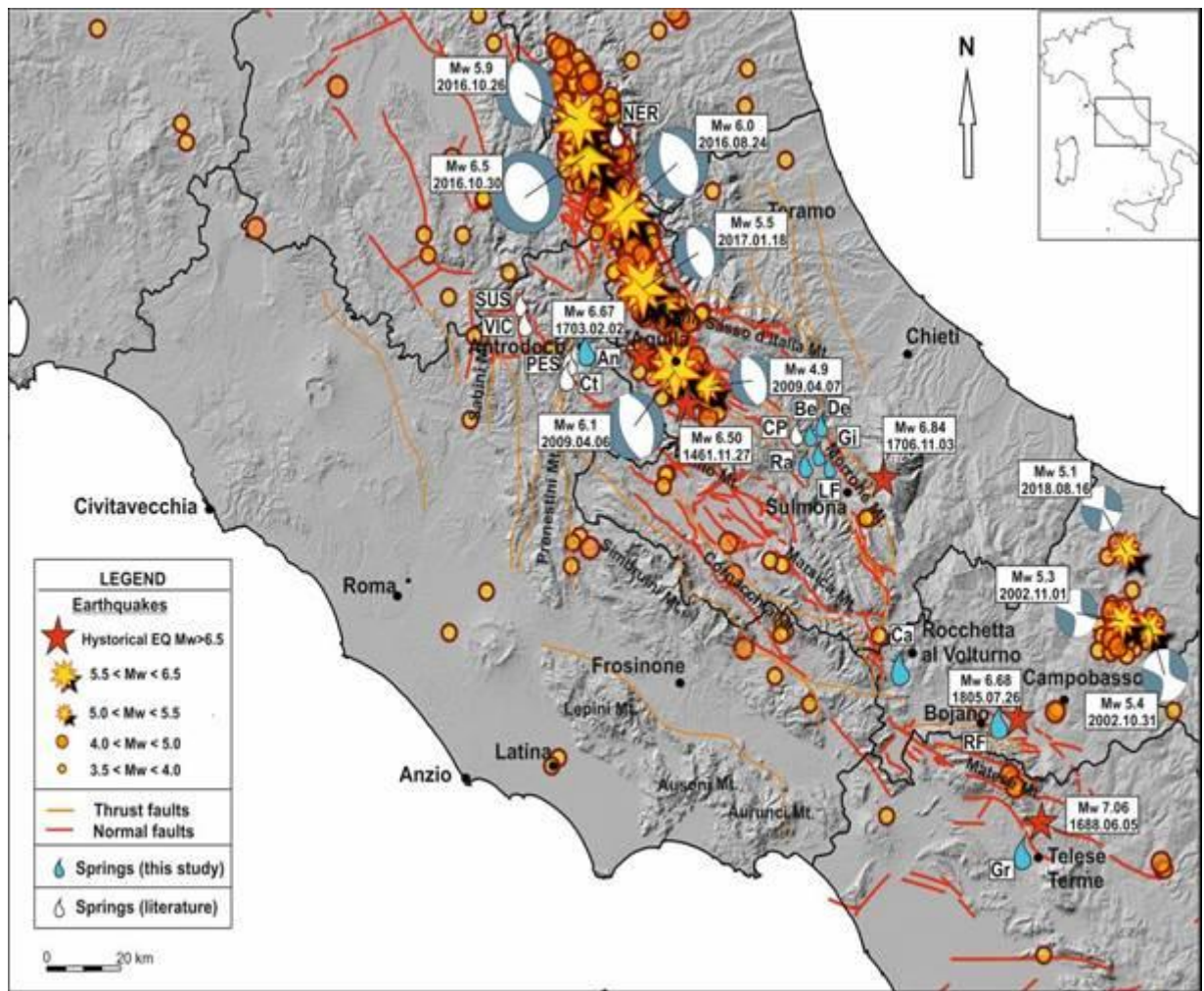


Figura 40. Siti di monitoraggio in Appennino centrale.

Lo studio isotopico condotto ha inoltre messo in luce una relazione lineare tra il rapporto $^{13}\text{C}/^{12}\text{C}$ della CO_2 e alcuni elementi in traccia presenti in soluzione quali Litio e Boro. Proprio quest'ultima osservazione ha aperto la strada alla possibilità, attraverso la modellazione idrogeochimica, di definire le temperature di equilibrio dei fluidi analizzati alla profondità di dissoluzione di questi elementi (Fig. 41). L'intervallo di temperatura per le acque campionate è stato dedotto da un'equazione basata sul rapporto Na/Li e sulla modellazione geotermica, ed è compreso tra 113-130 °C (Fig. 42). A livello generale, l'intervallo di temperatura calcolato concorda con quello misurato in pozzi profondi nell'Appennino settentrionale.

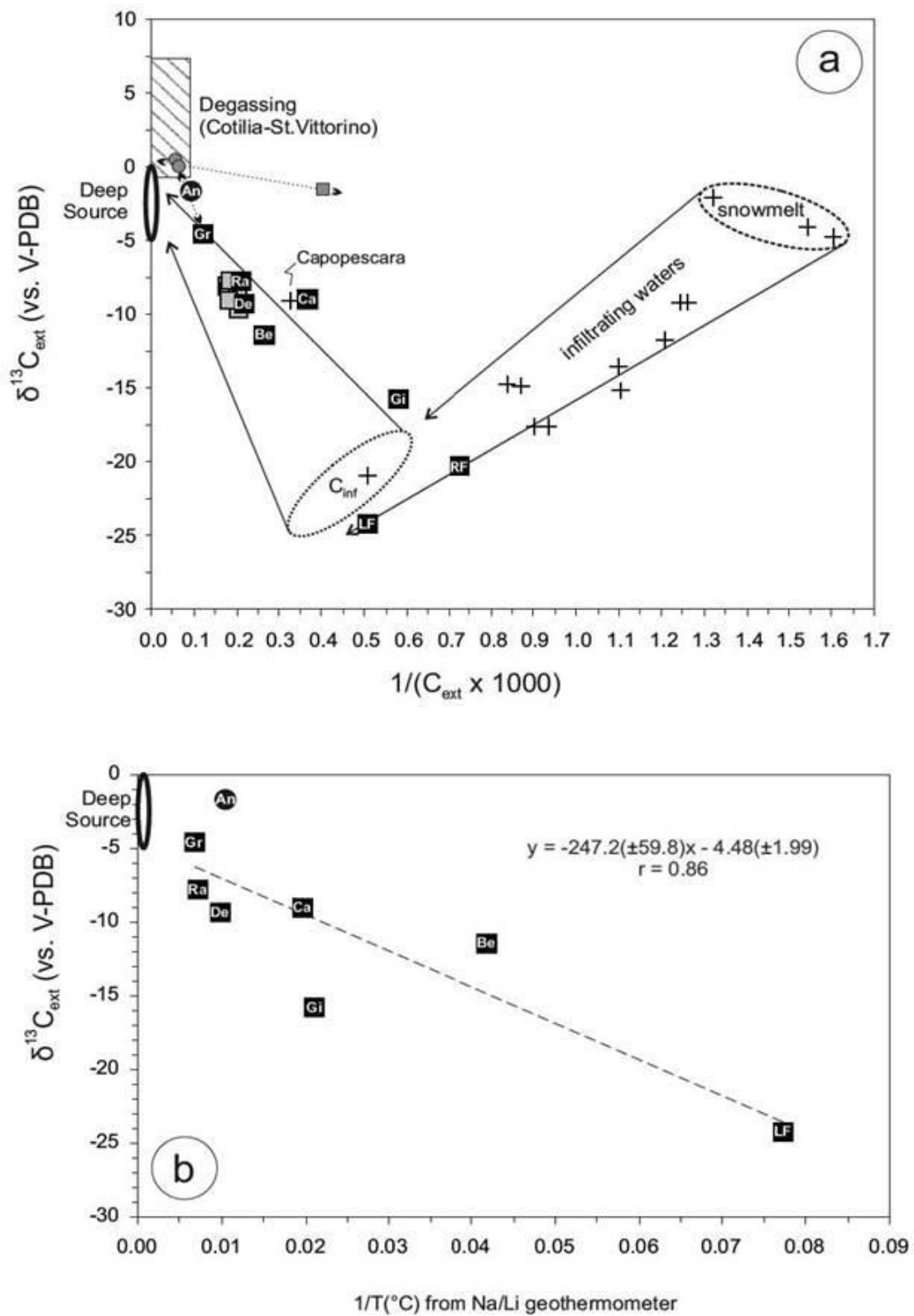


Figura 41. (a) Diagramma $\delta^{13}C_{ext} / 1/C_{ext}$. (b) $\delta^{13}C_{ext} / 1/T$, dove T = temperatura in $^{\circ}C$ ottenuta dall'applicazione del geotermometro Na/Li, versus $\delta^{13}C_{ext}$.

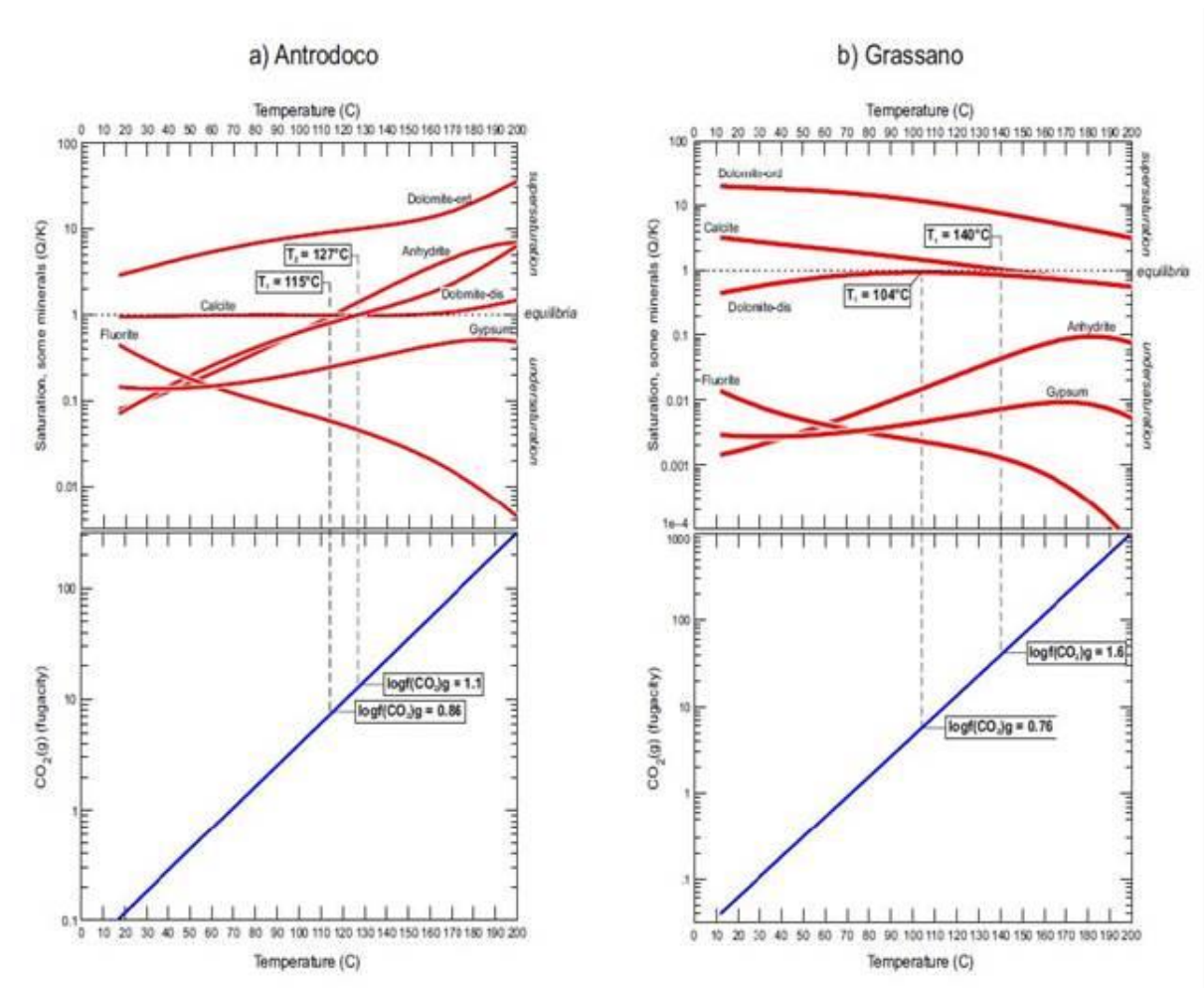


Figura 42. Modello geotermometrico di Antrodoto e Grassano.

Lo studio isotopico della CO₂ accoppiato al monitoraggio geotermometrico delle sorgenti potrebbe quindi aiutare a distinguere tra i contributi di gas e fluidi profondi e gas e fluidi superficiali. I risultati di questo studio indicano che le faglie svolgono un ruolo cruciale nel controllo della migrazione dei fluidi crostali e mantellici. Inoltre, rivelano che l'eventuale valutazione di potenziali precursori sismici richiede obbligatoriamente un lungo periodo di monitoraggio continuo e su ampie aree tale da definire il flusso di gas caratteristico di una determinata area ed una sua eventuale variazione sintomatica quindi di variazioni di stress lungo le principali direttrici di flusso ossia le faglie stesse.

8. Risultati: Precursori Sismici e Vulcanici in Islanda del Nord

8.1. Razionale e Stato dell'Arte

I campioni analizzati in questo studio sono stati prelevati dal pozzo artesiano HA-01 (Lat. 65.8722°N, Long. 17.4528°W) nella località di Hafralækur, nel nord dell'Islanda, all'interno della Tjörnes Fracture Zone, in corrispondenza delle valli fluviali dei fiumi Laxà e Skàlfandafljót. L'acqua che entra all'interno di questo pozzo ha una temperatura di 71-76°C, un pH di circa 10.2 (a ~ 25°C) e un contenuto in sali disciolti di circa 240 ppm, tipico delle acque sotterranee delle aree geotermiche a bassa temperatura nelle zone interne dell'Islanda. Inoltre, l'acqua analizzata è caratterizzata da miscelazione tra acque superficiali e acque profonde e da interazione acqua-roccia ([Skelton et al., 2019](#)).

Questo studio è stato svolto in collaborazione con il dipartimento di Scienze Geologiche di Stoccolma e con l'Istituto di Scienze della Terra di Reykjavik, i quali ci hanno fornito un database con tutti i parametri chimico-fisici e isotopici dell'acquifero analizzato. Lo studio è stato condotto per avere un termine di confronto con i dati ed i risultati ottenuti in Appennino centro-meridionale.

I cambiamenti idrogeochimici legati ai terremoti sono stati documentati sin dai tempi storici ([Manga e Wang, 2015](#)). La maggior parte di questi cambiamenti sono stati registrati in concomitanza e/o dopo eventi sismici ([Wakita 1975](#); [Igarashi et al., 1995](#); [Manga et al., 2003](#); [Cucci et al., 2019](#); [Kawabata et al., 2020](#); [Kim et al., 2019](#); [Hosono e Masaki 2020](#); [Sato et al., 2020](#); [Barberio et al., 2020](#); [Chiodini et al., 2020](#)); recentemente, tuttavia, le variazioni idrogeochimiche anomale prima di terremoti $M_w \geq \sim 5$ hanno iniziato a essere sistematicamente misurate e documentate ([Claesson et al., 2004](#); [Chen et al., 2013](#); [Skelton et al., 2014, 2019](#); [Chen et al., 2015](#); [Barberio et al., 2017](#); [De Luca et al., 2018](#); [Onda et al., 2018](#); [Boschetti et al., 2019](#); [Sano et al., 2020](#)). Infatti, la mancanza o la scarsità, fino a tempi recenti, di un monitoraggio idrogeochimico continuo ed a lungo termine finalizzato allo studio del ciclo sismico

([Ingebritsen e Manga 2014](#); [Skelton et al., 2019](#); [Zhou et al., 2020](#)) hanno notevolmente limitato la capacità degli scienziati ad identificare e comprendere appieno eventuali precursori sismici di natura idrogeochimica. Mentre le reti sismologiche e anche geodetiche (GPS) sono attive da molti anni in tutto il mondo, fornendo importanti informazioni sulla deformazione della crosta e sui cicli sismici (ad esempio, [Chiarabba et al., 2020](#)), le reti idrogeochimiche per l'identificazione dei precursori sismici hanno iniziato ad emergere solo di recente in Cina, Islanda, Italia, Giappone, Stati Uniti occidentali e pochi altri paesi (ad esempio, [Chaudhuri et al., 2013](#); [Hosono e Masaki, 2020](#); [Franchini et al., 2021](#)). Queste nuove reti o singole stazioni di monitoraggio hanno prodotto risultati significativi sulle variazioni idrogeochimiche pre-sismiche probabilmente connesse alle fasi dilatative preparatorie di terremoti medio-forti. In particolare, i cambiamenti pre-terremoto nella temperatura delle acque sotterranee (ad esempio, [Shi e Wang, 2014](#); [He e Singh, 2019](#)) e nella composizione chimica (ad esempio, [Claesson et al., 2004](#); [Barberio et al., 2017](#); [Onda et al., 2018](#); [Boschetti et al., 2019](#); [Nakagawa et al., 2020](#); [Skelton et al., 2019](#), [Shi et al., 2020](#); [Hosono et al., 2020](#), [Franchini et al., 2021](#)), nonché modifiche nella geochimica dei gas naturale (ad esempio, [Wakita et al., 1980](#); [King et al., 2006](#); [Sano et al., 2016](#); [Buttitta et al., 2020](#); [Martinelli et al., 2020](#)) sono stati adeguatamente documentati e interpretati come potenziali sismici precursori.

Come accennato in precedenza, stanno ora emergendo reti di monitoraggio idrogeochimico per l'identificazione dei precursori sismici, mentre i precursori delle eruzioni vulcaniche sono principalmente ricercati e identificati attraverso il monitoraggio sismico e geodetico ([Patanè et al., 2003](#); [Sparks, 2003](#); [McNutt, 2015](#)) o attraverso misurazioni geochimiche spesso (ma non solo) sulle emissioni prossimali come fumarole, sorgenti termali e laghi vulcanici ([Aiuppa et al., 2007](#); [De Moor et al., 2016](#)). Al contrario, il monitoraggio idrogeochimico intermedio o remoto dei vulcani per l'identificazione dei precursori dell'eruzione, sebbene utilizzato, è più raro ([Armienta e De la Cruz Reyna, 1995](#); [Caracausi et al., 2003](#)). Di

seguito, mostreremo che questo metodo remoto potrebbe essere adatto e affidabile oltre a facilitare il campionamento delle emissioni di fluido vulcanico prossimale.

Dal 2002, nel nord dell'Islanda è in funzione un sistema di monitoraggio idrogeochimico con l'obiettivo principale di identificare potenziali precursori dei terremoti. Una stazione di monitoraggio è stata impostata a Húsavík (HU01) e l'altra a Hafralækur (HA01) (Claesson et al., 2004, 2007; Skelton et al., 2014, 2019; Andrén et al., 2016). HA01, da cui provengono i campioni analizzati in questo studio, è costituito da un pozzo profondo 101 m situato a Lat. 65,8722 ° N e Long. 17.4528 ° O (Fig. 43). Questo pozzo è stato costantemente monitorato dal 2008. Il sistema di monitoraggio ha consentito agli scienziati di identificare i cambiamenti idrogeochimici (interpretati come potenziali precursori sismici) prima di tre grandi terremoti ($M_w > 5,0$) che si sono verificati al largo dell'Islanda settentrionale il 16 settembre 2002, 21 ottobre 2012 e il 2 aprile 2013, rispettivamente. Prima dei terremoti del 2012 M_w 5.6 e del 2013 M_w 5.4, sono state registrate anomalie significative nelle concentrazioni di Na, Ca, Si, $\delta^{18}\text{O}$ e $\delta^2\text{H}$ nelle acque sotterranee presso la stazione idrogeochimica HA01 (Skelton et al., 2014). Questi studi sono stati poi seguiti da modelli geochimici e studi statistici per spiegare e verificare interpretazioni precedenti (Andrén et al., 2016; Skelton et al., 2019). Inoltre, prima del terremoto del 2002 M_w 5.8 avvenuto al largo dell'Islanda settentrionale, sono state rilevate anomalie significative di Cu, Zn, Mn e Cr nelle acque sotterranee analizzate dal pozzo HU01 (a 20 km dal pozzo HA01) a Húsavík (Baia di Skjálfandi; Fig. 43) insieme agli spostamenti pre e post sismici delle concentrazioni nelle acque sotterranee di B, Ca, K, Li, Mo, Na, Rb, S, Si, Sr, Cl, SO_4 , $\delta^{18}\text{O}$ e $\delta^2\text{H}$ (Claesson et al., 2004).

Per espandere le analisi idrogeochimiche delle acque sotterranee HA01 monitorate e identificare ulteriori potenziali precursori di terremoti nel nord dell'Islanda, nel 2018 è stata stabilita una collaborazione internazionale tra l'Università di Stoccolma, l'Università d'Islanda a Reykjavík, l'Università Sapienza di Roma e il CNR-IGAG di Roma nell'ambito del Progetto HydroQuakes finanziato da Fondazione ANIA. Nell'ambito di questa collaborazione, le

concentrazioni di elementi in tracce nelle acque sotterranee campionate dal pozzo HA01 tra il 2010 e il 2018 sono state analizzate insieme ai dati di terremoti e vulcanici nello stesso periodo.

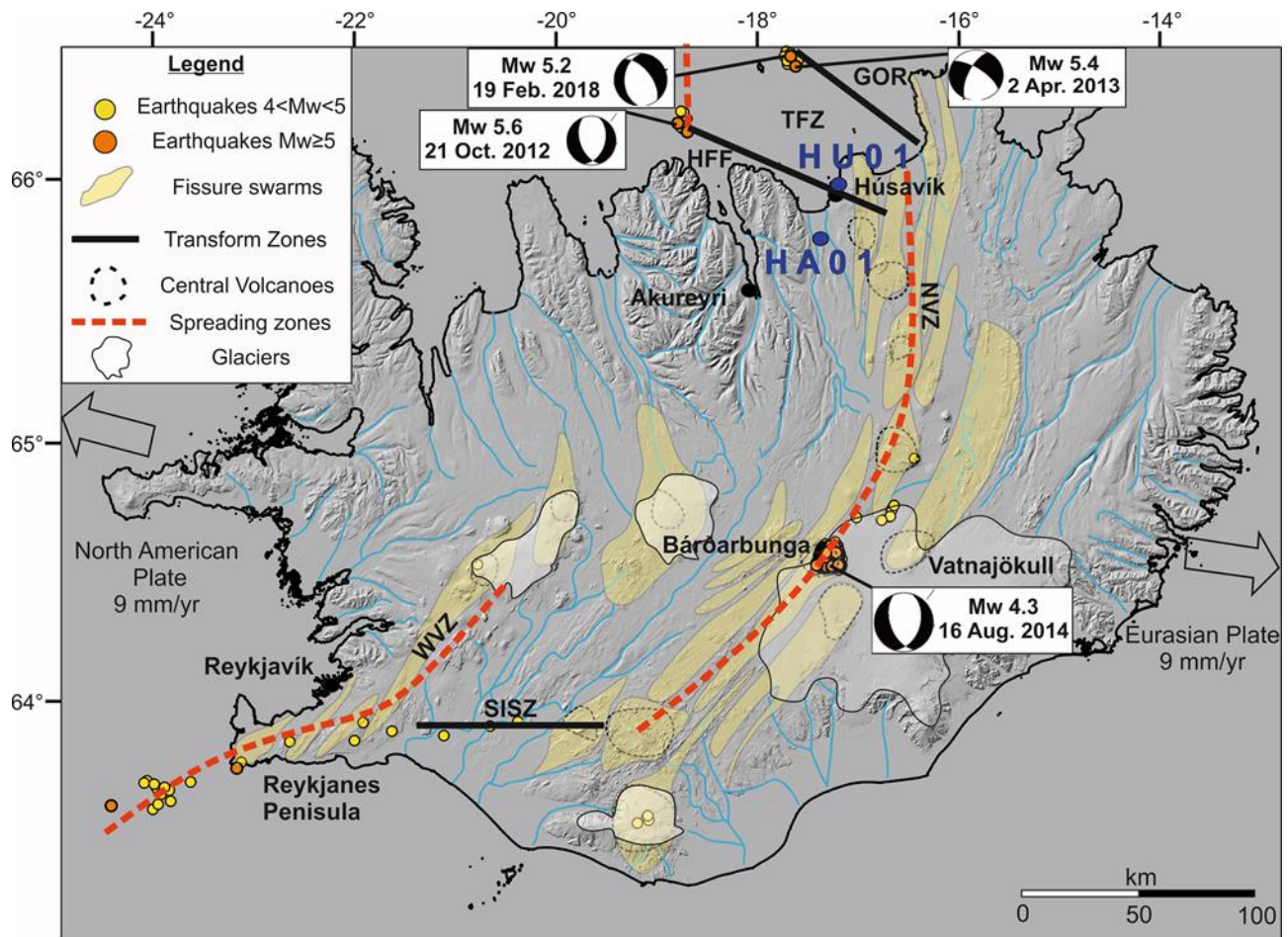


Figura 43. Mappa dell'Islanda. I siti di campionamento delle acque sotterranee a Hafralækur (HA01) e Húsavík (HU01), nel nord dell'Islanda, sono visualizzati con simboli blu. Sono anche mostrati il vulcano Bárðarbunga e i ghiacciai (ad esempio, Vatnajökull). Le zone di diffusione e le zone di trasformazione principale sono rappresentate rispettivamente con linee tratteggiate rosse e linee continue nere. Gli sciami di fessure vengono visualizzati come aree ombreggiate in giallo (da Árnason, 2020). Gli epicentri dei terremoti (2010-2018) sono rappresentati con punti arancioni e gialli a seconda della magnitudo (<http://www.vedur.is>). Vengono mostrati anche i meccanismi focali di terremoti selezionati (21 ottobre 2012, Mw 5.6; 2 aprile 2013, Mw 5.4; 16 agosto 2014, Mw 4.0; 19 febbraio 2018, Mw 5.2) (<http://www.globalcmt.org/>; Ekström et al., 2012).

Abbiamo quindi utilizzato analisi statistiche per identificare tendenze temporali e punti di cambiamento nelle serie temporali degli elementi in traccia, nonché calcoli geochimico-termodinamici per vincolare l'origine degli elementi osservati. I risultati mostrano nuovi potenziali precursori idrogeochimici di terremoti $M_w \geq \sim 5$ e potenziali precursori idrogeochimici remoti di eruzioni vulcaniche. Questi risultati sono integrati con precedenti risultati idrogeochimici ottenuti dallo stesso sistema di monitoraggio ([Skelton et al., 2019](#)) per una migliore comprensione dei processi idrogeochimici e fisici che si verificano durante le fasi preparatorie di terremoti medio-forti ed eruzioni vulcaniche in Islanda. Il nostro scopo principale è far progredire la scienza dei precursori idrogeochimici dei terremoti e delle eruzioni vulcaniche. I nostri risultati fanno parte di un primo passo provvisorio verso la formazione del background necessario per formulare protocolli nazionali volti all'identificazione dei precursori sismici e vulcanici e alla relativa mitigazione dei pericoli.

L'Islanda si trova sulla dorsale medio-atlantica tra i margini divergenti delle placche dell'Eurasia, a est, e il Nord America, a ovest (ad esempio, [Einarsson 1991, 2008](#)). In dettaglio, si trova tra la cresta Reykjanes, a sud, e la cresta Kolbeinsey, a nord ([Einarsson 1991, 2008; Árnadóttir et al., 2008; Fig. 43](#)). L'ambiente tettonico dell'Islanda è dominato da uno spostamento verso est della dorsale medio atlantica a causa di un punto caldo attualmente situato all'incirca sotto il ghiacciaio Vatnajökull, nel sud-est dell'Islanda ([Thordarson e Larsen, 2007](#)). Due zone di trasformazione collegano il segmento di cresta spostato alla dorsale medio atlantica: la zona sismica dell'Islanda meridionale (SISZ) a sud e la zona di frattura di Tjörnes (TFZ) a nord ([Fig. 43](#)). La TFZ attraversa l'area indagata in questo lavoro nel nord dell'Islanda.

La TFZ è una zona trasforme obliqua oceanica lunga circa 120 km e larga 70 km, che collega la Northern Volcanic Rift Zone, a sud, e l'estremità meridionale del sottomarino Kolbeinsey Ridge, a nord ([Einarsson, 1991, 2008; Stefansson et al., 2008](#)). Questa zona di frattura con orientazione WNW-ESE include due principali strutture trasformati, Grímsey Oblique

Rift (GOR) e Húsavík-Flatey Fault (HFF) (Fig.43; Gudmundsson et al., 1993, 2007; Rögnvaldsson et al., 1998 ; Stefánsson et al., 2008; Wästeby et al., 2014; Tibaldi et al., 2020).

L'attività sismica in Islanda è principalmente legata alle dinamiche di trasferimento estensionale e laterale associate alla cinematica della dorsale medio atlantica. L'attività sismica è quindi localizzata principalmente lungo i segmenti di cresta mentre è più rara nelle zone intraplacche. I terremoti nel nord dell'Islanda si verificano principalmente nella zona della frattura di Tjörnes (Gudmundsson, 2007), lungo la faglia di Húsavík-Flatey e la spaccatura obliqua di Grímsey (IMO, 2016; Fig.43). I movimenti di faglia nella zona di frattura di Tjörnes sono responsabili dell'alto livello di attività sismica di questa zona, che ha ospitato più di dieci terremoti $M_w > 6$ negli ultimi 300 anni (Gudmundsson et al., 1993, 2007; Rögnvaldsson et al., 1998; Stefánsson et al., 2008; Wästeby et al., 2014; Skelton et al., 2019). Inoltre, sono stati registrati terremoti moderati-forti associati all'attività di vulcani come Katla, Krafla e Bárðarbunga (Einarsson e Björnsson, 1979; Einarsson, 2008).

Durante il nostro periodo di monitoraggio (2010-2018), i principali eventi sismici e vulcanici verificatisi nell'Islanda centrale e settentrionale sono stati quattro terremoti $M_w \geq 5.0$ nella TFZ e un'eruzione vulcanica. I terremoti si sono verificati al largo dell'Islanda settentrionale lungo l'HFF occidentale nel 2012 (terremoti M_w 5,4 e 5,6 si sono verificati a Lat. 66,333 ° N e Long. -18,805 ° W, e Lat. 66,299 ° N e Long. -18,714 ° W, rispettivamente) , lungo il Grímsey Oblique Rift nel 2013 (terremoto M_w 5,4 avvenuto a Lat. 66,547 ° N e Long. -17,661 ° W), e nel 2018 (terremoto M_w 5,2 avvenuto a Lat. 66,586 ° N e Long. -17,708 ° W) (Fig. 43).

L'eruzione vulcanica è avvenuta a Holuhraun, appena a nord del ghiacciaio Vatnajökull, e faceva parte di un evento di fessurazione che ha avuto origine nell'area del vulcano Bárðarbunga (Fig. 43). L'evento di rifting è iniziato il 16 agosto 2014, con un dicco magmatico che si è propagato gradualmente per 48 km verso nord-est dal vulcano Bárðarbunga fino al 27 agosto, seguita da un'attività eruttiva iniziata il 29 agosto 2014 e terminata il 27 febbraio 2015 (Sigmundsson et al., 2015; Andren et al., 2016).

Il pozzo di monitoraggio idrogeochimico HA01, che è la fonte dei campioni d'acqua analizzati in questo documento, si trova nell'area di Hafralækur ([Fig. 43](#)) ed è installato in un'area geotermica a bassa temperatura, appena a sud della Tjörnes Fracture Zone (TFZ) e ~ 20 km a sud della città di Húsavík ([Andrén et al., 2016](#)). Nell'area di Hafralækur-Húsavík, il substrato roccioso è costituito principalmente da lave mafiche e intermedie dall'età terziaria all'età olocenica con sedimenti intercalati ([Jóhannesson, 2014](#)). Il pozzo HA01 è profondo 101 m e penetra in uno strato di sedimenti derivati dal basalto sotto il Younger Laxá Lava e successivamente tre flussi di lava ([Andrén et al., 2016](#)). Dal pozzo, l'acqua artesianica defluisce naturalmente dopo la circolazione in basalti e sedimenti derivati dal basalto. Il pozzo è rivestito fino a una profondità di 35 m, con filtri per l'ingresso dell'acqua posti a 65, 82 e 96 m, per un totale di 7,7 L / s. La falda freatica del pozzo è calda, con temperature di 71-76 ° C, e alcalina con un pH di ~10,2 (a 25 ° C). L'acqua di falda ha un basso contenuto di solidi disciolti (240 ppm), tipico delle acque sotterranee geotermiche fresche a bassa temperatura sui fianchi della zona di rift attiva in Islanda ([Kristmannsdóttir et al., 2010](#); [Skelton et al., 2014, 2019](#) ; [Andrén et al., 2016](#)).

8.2. Metodi

Abbiamo raccolto campioni d'acqua dal pozzo HA01, su base settimanale, da ottobre 2008 ad oggi (2021). In questo lavoro, consideriamo la finestra temporale da settembre 2010 a giugno 2018. Abbiamo raccolto diversi campioni per la determinazione degli elementi principali (cationi e anioni) e del contenuto di elementi in tracce e per l'analisi degli isotopi. Abbiamo filtrato i campioni di acque sotterranee in situ attraverso un filtro da 0,2 µm in bottiglie di polietilene lavate con acido. Abbiamo aggiunto Suprapur® HNO₃ concentrato (Merck KGaA, Darmstadt, Germania) a quei campioni (1 ml HNO₃ per 100 ml campione) raccolti per gli elementi principali da analizzare su un ICP-OES (spettrometro di emissione ottica al plasma accoppiato induttivamente). Abbiamo refrigerato (~ 5 ° C) e conservato i campioni a Húsavík (Islanda

settentrionale) e poi inviati all'Università di Stoccolma e all'Università dell'Islanda a Reykjavík per le analisi degli isotopi stabili ($\delta^{18}\text{O}$ e $\delta^2\text{H}$) e delle concentrazioni dei principali elementi, rispettivamente. Abbiamo inviato campioni di acqua acidificata a Roma per l'analisi della concentrazione di elementi in tracce ([Franchini et al., 2021](#) per metodi analitici dettagliati). Abbiamo effettuato quest'ultima analisi sulle stesse aliquote del campione precedentemente utilizzate per l'analisi degli elementi principali ([Skelton et al., 2014; 2019; Andrén et al., 2016](#)). Abbiamo misurato la concentrazione di oligoelementi disciolti (cioè litio, berillio, boro, alluminio, vanadio, cromo, manganese, ferro, cobalto, nichel, rame, zinco, gallio, arsenico, rubidio, stronzio, molibdeno, cadmio, indio, antimonio, cesio, piombo e uranio), presso il Laboratorio di Geochimica della Sapienza Università di Roma con una spettrometria di massa al plasma accoppiato induttivamente ICP-MS (X Series 2 Thermo Fisher Scientific) ([Ricolfi et al., 2020](#)). Per mantenere la stabilità degli oligoelementi nelle soluzioni fino all'analisi, nel laboratorio ICP-MS, abbiamo ricontrollato il pH dei campioni di acqua acidificata e abbiamo aggiunto Suprapur® HNO_3 fino a $\text{pH} < 2$, se necessario ([Marcovecchio et al., 2014](#)). Abbiamo utilizzato acqua ultrapura (Millipore, Milli-Q, 16 $\text{M}\Omega\text{ cm}$) per preparare i bianchi, soluzioni standard, diluizioni dei campioni e uno standard interno, Rh, per correggere la deriva strumentale ICP-MS. L'accuratezza analitica di questo metodo varia tra il 2% e il 5% ([Barberio et al., 2017; Nigro et al., 2017](#)). Abbiamo analizzato, dopo ogni decimo campione, il bianco e due materiali di riferimento standard (SRM1640a) acquistati dal National Institute of Standards and Technology (Stati Uniti) come campioni di acqua. La misurazione delle incertezze per tutti i vincoli è stata eseguita e controllata utilizzando una replica regolare di laboratorio dei campioni e confermando la precisione / calibrazione dello strumento su cicli regolari con soluzioni standard. I recuperi degli analiti di interesse erano compresi tra il 98,4 e il 106,3% e i recuperi dell'SRM1640a erano compresi tra il 91,2 e l'111,6%. Abbiamo utilizzato l'aggiunta di isotopi ^{206}Pb , ^{207}Pb e ^{208}Pb per misurare la concentrazione di piombo ([Ricolfi et al., 2020](#)).

Abbiamo anche applicato l'analisi dei componenti principali (PCA) ai campioni di acqua studiati. Questa analisi multivariata è uno strumento statistico utile per scoprire relazioni insospettite, riducendo la dimensionalità del set di dati, pur conservando le informazioni presenti nella struttura dei dati. È stato applicato con successo per spiegare la composizione idrogeochimica delle acque geotermiche in diversi contesti geologici ([Awaleh et al., 2020](#); [Boschetti et al., 2003](#); [Nicholson, 1993](#)). Per la PCA "classica" sono stati utilizzati codici diversi come OriginPro versione 2019b (OriginLab Corporation, Northampton, MA, USA) e SPSS versione 16 (rilasciata nel 2019; Armonk, NY: IBM Corp; IBM, 2019). Prima dell'estrazione PCA, l'adeguatezza del campionamento della matrice dei dati è stata verificata in termini di rapporto "soggetto a variabili" ([Bryant e Yarnold 1995](#); [Hutcheson e Sofroniu, 1999](#); [Hatcher e O'Rourke, 2013](#); [Garson, 2018](#)), Kaiser -Meyer-Olkin e il test di sfericità di Bartlett (IBM, 2019). I risultati vengono anche confrontati con Categorical PCA (CATPCA) e Robust PCA (RPCA; [Filzmoser e Todorov 2013](#); [Hubert et al., 2016](#)). Altri dettagli sono discussi di seguito nella sezione dedicata.

Inoltre, abbiamo utilizzato l'analisi del punto di cambiamento (change-points) sulla serie temporale di dati chimici. Un punto di cambiamento (CP) è il punto in cui una sequenza ordinata di dati ($y_1, y_2, \dots, y_n$) cambia le sue proprietà statistiche ([Skalska, 2017](#)). Alcuni codici disponibili gratuitamente possono risolvere il rilevamento e la valutazione statistica dei cambiamenti nelle tendenze dei dati ([Skalska, 2017](#)). Il programma di regressione Joinpoint (JRP), versione 4.8.0.1, è un pacchetto software che inserisce i dati in modelli di joinpoint (programma di regressione Joinpoint, 2020). Il software consente all'utente di verificare se un'apparente variazione di tendenza è statisticamente significativa. Una sequenza di test di permutazione (metodo Monte Carlo) identifica i punti di cambiamento tra le tendenze. La procedura si basa su un'applicazione sequenziale di test del tipo di rapporto di verosimiglianza ([Kim et al., 2000](#)). Questa breve descrizione non cerca di essere matematicamente o statisticamente esaustiva; pertanto, si rimanda il lettore alla letteratura di riferimento per maggiori dettagli. In questo studio le condizioni operative del codice erano le seguenti: i) per ovviare al fatto che le date di

campionamento degli oligoelementi non hanno periodicità regolare, errore standard del 5% (cioè superiore al 2% reale) è stato preso in considerazione per ciascuna concentrazione di dati grezzi prima dell'elaborazione; ii) come elaborazione del modello è stato scelto il Weighted Bayesian Information Criteria (WBIC). Quest'ultimo combina sia i tradizionali criteri di informazione bayesiana (BIC) che la sua modifica con una penalità più severa (BIC3) utilizzando un termine di penalità ponderato basato sulla caratteristica dei dati ([Joinpoint Regression Program, 2020](#)).

Per quanto riguarda i dati sismici, abbiamo considerato i terremoti dal 1 settembre 2010 al 31 dicembre 2018, ~ 800 eventi sismici ($M_w \geq 4$) si sono verificati in Islanda ([Fig. 43](#)). Questi terremoti erano per lo più legati all'attività vulcanica e al collasso della caldera di Bárðarbunga (in effetti, questi terremoti si sono verificati principalmente tra agosto 2014 e febbraio 2015) e all'attività sismica della faglia Húsavík-Flatey e della spaccatura obliqua di Grímsey nel nord dell'Islanda ([Fig. 43](#)). Tutti i dati sui terremoti selezionati provengono dal Global CMT ([Ekström et al., 2012](#)).

8.3. Risultati

Prima di osservare i dati chimici del pozzo HA01 monitorato sulla finestra temporale studiata e contro le attività sismiche e vulcaniche nello stesso periodo (cioè le serie temporali), abbiamo calcolato e mostrato tutti i coefficienti di variazione associati all'HA01 oligoelementi delle acque sotterranee in [Fig. 44a](#). L'intervallo di variabilità bassa (coefficiente di variazione $<0,5$) include Li, B, Al, V, Ga, As, Rb, Sr e Mo. L'intervallo di variabilità intermedio ($\geq 0,5$ e $<1,0$) include Cr, Co, Cu, Zn, Cd, In e Cs. L'intervallo di variabilità elevato ($\geq 1,0$) include Mn, Fe, Ni, Sb, Pb e U ([Fig. 44a](#)).

La maggior parte degli elementi con coefficienti di variazione $> 0,5$ hanno concentrazioni medie molto basse durante il periodo di campionamento, ovvero inferiori a 1 ppb o addirittura inferiori al limite di quantificazione dello strumento. Per questo motivo, abbiamo escluso questi

elementi (cioè Co, Cd, In, Cs, Cr, Mn Ni, Cu, Sb, Pb e U) dalle nostre successive analisi ed elaborazioni. Per lo stesso motivo abbiamo escluso anche Zn. Quest'ultimo elemento, infatti, nonostante una concentrazione media di 6,42 ppb, è stato rilevato solo in 29 dei 166 campioni analizzati. Sebbene la concentrazione di Fe fosse spesso al di sotto del limite di rilevamento dello strumento (ovvero, in 54 campioni su un totale di 166), nelle analisi seguenti l'abbiamo considerata la stessa per il suo ruolo documentato nei processi pre-sismici altrove ([Barberio et al., 2017](#); [Boschetti et al., 2019](#)). I restanti elementi (Li, B, Al, V, Ga, As, Rb, Sr e Mo) sono per lo più caratterizzati da bassi coefficienti di variazione ($<0,5$). Questi bassi coefficienti di variazione su una lunga serie temporale (8-9 anni) confermano l'idoneità di questi elementi come buoni indicatori per i cambiamenti legati agli eventi ambientali. In altre parole, anomalie nelle concentrazioni delle acque sotterranee sarebbero enfatizzate dalla stabilità delle serie temporali espresse anche dal basso coefficiente di variazione.

Per comprendere meglio la distribuzione statistica delle popolazioni analizzate, abbiamo anche rappresentato graficamente ([Fig. 44b](#)) le concentrazioni degli elementi selezionati (vedi sopra) (Li, Mo, As, Sr, Rb, B, V, Ga, Al e Fe) come trame di scatola e baffi. Ciascun riquadro rappresenta gli intervalli interquartili (25 ° -75 ° quartile) ed è separato in due parti dalla mediana. I baffi sono limitati dall'intervallo interquartile (IQR) con un fattore pari a 1,5. Tutti gli elementi selezionati hanno piccole caselle, il che significa che le popolazioni sono ben raggruppate attorno alla mediana. Inoltre, tutti gli elementi tranne As e Al hanno valori anomali (punti in [Fig. 44b](#)), che sono "valori anomali" rispetto alla mediana e al riquadro associato in quanto superano i baffi ([Fig. 44b](#)).

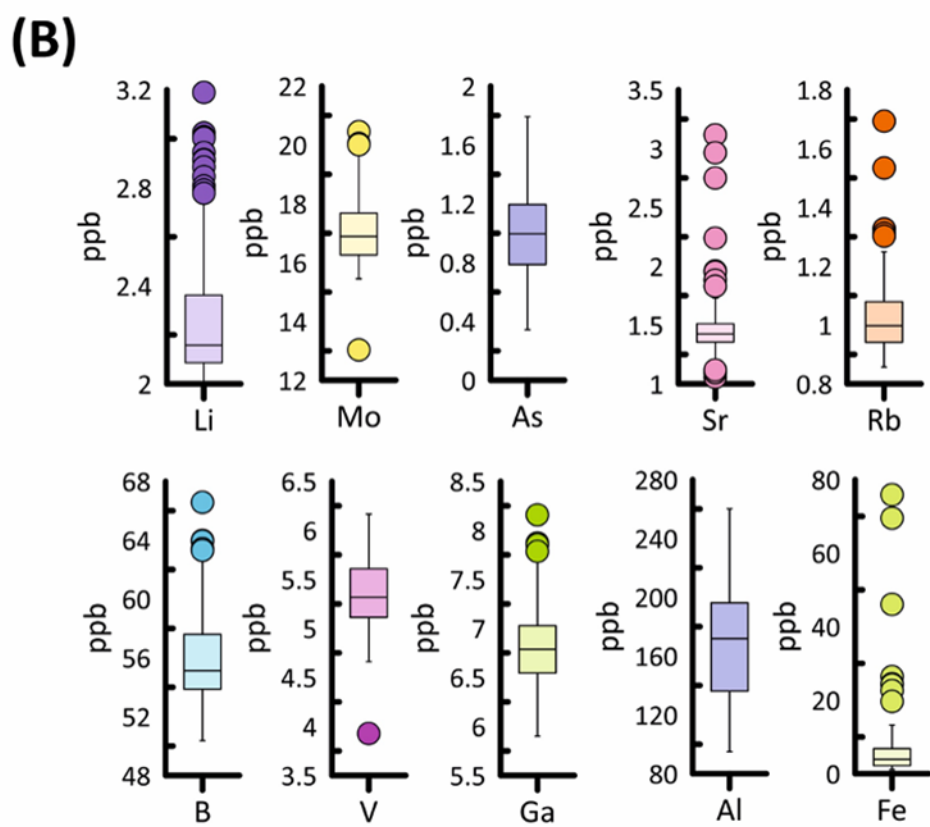
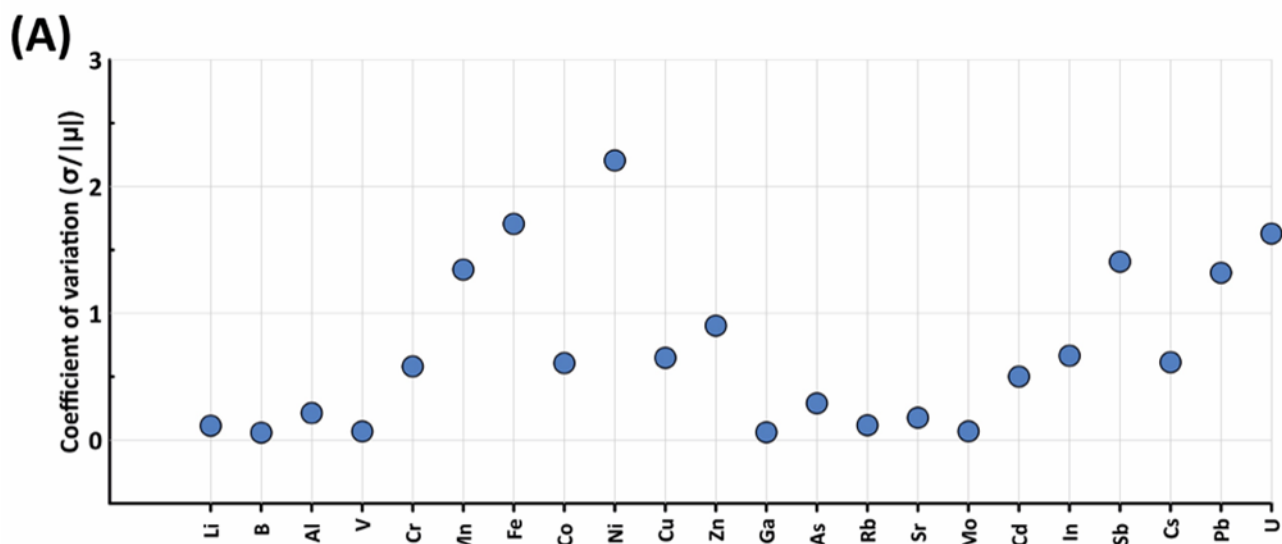


Figura 44. Variabilità degli elementi nella falda acquifera HA01. (a) Coefficienti di variazione per tutti gli oligoelementi. (b) Grafici box-and-whisker per gli oligoelementi selezionati in cui i punti rappresentano "valori anomali" di concentrazioni (ppb) rispetto alla mediana e al riquadro associato.

Le serie temporali delle concentrazioni di elementi in tracce precedentemente selezionate (Li, Mo, As, Sr, Rb, B, V, Ga, Al e Fe; vedere la sezione precedente) sono mostrate in [Fig. 45](#). La rappresentazione grafica di la serie storica permette di apprezzare immediatamente la straordinaria stabilità riscontrata nelle concentrazioni di Li, B, Mo, V, Ga, As, Rb, Sr e Al nell'arco di nove anni. Questa affermazione è confermata dalla bassa variabilità del campione intorno ai valori medi. Fe e Zn mostrano invece una deviazione standard molto elevata, sintomo di una maggiore variabilità intrinseca e/o potenziali difficoltà strumentali nella loro determinazione ([Fig. 45](#)). In dettaglio, in [Fig. 45](#), è possibile identificare due gruppi in base all'andamento della concentrazione nel tempo. Il primo gruppo è rappresentato da elementi come Li, Ga e Mo, mentre il secondo da B, V e Al. Questi gruppi di elementi mostrano comportamenti simili, in cui vengono riconosciute tendenze comparabili delle concentrazioni.

Le concentrazioni di Sr, Rb e Fe hanno registrato serie temporali molto stabili intorno ai loro valori medi, da cui si sono allontanate in modo significativo solo tra gennaio 2018 e la fine del campionamento ([Fig. 45](#)).

La serie temporale As è caratterizzata da valori di concentrazione molto bassi e variabili (ma entro un intervallo di concentrazione molto ristretto di circa 1 ppb). Non sono visibili tendenze chiare in questa stretta distribuzione durante il periodo di monitoraggio ([Fig. 45](#)).

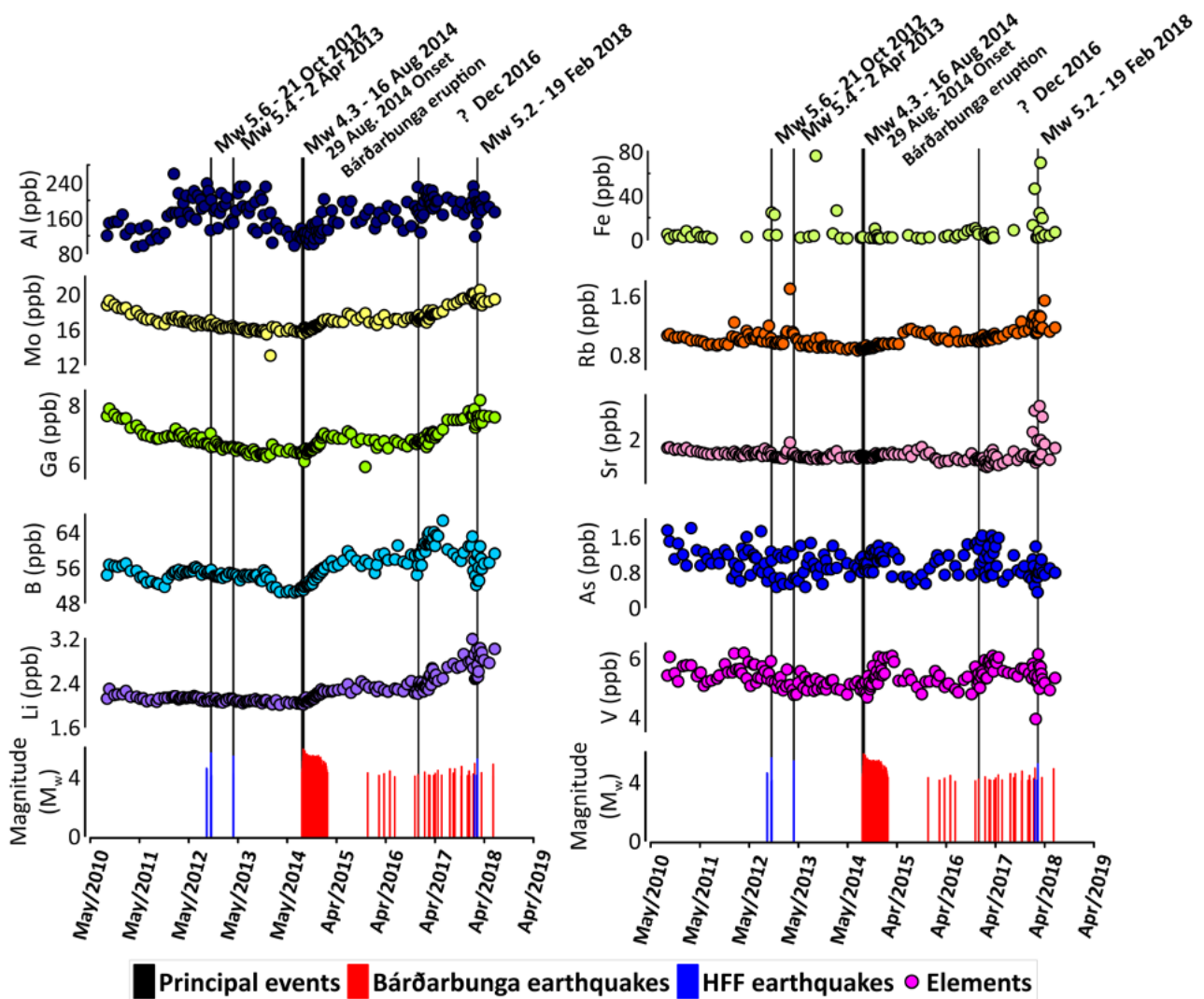


Figura 45. Serie storica delle concentrazioni di oligoelementi e dei maggiori terremoti ed eruzioni vulcaniche. Le concentrazioni di oligoelementi nelle acque sotterranee HA01 (ppb; 22 settembre 2010 - 25 giugno 2018) sono mostrate con cerchi di diversi colori. Gli eventi sismici ($M_w \geq 4$; 13 gennaio 2011 - 23 febbraio 2019) relativi alle attività del vulcano Bárðarbunga e della faglia Húsavík-Flatey (HFF) sono visualizzati rispettivamente con barre rosse e blu. I dati sui terremoti provengono dal Global CMT ([Ekström et al., 2012](#)).

Per identificare le possibili correlazioni tra gli elementi in tracce delle acque sotterranee analizzate e gli eventi geologici come i terremoti e l'attività vulcanica, confrontiamo le nostre serie temporali idrogeochimiche con le serie temporali di eventi sismici con $M_w \geq 4$ e gli episodi vulcanici principali (vulcano Bárðarbunga) per il periodo di monitoraggio in aree selezionate dell'Islanda ([Fig. 43 e 45](#)). Queste possibili correlazioni verranno ulteriormente approfondite di seguito attraverso metodi statistici, ovvero analisi delle componenti principali e dei punti di cambiamento. In sintesi, individuiamo le seguenti possibili correlazioni temporali:

(1) Un apparente aumento delle concentrazioni di B, Al e V (HA01) è iniziato circa cinque mesi (maggio 2012) prima dell'evento sismico M_w 5.6 che si è verificato al largo dell'Islanda settentrionale il 21 ottobre 2012 a circa 75 km del pozzo HA01. Successivamente (da luglio 2012), le concentrazioni di questi tre elementi sono tornate ai valori di fondo ([Fig. 45](#)). In precedenza erano stati identificati diversi potenziali precursori idrogeochimici di questo terremoto ([Skelton et al., 2014; 2019; Andrén et al., 2016](#)).

(2) Da gennaio 2014, B, Al e V hanno mostrato una sostanziale diminuzione delle loro concentrazioni (HA01) fino ad agosto 2014, quando è stata registrata una rapida inversione e aumento di tutti e tre gli elementi. In dettaglio, questo aumento è iniziato circa una settimana prima dell'inizio della sequenza sismica di Bárðarbunga e dell'evento di rifting (16 agosto 2014), che, a sua volta, ha annunciato l'eruzione vulcanica (iniziata il 29 agosto 2014) di circa due settimane ([Gudmundsson et al., 2016](#)). Quindi, l'inversione e l'aumento di B, Al e V (HA01) si sono verificati circa tre settimane prima dell'inizio dell'eruzione del Bárðarbunga, avvenuta a circa 140 km dal pozzo HA01. Inoltre, nel settembre 2014 (dopo l'inizio dell'eruzione vulcanica), le concentrazioni di Li, Ga e Mo hanno iniziato ad aumentare. B, Al, V, Li, Ga e Mo sono tornati ai valori di fondo nel febbraio 2015 ([Fig. 45](#)).

(3) Tutti gli oligoelementi considerati (cioè le concentrazioni di Li, B, Ga, Mo, Sr, Rb e Fe nelle acque sotterranee HA01) eccetto Al, V e As hanno superato la soglia $+ 2\sigma$ da gennaio 2018, circa sette settimane prima del terremoto di Mw 5.2, avvenuto al largo dell'Islanda settentrionale il 19 febbraio 2018 a circa 70 km dal pozzo HA01 ([Fig. 45](#)). Le concentrazioni di questi elementi sono rimaste elevate fino alla fine del nostro periodo di studio (giugno 2018).

(4) Alcune variazioni idrogeochimiche si sono verificate nel 2016-2017 (HA01) quando non si sono verificate attività sismiche e vulcaniche significative. In particolare, Li, Ga e Mo hanno mostrato un aumento sostanziale della concentrazione delle acque sotterranee (HA01) da dicembre 2016 a novembre 2017, mentre B, Al e V hanno mostrato un aumento sostanziale da gennaio 2017 a giugno 2017 ([Fig. 45](#)). Nello stesso periodo, anche la concentrazione di alcuni importanti elementi chimici nell'acqua HA01 ha mostrato variazioni anomale ([Skelton et al., 2019](#)). Le suddette possibili correlazioni tra tendenze idrogeochimiche ed eventi sismico-vulcanici verranno statisticamente testate di seguito.

Come accennato in precedenza e osservato nella [Fig. 45](#), i cambiamenti idrogeochimici prima dell'attività del Bárðarbunga del 2014 sono i più evidenti nelle serie temporali registrate. Mentre queste serie temporali saranno ulteriormente analizzate di seguito attraverso metodi statistici, qui proponiamo alcuni calcoli geochimici-termodinamici per comprendere le possibili fonti di oligoelementi (e le loro variazioni di concentrazione pre-vulcanica) negli ambienti vulcanici islandesi.

I terremoti sono tra i segnali più importanti nella previsione delle eruzioni, a causa del movimento del magma che aumenta lo stress delle rocce circostanti. Tuttavia, l'attività sismica nelle aree vulcaniche può essere caratterizzata da un'ampia variabilità, a seconda dell'ampio range di comportamento elastico e reologia del magma in aumento e delle rocce circostanti ([Marzocchi e Bebbington, 2012](#)). Tra i principali precursori vulcanici, i segnali geochimici possono essere importanti per prevedere le eruzioni vulcaniche ([Marzocchi e Bebbington, 2012](#)). Per rilevare i cambiamenti all'interno del sistema vulcanico sono stati utilizzati metodi di

monitoraggio basati sui cambiamenti chimici legati all'attività vulcanica. In particolare, il monitoraggio geochimico si è concentrato principalmente sulle emissioni di gas da fumarole o crateri e, meno frequentemente, gli studi hanno affrontato i cambiamenti nella geochimica delle acque sotterranee remote prima delle eruzioni vulcaniche ([Armienta et al., 2008](#)). Tuttavia, l'applicazione di metodi di monitoraggio geochimico dell'acqua (sorgenti, torrenti, ecc.) associata al vulcanismo si è dimostrata produttiva nella comprensione dei meccanismi legati all'attività vulcanica ([Armienta et al., 1995](#)). In un sistema geotermico attivo, come questo caso di studio in Islanda, i fluidi sono in grado di trasportare o depositare a distanza metalli che provengono da acqua di fonte, volatili magmatici e tramite dissoluzioni rocciose ([Kaasalainen et al., 2015](#); [Blomgren et al., 2019](#)). Ad esempio, B è altamente mobile durante l'interazione acqua-roccia nel sistema geotermico basaltico e quindi è un buon indicatore di lisciviazione delle rocce. B è una delle specie chimiche più sensibili ai cambiamenti nell'attività vulcanica. In effetti, lo spostamento del magma può portare alla collocazione del dicco che facilita la lisciviazione della roccia ospite. Per questo motivo, la composizione idrogeochimica delle sorgenti varia con i cambiamenti del modello di stress vulcanico ([Armienta et al., 2008](#); [Arnórsson e Andrésdóttir, 1995](#); [Kaasalainen et al., 2015](#)).

Il calcolo della mobilità relativa degli oligoelementi ([Aiuppa et al., 2000](#); [Gislason et al., 1996](#); [Koh et al., 2016](#)), ovvero il rapporto normalizzato sodio tra le concentrazioni in tracce rilevate nel pozzo HA01 e basalto ([Kokfelt et al., 2006](#); [Kaasalainen e Stefánsson, 2012](#); [Shorttle et al., 2013](#)) - conferma definitivamente che B è l'elemento più mobile nell'area studiata. Pertanto, per la suddetta idrosensibilità vulcanica di B, in questo studio, abbiamo effettuato un'analisi sulla relazione tra B e le concentrazioni di elementi in tracce nei fluidi dell'acquifero geotermico dell'area di Hafralækur ([Fig. 46](#)). In dettaglio, abbiamo confrontato i nostri campioni d'acqua (punti neri) con i dati di studi precedenti riguardanti: campioni di neve dal ghiacciaio Vatnajökull e l'altopiano NE del ghiacciaio durante l'eruzione del Bárðarbunga 2014/2015 (rombi bianchi; [Galeczka et al., 2017](#)), acqua campioni dal fiume Jökulsá á Fjöllum (JFR) durante

l'eruzione del Bárðarbunga 2014/2015 (quadrati azzurri; [Galeczka et al., 2016](#)), acque sotterranee fredde islandesi (triangoli verdi; [Kristmannsdóttir e Klemensson, 2007](#); [Kristmannsdóttir e Guðrúnardóttir, 2009](#); [Kristmannsdóttir, 2009](#); [Kristmannsdóttir 2011](#)) e acque sotterranee termali islandesi (triangoli arancioni; [Arnórsson, 1969](#); [Kristmannsdóttir e Klemensson, 2007](#); [Kristmannsdóttir, 2008](#); [Kristmannsdóttir e Guðrúnardóttir, 2009](#); [Kristmannsdóttir, 2011](#); [Kaasalainen e Stefánsson, 2012](#); [Kaasalainen, 2015](#)). La temperatura di transizione tra acque fredde e termali è di 10° C ([Kristmannsdóttir e Klemensson, 2007](#); [Kristmannsdóttir e Guðrúnardóttir, 2009](#); [Kristmannsdóttir, 2011](#)), in accordo con la definizione di Schoeller di acque termali (temperatura dell'aria o dell'acqua di superficie aumentata di 4 ° C) ([Schoeller, 1962](#)). Infatti, a Húsavík, la temperatura media annuale delle acque superficiali è di circa 5,6 ° C. La transizione tra acque fredde e termali avviene intorno a $\log B = 1$. I valori logaritmici tendono a far sfumare la variabilità degli elementi temporali, in particolare nei campioni con valori di coefficiente di variazione inferiori. Tuttavia, è possibile avere alcune indicazioni sull'origine dei costituenti in tracce, grazie anche al confronto con la concentrazione mediana di oligoelementi nei basalti islandesi ([Kaasalainen e Stefánsson, 2012](#)) e con i dati di letteratura delle acque termali islandesi a temperatura inferiore di o uguale a 100 ° C ([Arnórsson, 1969](#); [Kaasalainen e Stefánsson, 2012](#); [Kaasalainen et al., 2015](#)). I codici geochimici-termodinamici possono essere utilizzati per modellare gli equilibri di elementi principali e in tracce durante l'interazione acqua-roccia (ad esempio, modellazione del percorso di reazione; [Kaasalainen et al., 2015](#); [Marini, 2013](#)). Tuttavia, la bassa concentrazione di oligoelementi nelle acque sotterranee $T \leq 100$ ° C unita alla difficoltà di tenere conto di altri fenomeni come l'adsorbimento / assorbimento nei minerali (in particolare ossidi e idrossidi), la co-precipitazione in fasi complesse (come soluzioni solide o argille stratificate miste) e l'incompletezza dei dati termodinamici sulle specie in soluzione fanno sì che questi modelli debbano essere utilizzati con estrema cautela quando applicati a elementi in traccia ([Marini, 2013](#); [Oelkers et al., 2009](#)). Ciò è evidente nella [Fig. 46](#), dove soprattutto nel caso di Li e Rb, le acque del pozzo sono posizionate al di sotto del modello del percorso di reazione creato da [Kaasaleinen et al \(2015\)](#).

Quel modello è stato calcolato per acque geotermiche ad alte temperature in Islanda; tuttavia il primo tratto di percorso (basso contenuto di B) può essere conforme per acque a $T \leq 100^\circ \text{C}$, come nel caso del pozzo HA01. È importante osservare come i campioni HA01 siano raggruppati nel dominio di commutazione tra le acque superficiali di JFR ([Galeczka et al., 2016](#)) e le acque termali islandesi, che è approssimato dal contenuto massimo di boro rilevato in JFR durante il 2014-2015 Eruzione del Bárðarbunga ($\log B = 1.8$) ([Fig.46](#)). I campioni tendono ad essere più vicini al modello del percorso di reazione nel caso di Sr, Al e Fe, con il primo che non è molto mobile rispetto al boro. I campioni di acque sotterranee del pozzo HA01 hanno contenuti inferiori in Sr rispetto sia al modello del percorso di reazione che alle acque termali islandesi, probabilmente a causa dell'elevato pH dell'acqua sotterranea HA01 (cioè, precipitazione di calcite più veloce soprattutto vicino alle condizioni di co-precipitazione in zeoliti calciche ([Andrén et al., 2016](#))).

Le concentrazioni di Al e parzialmente Fe nelle acque sotterranee HA01 mostrano il miglior accordo con l'andamento dei campioni JFR verso le acque termali islandesi. Questi due elementi sono geochimicamente simili; possono infatti essere classificati come oligoelementi "immobili", probabilmente per la loro tendenza a formare colloidali ossido-idrossido. Tuttavia, Fe ha la maggiore variabilità nella parità di concentrazione di B, probabilmente a causa di condizioni redox variabili e / o per il fatto che il ferro risiede nelle strutture di particelle minerali argillose su scala nanometrica che subiscono cicli tra Fe (II) e Fe (III) ([Ilgen et al., 2019](#)). Diversamente, Mo è il secondo oligoelemento più mobile dopo B. Notevole anche la sua concentrazione nelle acque sotterranee HA01 perché prossima a quella dei basalti, molto più alta delle acque superficiali, e leggermente spostata verso concentrazioni più elevate rispetto ad altre acque termali islandesi ([Fig.46](#)). Il Mo è un elemento poco concentrato nei basalti, ma tende ad accumularsi nell'acqua proporzionalmente al tempo e alla temperatura di interazione ([Arnórsón e Óskarsson, 2007](#)). Ciò conferma che l'acqua sotterranea HA01 è antica, probabilmente originata dallo scioglimento glaciale e databile all'incirca al periodo pre-precoce dell'Olocene,

come suggerito dal valore del rapporto isotopico basso stabile dell'idrogeno, $\delta^2\text{H}$ (H_2O) ([Skelton et al., 2014](#)). È quindi evidente che l'analogia del contenuto B tra le acque del JFR e del pozzo HA01 prima e durante la crisi vulcanica 2014-2015 è una mera coincidenza, anche se la posizione del pozzo HA01 sul "trend di crescita" degli oligoelementi nelle acque è compatibile con un'origine da scioglimento glaciale. Infatti, la deglaciazione del primo Olocene (12–8,2 cal ka) e il riscaldamento furono associati in Islanda a due generazioni principali di "jökulhlaups" (mega-inondazioni da scoppio del ghiacciaio) attorno alla calotta glaciale del Vatnajökull, a circa 11,4-11,2 cal ka e ca 10,4-9,9 cal ka, e le principali emissioni di tefra dai vulcani subglaciali Grímsvötn e Bárðarbunga ([Van Vliet-Lanoë et al., 2020](#)).

Inoltre si indica l'evoluzione del JFR durante l'evento 2014-2015 (freccia viola) e anche una linea meno marcata rappresentativa della correlazione dei campioni tipici delle acque termali del nord dell'Islanda (tra cui c'è anche il pozzo HU01 ; [Kristmannsdóttir, 2008](#)) ([Fig.46](#)). Oltre al pozzo HA01, questi campioni mostrano un pH più basico (mediano pari a 9,7) rispetto agli altri (8,37 [Kristmannsdóttir e Klemensson, 2007](#); [Kristmannsdóttir e Guðrúnardóttir, 2009](#); [Kristmannsdóttir, 2011](#); 8,66 nelle acque NaCl [Kaasalainen e Stefánsson, 2012](#)). È interessante notare che i valori di pH basici sono tipicamente misurati dall'acqua proveniente dai ghiacciai e sono causati dall'isolamento della CO_2 atmosferica delle acque sotterranee ([Vigier et al., 2006](#)). La linea di correlazione (linea verde) è sempre vicina ai campioni HA01 ([Fig. 46](#)). Pertanto, questa linea può essere rappresentativa dell'andamento evolutivo delle acque nella zona di Hafralækur. Tuttavia, i campioni d'acqua dal pozzo HA01 rappresentano la transizione tra JFR e le acque termali (linea rossa verticale), evidente soprattutto nei grafici Al e Fe. Inoltre, le tendenze dei campioni HA01 e di altri campioni "di base" sono simili per elementi con affinità geochemica, come ([Fig. 46](#)): Al e Ga (mobilità diversa ma comportamento simile delle specie disciolte a causa del pH; [Elmi, 2009](#)), As e Mo (mobilità elevata simile e affinità con i solfuri) e Li e Rb (mobilità moderata simile e tendenza parallela al rapporto B / metallo alcalino nei basalti). Infine, una menzione speciale è necessaria per i metalli alcalini Li, Rb e Cs. Nei fluidi geotermici,

la concentrazione di questi elementi aumenta con l'aumentare della temperatura (Kaasalainen et al., 2015). Questo spiega anche perché l'andamento è diverso dal modello geochimico ad alta temperatura (linea tratteggiata), dato che il pozzo HA01 ha una T profonda pari a ca. 100 ° C (Fig. 46). Nella Fig. 47, la maggior parte dei campioni del pozzo HA01 sono raggruppati tra la composizione media dell'acqua meteorica e un rapporto in peso Li / Rb = 2,26, che è compreso tra quello del vetro basaltico (Li / Rb = 2,33, Berger et al., 1988 , che a sua volta è anche simile a MORB, Li / Rb = 2,26, Gale et al., 2013) e al rapporto mediano dei basalti toleiti islandesi, (Li / Rb = 2,18; Kaasalainen e Stefánsson et al., 2012), quest'ultimo essendo anche più arricchito di C (Fig. 47). In generale, i processi legati alla distribuzione di questi elementi nelle acque termali sono particolarmente evidenti ad alte temperature nel seguente intervallo: 150 <T <350 ° C (Kaasalainen et al., 2015; Giggenbach, 1991; Seyfried e Bischoff, 1979; Seyfried , 1987). In un tale intervallo di temperatura, l'assorbimento di Li su quarzo o Cs su zeoliti è più pronunciato (Giggenbach, 1991).

In sintesi, il calcolo della mobilità relativa degli oligoelementi conferma che B è altamente mobile durante l'interazione acqua-roccia nel sistema geotermico ospitato basaltico. In particolare, l'analisi della relazione tra B e le concentrazioni di oligoelementi nei fluidi dell'acquifero geotermico dell'area di Hafraðækur ci permette di confermare che i campioni d'acqua dal pozzo HA01 rappresentano la transizione tra JFR e le acque termali (Fig. 46). Inoltre, la notevole concentrazione di Mo conferma che l'acqua sotterranea HA01 è antica, probabilmente originata dallo scioglimento glaciale, e databile all'incirca all'epoca pre-Olocene (Arnórsson e Óskarsson, 2007; Skelton et al., 2014).

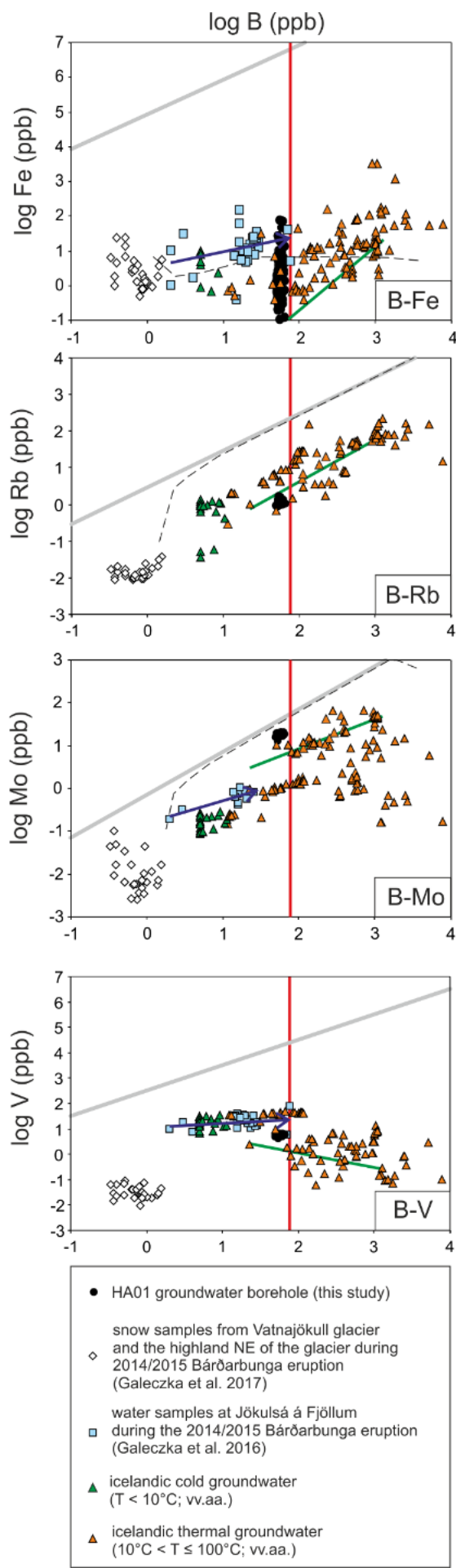
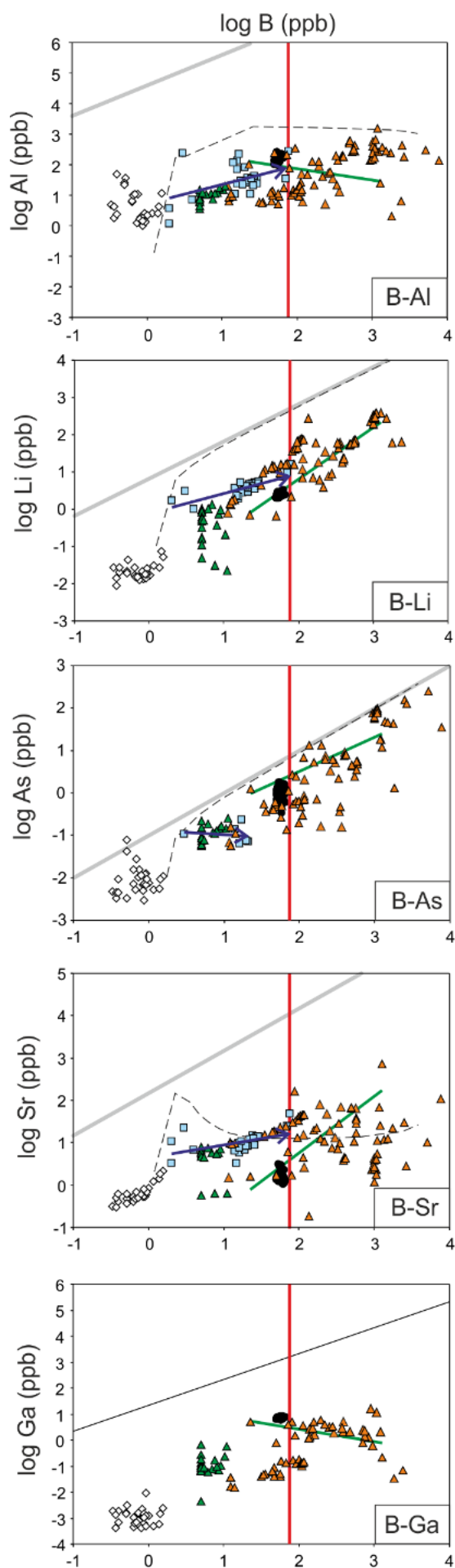


Figura 46. Relazioni tra B e le concentrazioni di oligoelementi nelle acque sotterranee HA01. La linea nera continua raffigura i rapporti boro / elemento secondo Kaasalainen e Stefánsson (2012, e riferimenti ivi contenuti), ad eccezione di Ga (valore Ga mediano da Arnórsson, 1969; De Argollo, 1978; Willis, 1979; Reimann e De Caritat 1998). La freccia viola mostra la linea di tendenza degli oligoelementi nei campioni del fiume Jökulsá á Fjöllum (quadrati bianchi) durante l'eruzione del Bárðarbunga 2014-2015 (Galeczka et al., 2016); la linea rossa verticale mostra la concentrazione massima di boro rilevata nel fiume durante quel periodo ($\log B = 1,8$). Vengono mostrati anche campioni di neve durante gli stessi periodi per confronto (diamanti bianchi; Galeczka et al., 2017). Le linee tratteggiate rappresentano la modellazione del percorso di reazione per l'acqua geotermica ad alta temperatura (acqua meteorica - interazione basalto a 260 ° C; Kaasalainen et al., 2015). I triangoli verdi e arancioni sono rispettivamente acque fredde islandesi ($T < 10$ ° C) e acque termali (10 ° C $< T \leq 100$ ° C) (vedere il testo principale per un elenco completo di riferimento); la linea verde rappresenta il miglior adattamento delle acque termali ad alto pH nel nord dell'Islanda.

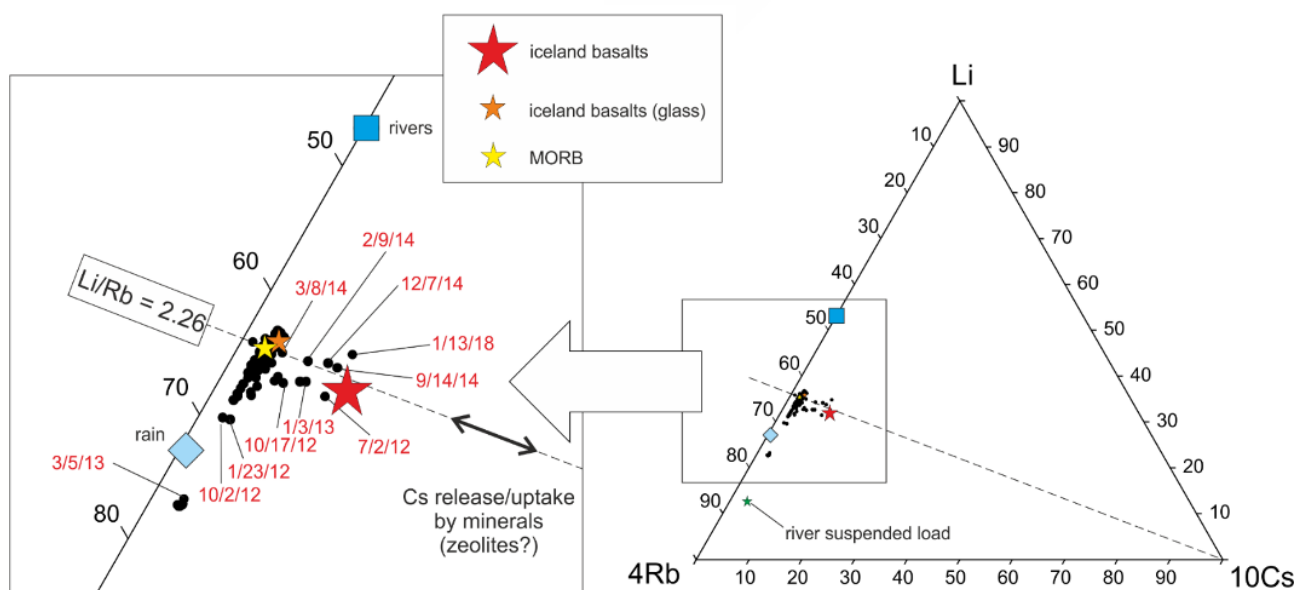


Figura 47. Diagramma ternario Li-Rb-Cs. La percentuale di elementi dai valori di concentrazione di ppb (acque) o ppm (rocce) è riportata sui lati del diagramma. I punti neri mostrano il set di dati della traccia di monitoraggio del pozzo HA01. $Li / Rb = 2,26$ è il valore mediano di quel set di dati. Vengono mostrati per confronto anche il basalto mediano (Kaasalainen e Stefánsson, 2012), il vetro basaltico (Berger et al., 1988), MORB (Gale et al., 2013), fiume e acque piovane (Kaasalainen e Stefánsson, 2012). Punti neri con etichette della data di campionamento come MM / GG / AA.

In questo studio, alcuni componenti principali precedentemente studiati come Ca, Na, Si, K (Skelton et al., 2014, 2019) sono stati aggiunti al database degli elementi in traccia (Li, B, Al, V, Ga, As, Rb, Sr, Mo) per far emergere quante più informazioni possibili dalla PCA (Principal Component Analysis). Questo aiuta anche a compensare la mancanza di alcuni oligoelementi, non inseriti nell'elaborazione PCA come al di sotto del limite di quantificazione. In questo modo, è stata ottenuta una matrice di dati di 13 variabili (gli elementi) e 156 soggetti (i campioni), che

concordano sia con il rapporto "soggetto a variabili" di [Bryant e Yarnold \(1995\)](#), $STV > 5$ e con altre regole pratiche relative alla dimensione dei soggetti (Garson, 2018): soggetti = variabili x 5 o soggetti > 100 ([Hatcher e O'Rourke, 2013](#)); soggetti > 150 ([Hutcheson e Sofroniu, 1999](#)). I componenti principali sono stati estratti dal codice OriginPro, utilizzando la matrice di correlazione. Risultati abbastanza simili sono stati ottenuti dal codice SPSS, che ha l'opzione aggiuntiva di ruotare i componenti estratti utilizzando Varimax (IBM, 2019). Con quest'ultimo codice, sia la misura Kaiser-Meyer-Olkin dell'adeguatezza del campionamento ($KMO = 0,746$) che il test di sfericità di Bartlett (livello di significatività $< 0,05$) indicano che la PCA è utile per l'interpretazione del set di dati. Come suggerito dal gomito del diagramma, il giusto numero di componenti era quattro, il che spiega il 75% della varianza cumulativa dei dati ([OriginLab, 2019](#)). Tuttavia, considerando che la varianza associata al quarto componente, (PC4), è inferiore al 10% e che il terzo componente, (PC3), era principalmente associato a un elemento in traccia, i risultati PCA vengono interpretati utilizzando un grafico binario che mostra sia gli autovettori variabili che i punteggi PC1 e PC2 relativi ai campioni ([Fig. 48](#)). In quel grafico, As è rappresentato sul baricentro del diagramma. Sono evidenti tre principali associazioni delle altre variabili: i) una correlazione tra i vettori Na e Si, rappresentata principalmente dal lato positivo di PC2 (asse Y); ii) la relazione tra i vettori K e Ca, orientati verso il quadrante negativo di [Fig. 48](#); iii) il raggruppamento dei vettori degli oligoelementi sul lato positivo di PC1. Inoltre, i punteggi del campione mostrano una distribuzione in senso antiorario a partire dal 2010 (quadrante alto / destro, asse Y, PC2). Successivamente, i campioni 2012-2013 sono distribuiti appena sopra il lato positivo di PC2 rappresentato principalmente da vettori variabili Na e Si. Ciò concorda con le variazioni chimiche rilevate durante gli eventi di sciame di quel periodo ([Skelton et al., 2014](#)), che erano correlate alle reazioni labradorite-analcime riportate in [Andrén et al. \(2016\)](#). Il successivo raggruppamento dei campioni è sul negativo (lato sinistro) di PC1, che sembra essere correlato a un periodo di minore concentrazione chimica della maggior parte degli oligoelementi descritti da PC1 (da giugno 2013 a giugno 2014). Successivamente, la variabilità chimica dei campioni raccolti nella seconda metà del 2014 viene progressivamente spostata

verso il vettore K. In particolare, i campioni raccolti dopo gli sciame sismici al vulcano Bárðarbunga (agosto 2014) sembrano non solo legati a quegli eventi sismici, ma anche alle variazioni del flusso di calore in quella zona (Reynolds et al., 2019). Infatti, i campioni di novembre 2014, che corrispondono alla massima potenza termica prodotta dall'intrusione magmatica (Reynolds et al., 2019), sono esattamente in cima al vettore K (Fig. 48). I campioni raccolti dalla fine del 2014 alla fine del 2017 / inizio 2018 migrano gradualmente verso il quadrante inferiore destro, vicino all'apice dei vettori B e Li, e successivamente (gennaio-febbraio 2018) verso il quadrante superiore destro della Fig. 48. La maggior parte probabilmente, questo potrebbe essere collegato a ulteriori eventi di potenza termica, che sono continuati fino al 2017 con un'intensità inferiore (Reynolds et al., 2019). Di conseguenza, la variazione delle serie temporali delle temperature profonde dedotta dalle equazioni geotermometriche Na / K (Verma e Santoyo, 1997) e Na-K-Ca (Fournier e Truesdell, 1973; Fournier e Potter, 1979; Fournier, 1989) i campioni HA01 mostrano una temperatura massima alla fine del 2014 e altri salti minori nella seconda metà del 2016. Infine, il progressivo spostamento temporale dei campioni verso i vettori degli oligoelementi, principalmente correlato al lato positivo di PC1 (Fig. 48), concorda con il fatto che gli eventi pre-sismici / sismici relativi al 2018 (es. Terremoto Mw 5.2, 19 febbraio 2018) sono rilevabili solo con oligoelementi.

Una seconda analisi PCA è stata eseguita utilizzando la matrice di correlazione degli oligoelementi al solo scopo di interpretarne al meglio il comportamento. I risultati del KMO (0,721) e del test di Bartlett (livello di significatività $\ll 0,05$, rispettivamente) certificano ancora una volta l'idoneità dei dati per il rilevamento della struttura. Le caratteristiche principali di questa analisi sono: i) le due componenti principali che spiegano il 60% della varianza cumulativa confermano il clustering V, B, Al e Li, Ga, Mo menzionato nella sezione precedente, quest'ultimo gruppo principalmente spiegato da PC1 asse; ii) all'estremo del lato negativo di PC1, i campioni raccolti prima dell'eruzione del Bárðarbunga vengono raggruppati, confermando la loro diminuzione della concentrazione prima di quell'evento; iii) sul lato opposto di PC1, i campioni

dell'inizio del 2018 sono ben distinti come valori anomali non solo da Li, Ga, Mo ma anche da Rb. I campioni raccolti durante gli sciame sismici 2012-2013 sono indistinguibili dagli altri perché ricadono nel baricentro del diagramma, a conferma che gli eventi sismici avvenuti in quel periodo non sono evidenziati da oligoelementi. Considerando che PC1 spiega la maggior parte della varianza cumulativa, potrebbe essere utilizzata come singola variabile che comprende tutti gli oligoelementi e riduce le informazioni di base non necessarie. Sia la rotazione Varimax che i metodi alternativi di estrazione dei componenti come Categorical PCA (CATPCA; [Ma et al., 2016](#)) o Robust PCA (RPCA; [Jung et al., 2014](#)) non aumentano né la percentuale di varianza spiegata da PC1 né la discriminazione capacità dei suoi punteggi. Infatti, è evidente come i punteggi relativi al PC1 estratti dalla PCA “classica” abbiano il picco più alto vicino alla data dell'eruzione del Bárðarbunga del 2014 e il più basso sugli eventi di fine 2017 / inizio 2018 rispetto a quelli ottenuti da Varimax-ruotato , CATPCA o ROBPCA.

In sintesi, la Principal Component Analysis (PCA) indica che gli eventi sismici verificatisi nel periodo 2012-2013 non sono stati preceduti da cambiamenti significativi nelle concentrazioni di elementi in traccia, mentre gli eventi sismici del 2018 sono stati preceduti solo da cambiamenti di elementi in traccia (e non da cambiamenti di elementi importanti). Inoltre, la variabilità chimica dei campioni di acque sotterranee raccolti dopo lo sciame sismico pre-eruttivo del vulcano Bárðarbunga (agosto 2014) non sembra semplicemente correlata a quell'evento sismico, ma piuttosto alle variazioni di flusso di calore in quella zona connesse con l'evento di rifting e Bárðarbunga eruzione ([Reynolds et al., 2019](#)).

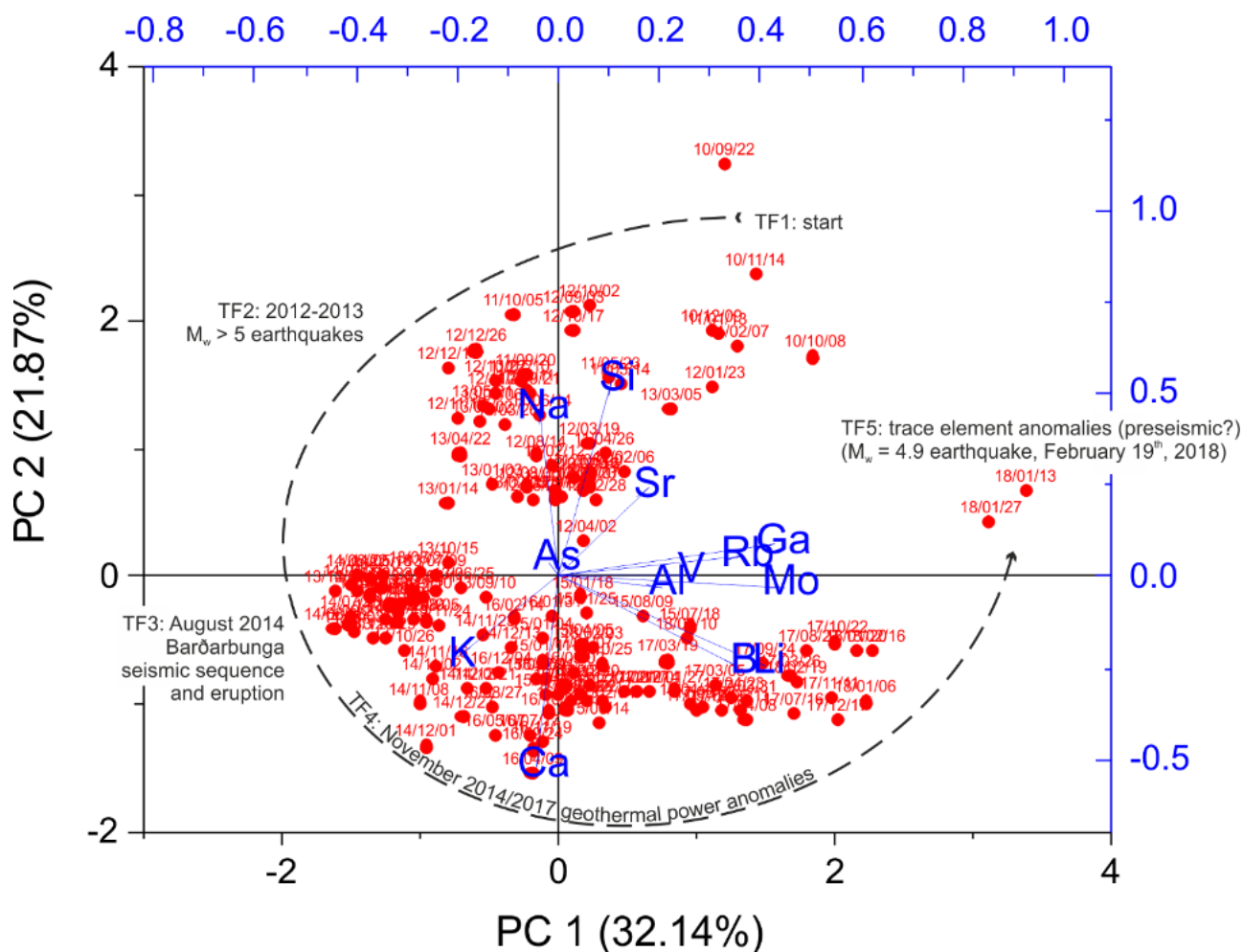


Figura 48. Grafico dell'analisi dei componenti principali (PCA). Sono riportati sia i carichi delle variabili (autovettori, in blu) che i punteggi assegnati ai punti di campionamento (pallini rossi con etichette della data di campionamento come AA / MM / GG), in relazione alle prime due componenti (PC1 e PC2). La curva tratteggiata rappresenta un percorso di evoluzione temporale approssimato della distribuzione dei punteggi del campione, che sembra contrassegnato da 5 intervalli di tempo (TF #).

Il rilevamento del punto di cambiamento (CP) nei dati di serie temporali dei sei cluster di elementi in traccia rilevati dall'asse PC1 (B, Al, V, Li, Ga e Mo; Fig. 49) rivela che ciascuno di essi ha almeno uno CP all'interno di un periodo centrale, che è caratterizzato dagli eventi sismici

avvenuti prima e durante l'eruzione del Bárðarbunga (Fig. 49; Scheda Supplementare CP). Rispetto al primo terremoto, all'eruzione principale e ai successivi eventi sismici, il periodo segnato dai PC ha un intervallo di date più ampio. Le date contrassegnate dai CP vanno dal 10 novembre 2013, per Al fino al 22 novembre 2015, per Ga, con l'inizio della sismicità pre-vulcanica (16 agosto 2014) e gli eventi eruttivi del Bárðarbunga (29 agosto 2014) approssimativamente a metà della serie storica (Fig. 49). I PC di Al dovrebbero essere presi con cautela perché Al è un elemento a bassa mobilità. Tuttavia, il primo Al CP è seguito da un CP in boro (il più mobile di tutti gli oligoelementi) il 1 ° dicembre 2013. Quest'ultimo CP segna l'inizio di una tendenza al ribasso della concentrazione, che poi si inverte l'8 marzo 2014. È difficile spiegare, elemento per elemento, le cause di queste variazioni. Tuttavia, è interessante notare come i primi CP siano coevi all'accumulo di stress rilevato nella stazione sismica BRE dell'Islanda settentrionale. Quella stazione si trova immediatamente sopra il piano di faglia della faglia trasforme di Húsavík-Flatey e monitora la divisione delle onde di taglio (Hong et al., 2020). Al BRE, l'accumulo di stress connesso all'evento Bárðarbunga era correlato alla sovrappressione del fluido delle microfratture. È iniziato nell'agosto 2013, un anno prima della prima scossa sismica pre-vulcanica a Bárðarbunga (Hong et al., 2020). Pertanto, i primi CP rilevati qui descritti potrebbero essere legati alla sovrappressione del fluido nelle microfratture prima dell'evento sismico principale. Diversamente, le variazioni termiche tardive legate all'eruzione del Bárðarbunga, che persistono fino alla fine del 2015 (Reynolds et al., 2019), sembrano essere contrassegnate dai CP di V e Ga, dalla K nel PCA (Fig. 49) , e dall'analisi geotermica utilizzando i principali costituenti chimici come descritto nella sezione precedente.

Il secondo periodo, caratterizzato da almeno un CP in tutti gli elementi tranne Ga, è posizionato poco prima del terremoto di Mw 5.2 del 19 febbraio 2018 (Fig. 49). Prima di quell'evento sismico, gli elementi mobili hanno due (Mo) o tre (B, Li) CP. In particolare, dopo un trend in aumento, B inizia una concentrazione decrescente il 23 aprile 2017, circa un mese prima rispetto ad altri elementi. Quindi, sia B che Li iniziano un brusco calo il 1 ° gennaio 2018,

seguito da un aumento il 3 febbraio 2018, cioè due settimane prima dell'evento sismico. Va notato che il diagramma ternario degli elementi alcalini (Fig. 47) mostra anche un valore anomalo al 13 gennaio 2018. Le tendenze dei precursori e dei relativi CP, sebbene non supportati da tutti gli elementi in traccia (5-6), potrebbero avere un ruolo più significativo dell'interazione acqua-roccia, in particolare della diversa solubilità -e composizione chimica- tra la fase vetro e cristallina della roccia (Fig. 47), o al ruolo di adsorbimento / desorbimento svolto dalle fasi minerali secondarie nelle fratture dell'acquifero (argille, zeoliti).

Infine, Mo e Ga hanno un PC il 10 luglio 2011, mentre Al mostra due PC, il primo il 5 ottobre 2011 e il secondo il 23 gennaio 2012, rispettivamente (Fig. 49). Non essendo confermato da altri elementi altamente mobili come B e Li, quel presunto lasso di tempo ha una "bassa significatività" o "bassa probabilità" (4 CP in 3/6 elementi; Fig. 49). Ciò è stato confermato dalla PCA, che non ha trovato alcuna struttura nei dati degli oligoelementi di quel periodo (Fig. 48). Da ottobre 2008 a settembre 2012, sono stati rilevati cambiamenti improvvisi anche in $\delta^{18}\text{O}$, accompagnati da concentrazioni in costante diminuzione dei costituenti principali (Na, Si, Ca) (Skelton et al., 2014). Questi sono stati collegati a una progressiva diminuzione della proporzione di acque sotterranee interessate dall'interazione acqua-roccia (Skelton et al., 2014). Pertanto, in assenza di una migliore spiegazione sulla loro origine, questi PC potrebbero essere classificati come "falsi positivi" o non direttamente correlati ad eventi sismici.

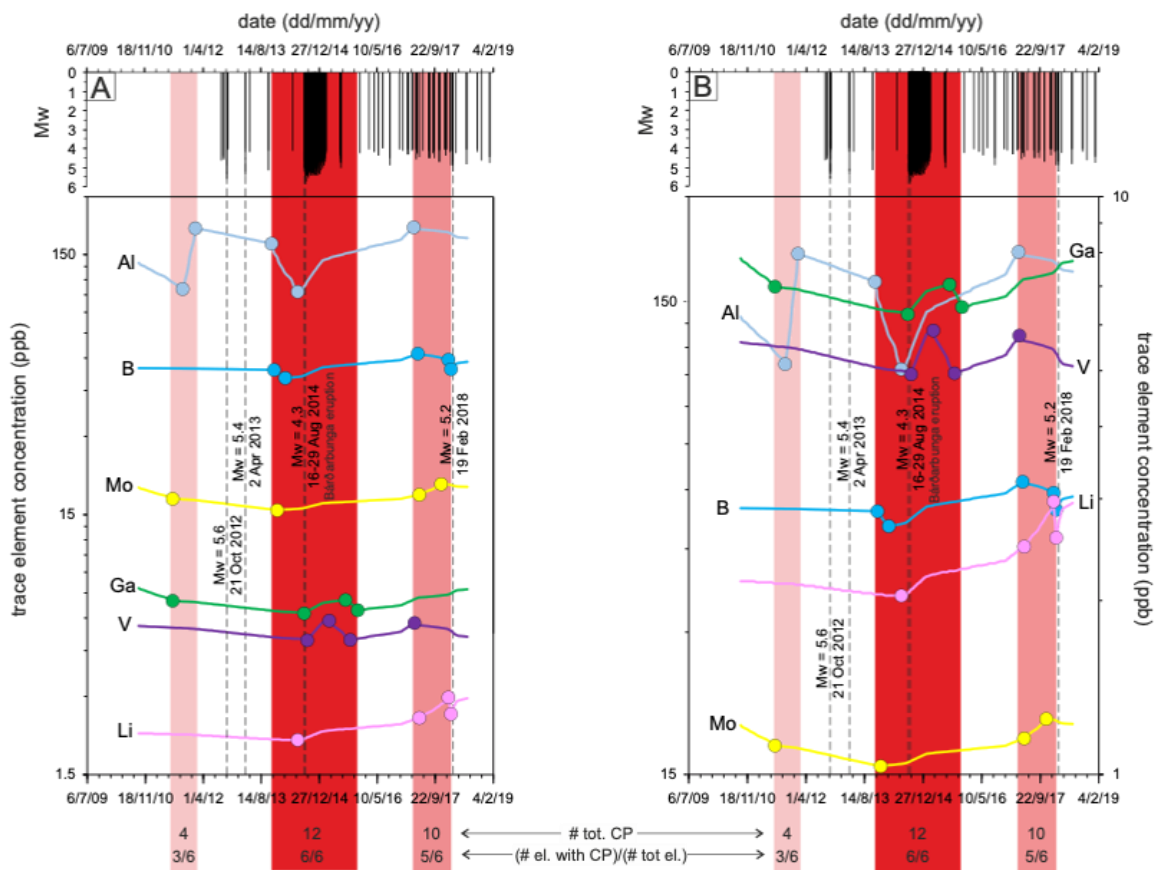


Figura 49. Diagramma Change Point (CP). Confronto tra le date del terremoto (parte superiore dei diagrammi, barre nere verticali e linee tratteggiate; scala del momento di magnitudo Mw) e i punti di cambiamento statisticamente significativi (CP) e le tendenze analizzate dal codice JRP (cerchi colorati e percorsi, rispettivamente; Programma di regressione Joinpoint 2020) relativi ai sei elementi raggruppati su PC1 (Al, B, Ga, Li, Mo e V). In (A), la scala di concentrazione ppb degli elementi è riferita all'asse sinistro log10. In (B), per mostrare meglio la pendenza dell'andamento di ogni elemento tra i CP, la concentrazione elementare entro la prima decade è stata suddivisa sull'asse secondario a destra. Lungo i percorsi, i gomiti non contrassegnati da cerchi rappresentano variazioni statisticamente non significative degli andamenti. In entrambi i diagrammi, i periodi verticali ombreggiati in rosso evidenziano tre diversi intervalli di tempo aventi una diversa densità di punti di cambio (fondo dei diagrammi): maggiore è il numero di punti di cambio (# tot CP) o gli elementi con CP sul totale (# el. CP / 6), più scuro è il tono rosso.

I cambiamenti idrogeochimici registrati prima e immediatamente dopo l'inizio dell'eruzione del Bárðarbunga del 2014 sono i più evidenti nelle serie temporali registrate (Fig. 45), come mostrato anche dalle analisi statistiche PCA e CP (Figg. 46 e 47, rispettivamente). In particolare, le concentrazioni di B e Al mostrano riduzioni significative, insieme a un trend di Mo appiattito a causa della stabilizzazione della concentrazione, da circa otto mesi prima dell'eruzione del Bárðarbunga (Fig. 47). Successivamente, gli stessi elementi iniziano una concentrazione che aumenta prima dell'evento di rifting e della successiva eruzione vulcanica. Inoltre, anche per le concentrazioni di Li, V e Ga è stato registrato un modello temporale simile, con l'inversione delle concentrazioni avvenuta circa due mesi (Li) o un giorno (Ga) prima dell'inizio dell'evento di rifting e un mese (V) dopo esso (Fig. 47). Interpretiamo questi segnali idrogeochimici come collegati con il grande evento di rifting di Bárðarbunga e l'eruzione e quindi i cambiamenti nelle concentrazioni di B, Al, Mo e Li, V, Ga sono considerati potenziali precursori vulcanici remoti.

Come accennato in precedenza, studi precedenti hanno documentato la sensibilità idrogeochimica ai terremoti delle acque sotterranee del pozzo HA01, almeno per alcuni costituenti principali (principalmente Na e Si) e rapporti isotopici stabili della molecola d'acqua (Skelton et al., 2014; Skelton et al., 2019). In questo studio, né le analisi PCA né CP sono state in grado di rilevare anomalie di concentrazione significative o variazioni di tendenza prima e dopo l'evento sismico Mw 5.6 del 21 ottobre 2012.

Diversamente, i cambiamenti idrogeochimici pre-sismici si sono verificati prima del terremoto di Mw 5.2 del 2018 (19 febbraio). Tutti gli oligoelementi considerati eccetto Al, V e As (cioè Li, B, Ga, Mo, Sr, Rb e Fe) hanno aumentato significativamente le loro concentrazioni nelle acque sotterranee da circa sette settimane prima del terremoto (Fig. 45). Un raggruppamento di elementi simili e una tendenza all'aumento contrassegnati da punti di cambiamento significativi sono stati statisticamente dimostrati dalle analisi PCA e CP, rispettivamente. È

interessante notare che nessuno dei principali elementi chimici né il rapporto isotopico stabile ossigeno-idrogeno dell'acqua (cioè $\delta^{18}\text{O}$ e $\delta^2\text{H}$) hanno modificato in modo significativo la loro concentrazione nelle acque sotterranee prima di questo terremoto (Skelton et al., 2019). Questa evidenza è un indizio significativo che gli oligoelementi possono essere idrogeochimicamente sensibili alla deformazione crostale pre-sismica, in particolare per i terremoti di magnitudo intermedia come quello verificatosi il 19 febbraio 2018, al largo dell'Islanda settentrionale (Mw 5.2). Tuttavia, i principali elementi e isotopi delle acque sotterranee sono fondamentali per ottenere una panoramica completa. Ulteriori prove sono infatti necessarie in futuro per supportare o confutare questa idea anche perché, nel caso del terremoto Mw 5.4 del 2013, sono state registrate anomalie idrogeochimiche pre-sismiche nelle concentrazioni di elementi maggiori (Skelton et al., 2014, Skelton et al., 2019; Andrén et al., 2016), mentre è stata riscontrata qualsiasi anomalia negli stessi campioni riguardo agli oligoelementi (Fig. 45). La deviazione dall'equilibrio tra labradorite e analcime è stata invocata da Andrén et al. (2016) per spiegare le variazioni di Na e Si durante gli eventi sismici 2012-2013. Questo processo è stato innescato da un nuovo input delle acque sotterranee dell'Olocene (Skelton et al., 2014; Skelton et al., 2019), che probabilmente ha un contenuto di oligoelementi inferiore rispetto agli altri due membri coinvolti nella miscelazione (un'acqua meteorica pre-Olocene e un componente arricchito con ^{18}O a causa dell'interazione con il basalto; Skelton et al., 2014). Pertanto, le variazioni nei rapporti isotopici stabili documentate prima del terremoto del 2012 (Skelton et al., 2014) e la diminuzione generalizzata e attenuata della concentrazione di oligoelementi (Fig. 45), ma contrassegnata da punti di cambiamento di Al, Mo e Ga nel mese di luglio 2011 (Fig. 49), sono probabilmente legati a questi cambiamenti idrologici / permeabilità. In effetti, va notato che la componente acqua ^{18}O esaurita, cioè influenzata dall'interazione acqua-roccia, ha mostrato un input significativo da aprile 2011 a maggio 2012 (Fig. 45b in Skelton et al., 2014). Le relazioni geochimiche tra Al e Ga, evidenziate anche da tendenze simili in Fig. 49, e come Mo non sia concentrato in una moderna componente di acque sotterranee erano già state sottolineate in precedenza.

Al contrario, nel corso del 2014 si registrano anomalie pre-eruttive significative negli oligoelementi (Figg. 48 e 49) senza anomalie significative riguardanti gli elementi maggiori (Skelton et al., 2014, 2019). Il ruolo complesso e la sensibilità dei potenziali precursori idrogeochimici, nonché il ruolo di fattori di influenza come il tipo, la distanza e l'ampiezza degli eventi geologici causali (ad es. terremoti, eruzioni vulcaniche o altro) oltre al contesto geologico del sottosuolo (specificità del sito) è solo all'inizio del processo di comprensione.

Inoltre, la nostra interpretazione dei cambiamenti idrogeochimici registrati come potenziali precursori sismici o vulcanici è messa in dubbio dall'osservazione che, nel 2016-2017, alcune variazioni idrogeochimiche si sono verificate quando non sono state registrate attività sismiche e vulcaniche significative. In particolare, due triplette elementari (cioè Li, Ga, Mo e B, Al, V) hanno mostrato un sostanziale aumento della concentrazione delle acque sotterranee nei periodi del 2016 e del 2017, rispettivamente (Fig. 45). Le analisi PCA hanno dimostrato che il raggruppamento di oligoelementi con K avvenuto dalla fine del 2014 alla fine del 2017 / inizio 2018 potrebbe essere correlato alla fase termica che segna la transizione tra la fase post eruttiva del Bárðarbunga e l'evento sismico avvenuto durante il 2018 (Fig. 48). Negli stessi periodi, anche la concentrazione di alcuni importanti elementi chimici nell'acqua HA01 ha mostrato variazioni anomale (Skelton et al., 2019), probabilmente causate da una rottura di una barriera idrologica dovuta alla sovrappressione del fluido e / o alla lenta deformazione.

Dai risultati di cui sopra, ipotizziamo che i seguenti cambiamenti idrogeochimici nelle concentrazioni di elementi in tracce potrebbero contribuire a previsioni affidabili di eventi geologici futuri. In particolare, interpretiamo:

(1) le variazioni idrogeochimiche nelle concentrazioni di B, Al, Mo e Li, V, Ga registrate, rispettivamente, prima e immediatamente dopo l'inizio dell'eruzione del Bárðarbunga del 2014 come potenziali precursori e postcursori vulcanici remoti, rispettivamente.

(2) i cambiamenti idrogeochimici nelle concentrazioni di Li, B, Ga, Mo, Sr, Rb e Fe, verificatisi prima del terremoto Mw 5.2 del 2018, come potenziali precursori del terremoto,

indicando che gli elementi in traccia possono essere idrogeochimicamente sensibili alla deformazione crostale pre-sismica, in particolare per terremoti di magnitudo intermedio-forte.

Le nostre interpretazioni devono essere ulteriormente confermate e validate da futuri monitoraggi idrogeochimici, che devono sempre comprendere le analisi dei principali elementi e isotopi delle acque sotterranee per ottenere una panoramica completa.

Il monitoraggio idrogeochimico a lungo termine degli oligoelementi ha confermato di essere un metodo promettente per identificare potenziali precursori di eventi geologici significativi come terremoti $M_w \geq 5$ ed eruzioni vulcaniche remote. Questo metodo dovrebbe essere integrato da un ulteriore monitoraggio idrogeochimico come le concentrazioni dei principali elementi e isotopi nelle acque sotterranee. Il ruolo di ciascun elemento (principale, traccia e isotopo) come potenziale precursore può essere diverso e deve essere chiaramente identificato e compreso in funzione di molti fattori influenzanti come la specificità del sito (cioè la geologia del sottosuolo) e il tipo, la distanza e magnitudo degli eventi geologici (es. terremoti o eruzioni vulcaniche).

I risultati ottenuti confermano che B è altamente mobile durante l'interazione acqua-roccia nel sistema geotermico basaltico ospitato. Pertanto, questo oligoelemento mostra una rilevante idrosensibilità vulcanica in quanto è un buon indicatore della lisciviazione delle rocce.

Principal Component Analysis (PCA) può aiutare a identificare il ruolo specifico degli elementi in diversi eventi, evidenziando che circa 115 eventi sono meglio spiegabili con i principali costituenti (ad esempio, 2012 e 2013 $M_w > 5$ terremoti; 2014-2017 anomalie di potenza termica) e altri con oligoelementi (ad esempio, eruzione del Bárðarbunga del 2014; terremoto di M_w 5.2 del 2018). L'analisi del punto di cambiamento (CP) su uno specifico cluster di elementi identificati dalla PCA aiuta a convalidare statisticamente la variabilità del trend nelle serie temporali. Gli oligoelementi mostrano comportamenti diversi sia tra i terremoti vulcanici e tettonici, sia tra i terremoti tettonici $M_w > 5$ verificatisi nel 2012-2013 e nel 2018. In particolare, i contributi delle acque sotterranee moderne influenzate dall'interazione acqua-roccia avvenuto

un anno prima del terremoto del 2012 sembra essere coevo con i punti di cambiamento rilevati nei trend di concentrazione di Al, Mo e Ga.

I cambiamenti idrogeochimici pre e post eruttivi nelle acque sotterranee dal pozzo HA01, che si trova a una distanza superiore a circa 140 km dal vulcano Bárðarbunga, non dovrebbero sorprendere. Tutte le faglie sismicamente attive hanno involucri di fluidi dei pori ad alta pressione critica. In effetti, un aumento dell'accumulo di stress è stato rilevato nel sistema di faglia Húsavík-Flatey prima dell'inizio della crisi sismica dell'episodio vulcanico di Bárðarbunga ([Hong et al., 2020](#)). Di conseguenza, sebbene entrambe le stazioni che monitorano la divisione delle onde di taglio e il pozzo HA01 nel nord dell'Islanda siano a oltre 100 km da Bárðarbunga, sembrano così sensibili ai cambiamenti di stress che dovrebbero registrare l'accumulo di stress e le variazioni chimiche prima delle eruzioni di Bárðarbunga.

Certamente, la diffusione di siti e reti di monitoraggio idrogeochimico a lungo termine su territori sismici e vulcanici (ad esempio, [Franchini et al., 2021](#)) consentirà agli scienziati di compiere progressi significativi nella scienza dei precursori del rischio geologico.

9. Conclusioni

(1) Confronto nazionale ed internazionale: A livello nazionale ed internazionale, molti gruppi di ricerca in Italia, Cina, Giappone, Israele e altrove stanno cominciando progetti simili ad HydroQuakes con tecnologie e metodi simili a quelli proposti dal gruppo di lavoro che scrive la presente relazione. Dunque, il confronto nazionale ed internazionale con altri gruppi di ricerca che lavorano sugli stessi temi (previsione dei terremoti) risulta di grande conforto e suggerisce che le idee e le metodologie proposte per e nell'ambito di HydroQuakes siano molto promettenti per la scienza della previsione dei terremoti.

(2) Metodi e tecnologia: Alcune delle stazioni sotto monitoraggio per il progetto HydroQuakes (Sulmona e Matese-Beneventano) sono state dotate di sonde in situ che permettono il monitoraggio in continuo di alcuni parametri chimico-fisici. In particolare, la stazione di Bojano è stata dotata di uno strumento in situ (spettrometro di massa) di marca Hiden e fabbricazione inglese che è in grado di determinare le concentrazioni di gran parte dei gas disciolti in soluzione fino a massa atomica 200 amu. Si tratta del primo esperimento/installazione di questo tipo al mondo. Su tale esempio, altri gruppi di ricerca in Italia stanno acquistando due strumenti identici per la loro installazione in altre sorgenti dell'Italia centro meridionale in aree sismicamente attive. Anche in questo caso, il confronto con altri gruppi di ricerca risulta molto confortante per le tecnologie ed i risultati adottati ed ottenuti nell'ambito del progetto HydroQuakes. Inoltre, le sonde installate in situ, compreso lo spettrometro di massa Hiden, sono state tutte collegate a un sistema di acquisizione online sviluppato da Digimatic s.r.l. (<http://www.digimatic.it/Home.html>) che consente agli operatori di visualizzare e scaricare tutti i dati acquisiti in tempo reale. La piattaforma digitale consente agli utenti autorizzati di visualizzare la posizione georeferenziata dei siti, consultare i manuali degli strumenti collegati e verificarne il corretto funzionamento. Il trasferimento in remoto dei dati avviene tramite un collegamento delle sonde via GPRS, grazie all'utilizzo di una SIM telefonica, a un server

stabilito presso il dipartimento di Scienze della Terra (Sapienza Università di Roma) al quale si può accedere tramite computer o dispositivi mobili in qualsiasi momento e da ogni luogo. Anche in questo caso, dalla letteratura scientifica attuale, tale sistema di controllo da remoto risulta essere il primo al mondo per l'ambito scientifico di HydroQuakes.

(3) *Appennino centrale*: il monitoraggio effettuato sulle stazioni di Sulmona e Matese-Benevento a partire dall'inizio del progetto HydroQuakes ha prodotto alcuni risultati interessanti. Durante il progetto, nell'area investigata da HydroQuakes non ci sono stati terremoti forti e intermedi ($M_w \geq 5.0$). Ci sono stati però tre terremoti che sono stati oggetto di attento studio: ossia il terremoto di Collelongo (M_w 4.1, 1 gennaio 2019) di Balsorano (M_w 4.4, 7 novembre 2019) e di San Leucio del Sannio (M_w 3.9, 16 dicembre 2019). Il risultato più interessante è che tali terremoti (eccetto quello di Collelongo) non sono stati sostanzialmente preceduti da anomalie idrogeochimiche. Questa evidenza potrebbe suggerire che tali anomalie possano insorgere sostanzialmente solo con terremoti intermedi e forti ($M_w \geq 5.0$). Il terremoto di Collelongo, che è avvenuto su una faglia appenninica molto grande (la faglia generatrice del grande terremoto di Avezzano del 1915) a profondità di circa 16-17 km è però stato preceduto da debolissime anomalie idrogeochimiche. Le stesse potrebbero essere proprio connesse a rotture pre-sismiche lungo una faglia molto grande a grandi profondità crostali (c. 17 km).

(4) *Precursori fossili*: Con l'avanzare della conoscenza dei potenziali precursori idrogeochimici dei terremoti, diventa necessaria una conferma e validazione di tali precursori tramite strutture fossili generate da paleofluidi per comprendere la frequenza e l'affidabilità di tali potenziali precursori. HydroQuakes insieme ad uno precedente in Islanda (Andrén et al., 2016) hanno questo merito, indicando la futura ricerca necessaria per validare, attraverso strutture fossili, potenziali precursori idrogeochimici dei terremoti. Allo stesso tempo, tale conferma o validazione è fattibile solo se i dati paleofluidali provengono da strutture pre-

/co-sismiche chiaramente identificate (es. vene, micromineralizzazioni e relative inclusioni di fluidi). HydroQuakes e alcuni studi precedenti sopra citati contribuiscono all'identificazione di microstrutture pre-/co-sismiche legate ai paleofluidi lungo le faglie, dove tali microstrutture sono quindi fondamentali non solo per la comprensione dell'attrito di faglia ma anche per il progresso della conoscenza dei segnali precursori dei terremoti.

(5) *Islanda del Nord*: I risultati del lungo monitoraggio in Islanda settentrionale forniscono interessanti evidenze per quanto riguarda le relazioni tra terremoti, eruzioni vulcaniche e anomalie idrogeochimiche. Alcune anomalie idrogeochimiche infatti precedono l'eruzione del Bárðarbunga del 2014 e relativi terremoti precursori così come deboli anomalie idrogeochimiche precedono alcuni terremoti di magnitudo intermedia ($M_w \geq 5.0$) nel nord dell'Islanda. In particolare: (a) le variazioni idrogeochimiche nelle concentrazioni di B, Al, Mo e Li, V, Ga registrate, rispettivamente, prima e immediatamente dopo l'inizio dell'eruzione del Bárðarbunga del 2014 possono essere interpretate come potenziali precursori e postcursori vulcanici remoti, rispettivamente; (b) i cambiamenti idrogeochimici nelle concentrazioni di Li, B, Ga, Mo, Sr, Rb e Fe, verificatisi prima del terremoto M_w 5.2 del 2018 nel nord dell'Islanda possono essere interpretati come potenziali precursori del terremoto, indicando che gli elementi in traccia possono essere idrogeochimicamente sensibili al regime pre-sismico di deformazione crostale, in particolare per terremoti di magnitudo intermedio-forte ($M_w \geq 5.0$).

(6) *Modello geochimico*: Mentre il modello fisico di deformazione pre-sismica che possa spiegare le eventuali anomalie idrogeochimiche pre-sismiche è sostanzialmente noto, quello geochimico non ancora. Nell'ambito di HydroQuakes è stato sviluppato un tale modello. In sostanza, tale modello permette di distinguere la CO_2 proveniente dalla crosta intermedia e profonda dalla CO_2 di origine più superficiale. Nel caso della sequenza sismica di Anatrice-Norcia (2016-2017), tale modello ha permesso di individuare un cospicuo apporto di CO_2 profonda dalla crosta nelle falde acquifere

superficiali. Tale apporto ha reso le acque più aggressive del solito e tale aggressività nei confronti delle rocce incassanti è all'origine dell'apporto di metalli e metalloidi in quantità notevolmente maggiore del solito alle sorgenti in superficie. Tale modello geochimico quindi spiega le anomalie idrogeochimiche pre-sismiche in Appennino centrale ma pensiamo possa essere anche esportato altrove con opportune modifiche chimico-fisiche e termodinamiche.



Appendice: Articoli Scientifici Derivati dal Progetto HydroQuakes

Dal Progetto HydroQuakes sono derivati, ad oggi, sei articoli scientifici. Quattro dei sei articoli sono già pubblicati su riviste scientifiche internazionali mentre gli ultimi due sono in fase di revisione da parte di altre riviste scientifiche internazionali e riteniamo possano essere a breve pubblicati. Ringraziamo la Fondazione ANIA ed in particolare il Dott. U. Guidoni con i suoi collaboratori per il sostegno alle ricerche ed il permesso a pubblicare i relativi risultati scientifici. I sei articoli sono di seguito elencati e riportati per intero nelle pagine successive. Per tali articoli, ci si è avvalsi della collaborazione di numerosi colleghi italiani e stranieri, che ringraziamo per il proficuo scambio di idee.

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Geochemistry, Geophysics, Geosystems

RESEARCH ARTICLE

10.1029/2018GC008117

Key Points:

- Geochemical processes behind water anomalies prior to the 2016 earthquakes in Italy are investigated by chemical models
- Increased concentrations of As and V, a slight B increase, and a concomitant lowering of B isotope ratio occurred due to mineral desorption
- Desorption was triggered by an excess of deep CO₂ in groundwater, which occurred prior to the mainshock due to preseismic crustal dilation

Supporting Information:

- Supporting Information S1
- Table S1
- Data Set S1

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CO₂ Inflow and Elements Desorption Prior to a Seismic Sequence, Amatrice-Norcia 2016, Italy

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Abstract The 2016 Mw ≥ 6.0 Amatrice-Norcia earthquakes (central Apennines, Italy) and the related seismic sequence were associated with increases in arsenic and vanadium concentrations recorded in groundwater springs a few months before the earthquakes occurred. To evaluate these signals as reliable seismic precursors and effective predictive tools, we studied the geochemical processes that caused these anomalies. Using chemical and isotope models, we show that increased concentrations of arsenic and vanadium, a slight increase in boron concentrations, and a concomitant lowering of the boron isotope ratio may be due to mineral desorption (e.g., from iron oxides and/or clays). We argue that a displacing effect on the trace elements sorbed on minerals was triggered by an excess of deep CO₂ in groundwater, which occurred prior to the main seismic event as a result of preseismic crustal dilation. Our observations confirm the pivotal role of CO₂ in the release of trace elements by alteration of solid phases and provide a new understanding of earthquake-related water chemical anomalies.

1. Introduction

Natural disasters have a great socioeconomic impact. In the last decades, studies of earthquake precursors have shown that geophysical and geochemical changes may occur prior to earthquakes of magnitude greater than 5 (Ingebritsen & Manga, 2014). Although many observed seismic precursors are related to the stress buildup before an earthquake and its following release, the effect on the different geochemical parameters and their amounts may vary depending on many factors (e.g., geodynamics, tectonics, rocks and minerals composition, and hydrology). As a result, it is very difficult to relate the geochemical anomalies to a specific process and prove that are really associated with earthquakes. Despite this, water chemical anomalies are increasingly recorded at distances between 20 km and more than 200 km from strong earthquake epicenters (Andr n et al., 2016; Chen et al., 2015; Claesson et al., 2004; De Luca et al., 2018; Grant et al., 2011; Huang et al., 2012; Igarashi et al., 1995; Inan et al., 2012; Ingebritsen & Manga, 2014; Sano & Wakita, 2016; Skelton et al., 2008, 2014, 2019; Wakita et al., 1988; Wang & Manga, 2010; W steby et al., 2014; Zeng et al., 2015).

The 2016 Amatrice and Norcia mainshocks (24 August and 30 October, respectively; Figure 1b; Chiaraluce et al., 2017; Falcucci et al., 2018) involved significant pore pressure changes and fluid movement, both at deep and shallow crustal levels (De Luca et al., 2018; Petitta et al., 2018; Tung & Masterlark, 2018), which were preceded by hydrogeochemical anomalies recorded since April 2016 in the springs of the central Apennines (Barberio et al., 2017; De Luca et al., 2018). Increases in the concentrations of arsenic and vanadium were recorded in groundwater issuing from springs monitored in the Sulmona area (S1 to S7 in Figure 1b), roughly 70 km to the southeast of the epicentral area and in a spring within the epicentral area (S8 in Figure 1b; Barberio et al., 2017). S1 to S4 are fed by deep groundwater flow, while S5–S7 are fed by local aquifers.

A preseismic and coseismic elemental contribution from bituminous-asphaltic and/or hydrothermal fluids was hypothesized (Barberio et al., 2017). However, neither additional trace elements (e.g., Ba, Ni, and Mn) nor salinity and oxygen-hydrogen stable isotope ratio changes—which should be a consequence of hydrocarbon decomposition (Bolliger et al., 1999; Tissot & Welte, 1984) and fluid mixing, respectively—were detected (Barberio et al., 2017). The possible cause of the anomalies must explain the steady characteristics of groundwater flow and the simultaneous increase of selected trace elements.

Below, partly based on previous data (Barberio et al., 2017), we explain the geochemical processes that led to the increase in As and V concentrations in groundwater, providing a new perspective on the possible link

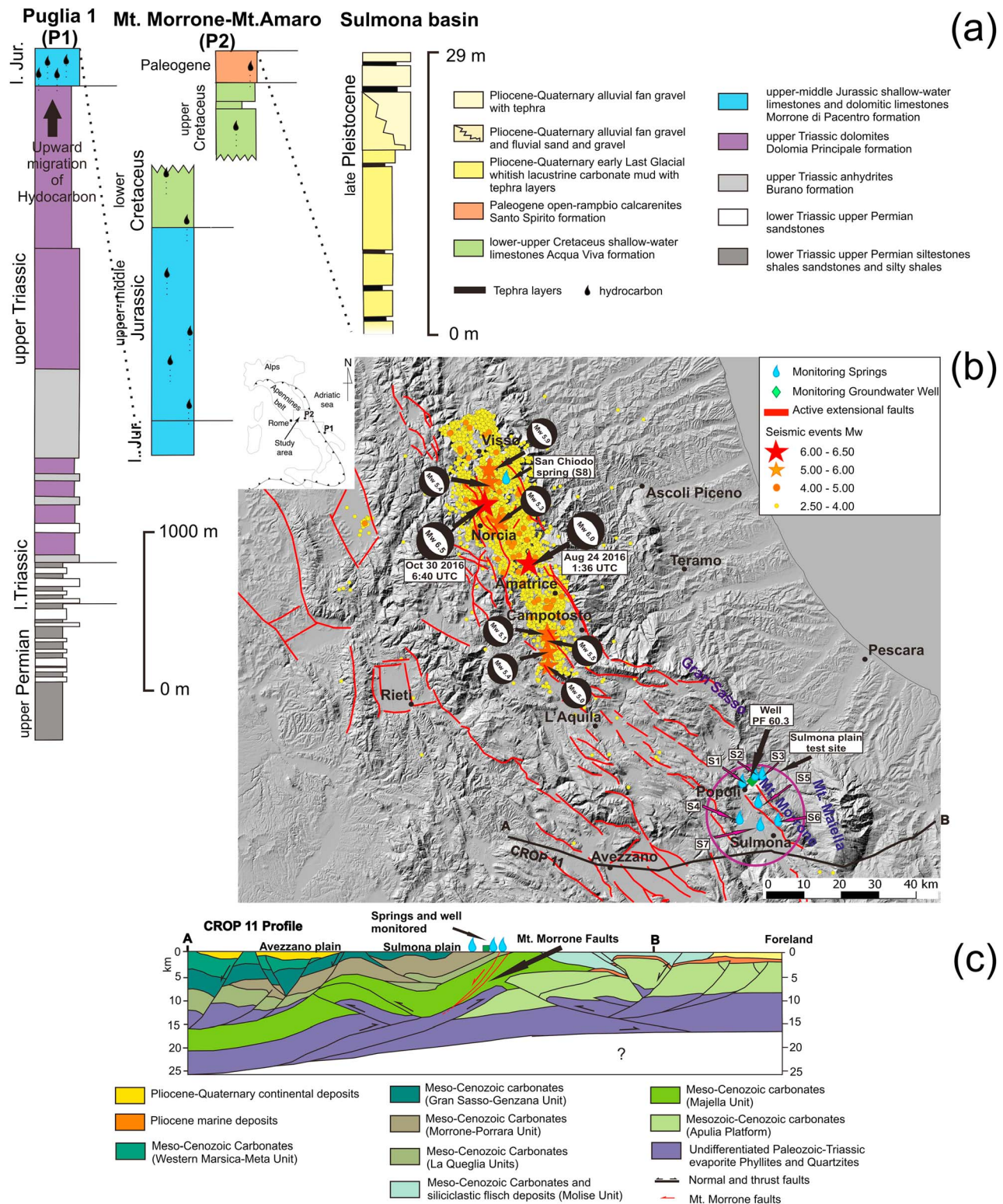


Figure 1. (a) Synthesis of stratigraphic logs from the Apulian-Adriatic foreland of the Apennines fold-thrust belt. See the well location in the upper-right inset of (b). (b) Map of central Apennines (see location in upper-left inset) showing earthquake epicenters of the 2016 to 2017 sequence. Locations of the monitoring well and springs analyzed in this work are displayed by blue drops and green squares, respectively. Earthquake epicenters are from the INGV database (available online at <http://cnt.rm.ingv.it/>). Active faults (red lines, all extensional) are from the Ithaca database (available online at <http://www.isprambiente.gov.it/en/projects/soil-and-territory/italy-hazards-from-capable-faulting>). (c) Interpretation of the CROP-11 deep seismic profile (modified after Patacca et al., 2008). See A-B profile track in (b). Note the location and depth of the extensional Mt. Morrone fault system (red faults) adjacent to the well and springs considered in this paper.

with deep CO₂ input. We present new data on boron isotope ratios that supports the potential role of elemental desorption from secondary solid phases (e.g., iron oxides and clays).

2. Setting

The Apennines (Figure 1) form a fold-thrust accretionary wedge that has progressively migrated eastward, toward the Adriatic foreland. Post-orogenic extension and normal faults have created numerous intramountain basins (Pliocene-Quaternary; Billi et al., 2006; Cavinato & DeCelles, 1999). In the study area (Sulmona plain; Figure 1b), located in the seismically active central Apennines (Galli et al., 2008), one of these extensional faults is the Mt. Morrone fault, striking NW-SE by roughly 25 km and dipping toward the SW by 50–60° (Figure 1c). This fault is considered to have been responsible for past earthquakes greater than Mw 6.5. Its most recent activation occurred during the second century Anno Domini (AD) (Ceccaroni et al., 2009; Galadini & Galli, 2001; Galli et al., 2008; Gori et al., 2011).

In the Sulmona area, the pre-orogenic succession consists of Meso-Cenozoic limestone and dolostone and Triassic evaporite with anhydrite and dolomite (units are thrust one over the other), as well as Permian-Triassic phyllite and quartzite (which makes up the crystalline basement; Parotto et al., 2003; Patacca et al., 2008). The fractured carbonates correspond to primary aquifers hosting regional groundwater flows (>10 m³/s from main springs) that converge from different hydrogeological units toward the study area. Minor springs are frequently characterized by mixing between regional flow and deep fluids, as in the sampled springs (Petitta et al., 2018). Moreover, two springs manifesting hydrocarbon seeps (Rusi et al., 2018) occur on the eastern side of Mt. Morrone. Source rocks consist of Upper Triassic layered or massive bituminous dolostone (Rusi et al., 2018). The syn-orogenic succession consists of hemipelagic marls overlain by sandstones with marl- and clay-rich interbeds (Brandano et al., 2010; Carminati et al., 2007), the latter of which correspond to the regional aquiclude. The post-orogenic deposits are mainly fluvial-lacustrine and gravel deposits (Quaternary), acting as aquitards with local groundwater flow. These deposits host well-preserved thin volcanoclastic layers (tephra), derived from the explosive activities of the peri-Tyrrhenian volcanoes or intra-Apennine centers (D'Orefice et al., 2006; Giaccio et al., 2013; Peccerillo, 2017; Figure 1a).

3. Data and Methods

The hydrogeochemical and hydrogeological data used in this work derive from the monitoring sites located in the Sulmona area (Barberio et al., 2017; Petitta et al., 2018) between the Gran Sasso and Morrone carbonate fractured aquifers, where regional groundwater flow paths converge to feed basal springs (Figure 1). The Morrone carbonate aquifer is bounded by low permeability layers; in the northern sector, these layers are constituted by the thrust zone between the Gran Sasso (top) and Mt. Morrone (bottom) carbonate units, where siliciclastic low-permeability deposits also outcrop. In the eastern sector, the low permeability limit is represented by the thrust zone between the Mt. Morrone unit (top) and the Laga siliciclastic flysch unit (bottom; Salvati, 2002); in the western sector, the Mt. Morrone active extensional fault partially isolates the deep carbonate aquifer from the local shallow aquifers located in the Plio-Quaternary continental clastic deposits of the Sulmona intramountain basin (Figure 1).

In this area, irregularly since July 2014 and systematically since January 2016, we hydrogeochemically monitored a group of seven springs fed both by the Mt. Morrone and by the Gran Sasso carbonate aquifers (Barberio et al., 2017; Petitta et al., 2018). The discharge area, corresponding to the Sulmona Plain and its northern prolongation (Popoli Gorges), receives groundwater flow both from regional aquifers, high and steady discharge springs, and locally from springs in the form of deep fluid contribution. The hydrogeological framework clearly indicates this area as a focal point of regional groundwater flow with deep flowpaths; for this reason, it is considered valuable for the monitoring aims of this research. Indeed, the stability of groundwater flow, showing minimal seasonal oscillations, allows for an optimal evaluation of groundwater changes due to reasons other than hydrogeological causes (i.e., seasonal recharge/discharge cycles, surface water/groundwater interaction, and lateral flow or leakage). The monitored springs were selected for their regime and chemical content as being representative of regional and deep groundwater flowpaths. These springs also exhibit hydrogeological and chemical stabilities, which indicates that the influence of seasonal and local hydraulic contributions is very limited and clearly identifiable (Barberio et al., 2017).

Samples from these springs were collected on a monthly basis. In particular, labile physical-chemical parameters (temperature and pH) were measured at the sampling site (Barberio et al., 2017), using a WTW Multi 3420 probe. New redox data (Eh in mV) measured from 28 April 2017 to 04 October 2017 using a WTW pH/Cond 3320 probe are shown in the supporting information Table S1. Water aliquots of the samples were analyzed in the laboratory for major cations, anions, and trace element content (along with $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ isotope ratios, here not discussed due to their nonsignificant variations; Barberio et al., 2017). Water aliquots for major and trace cations were acidified at 1% v/v by adding 65% p/p HNO_3 Suprapur[®] (Merck-Millipore). According to Standard Methods (Clesceri et al., 1999), the analytical accuracy on major ions ionic balance and on trace elements determination was better than 5%. The Limit of Quantification of As and V by inductively coupled plasma mass spectrometry (ICP-MS) was $0.01 \mu\text{g/L}$. We refer the reader to the previously published manuscript for further details on these analytical methods and on the statistical significance of As and V anomalies (Barberio et al., 2017). In this new study, new data elaborations and interpretations are furnished along with new B and Sr isotope analyses on selected samples.

The total dissolved solids (TDSs) are calculated by summing the concentrations (in milligrams per liter; Barberio et al., 2017) of the primary dissolved constituents as follows (Clesceri et al., 1999; Table S1):

$$\text{TDS} = [0.5 \times (\text{Alk as } \text{HCO}_3^-)] + \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+ + \text{Cl}^- + \text{SO}_4^{2-}.$$

In the Table S1, the molality concentrations, activities, and mineral saturation indexes (S.I.) of the sampled waters (Barberio et al., 2017) are calculated using the PhreeqcI code (Phreeqc Interactive), version 3, using the *lnl.dat* thermodynamic data set, which employs the Debye-Hückel theory for the activity calculation (Parkhurst & Appelo, 2013). Contrastingly, the *phreeqc.dat* data set was used for calculations at $P > 10^{-1} \text{ MPa}$ (e.g., Figure 4). The total molality (molar per kilogram H_2O) of Ca, Mg, SO_4 , and $\text{C}(4) = \text{TDIC}$, resulting from speciation at the pH-T-P sampling conditions of spring water samples (Barberio et al., 2017), was used for the calculation of Ccarb and Cext parameters (Chiodini et al., 2000; Martini, 2016; Table S1).

The standard properties of hydrous ferric oxide (HFO, FeOOH) was used for surface complexation modeling (SCM; Dzombak & Morel, 1990; Parkhurst & Appelo, 2013; Zhu & Anderson, 2002): molecular formula weight = 89 g/mol; surface area = $600 \text{ m}^2/\text{g}$, strong site density = 0.005 mol/mol ; weak site density = 0.2 mol/mol . Following adsorption modeling by the S3 water (17 December 2015 sample) and HFO surfaces at different equilibria conditions and weights, desorption was modeled by the infiltration of 16 (HFO sites coupled to ferrihydrite-water equilibria) or 20 (HFO weights: 0.25, 34, and 334 g) pore volumes, using the S1 water (17 December 2015 sample) as recharging water at increasing CO_2 fugacity (Parkhurst et al., 2011). Calcite saturation was fixed during modeling calculation (Data Set S1).

Boron ($^{11}\text{B}/^{10}\text{B}$) and strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) isotope ratios were obtained by multicollector thermal ionization mass spectrometry (MC-TIMS) measurement (Triton, Thermo Scientific) at the University of Calgary (Elhamel, 2014; Wieser & Tutas, 2009). Analyses were performed on 0.45- μm filtered S1 (both $^{11}\text{B}/^{10}\text{B}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) and S8 (only $^{87}\text{Sr}/^{86}\text{Sr}$) samples, following column pretreatment to avoid an analytical background and taking into account the B and Sr concentrations. For boron, the delta values in permil of the isotope ratios ($\delta^{11}\text{B} \text{ ‰}$) were calculated against the reference material NIST SRM 951 (boric acid), whereas for strontium, ratios $^{87}\text{Sr}/^{86}\text{Sr}$ were normalized to NIST SRM 987 (strontium carbonate). The external reproducibility (2σ) was better than $\pm 2\text{‰}$ for $\delta^{11}\text{B}$ and ± 0.00002 for $^{87}\text{Sr}/^{86}\text{Sr}$. The results are shown in the final sheet of Table S1. A more detailed discussion of the methodology can be found in Supporting Information S1 (Barbieri et al., 2005, 2017; Bethke, 2008; Blanc et al., 2012; McArthur et al., 2012; Giaccio et al., 2013; Boschetti et al., 2017).

4. Modeling Pre-Seismic and Co-Seismic Geochemical Processes

4.1. “Deep CO_2 ” Input

The involvement of deep CO_2 -bearing fluids in the triggering of earthquake sequences has been widely debated (Miller, 2013; Weinlich, 2014). A carbon mass balance of the involved water describing the origin of total dissolved inorganic carbon (TDIC) can be represented as follows (amounts expressed as m = molality; see the Supporting Information S1 for details) (Chiodini et al., 2000):

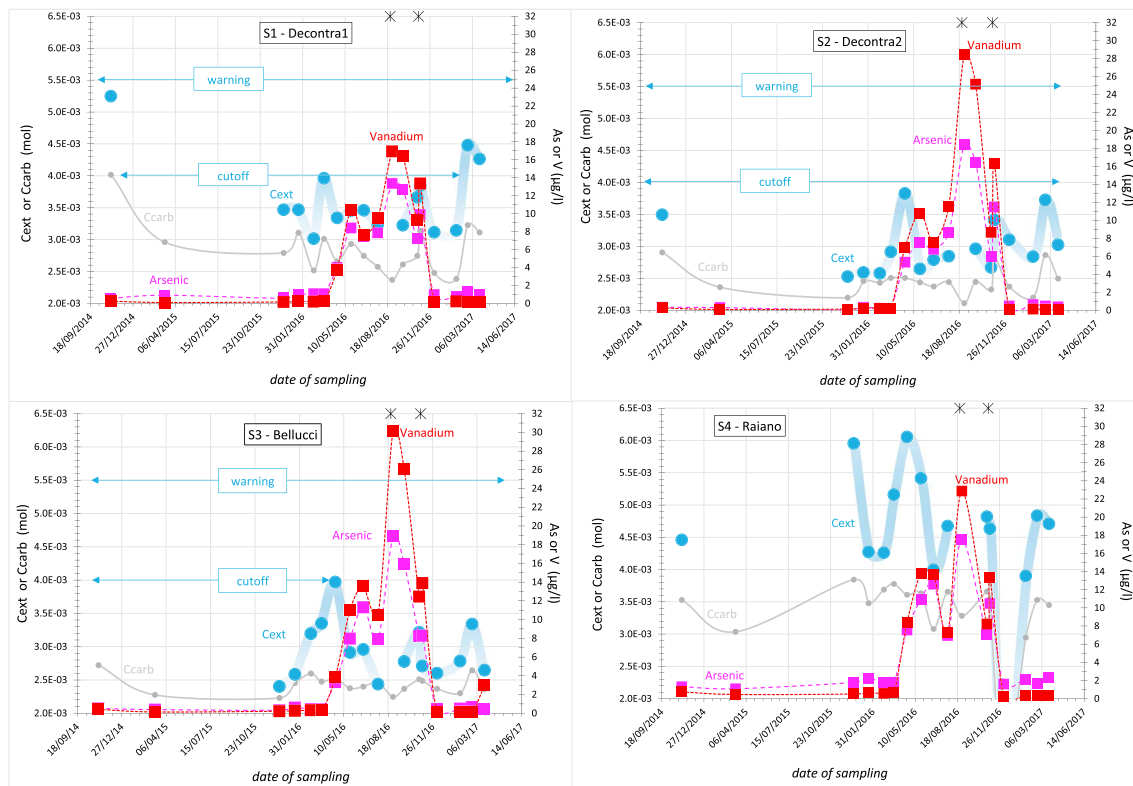


Figure 2. Time series for Cext-Ccarb (big blue-small gray dots joined by solid lines) and As-V (pink-red squares joined by dashed lines) of the S1–S4 springs. The dimension of the data points is greater than analytical accuracy (5%). Cutoff and warning threshold refer to Cext values of 4.0E-03 and 5.5E-03 m, respectively (Chiodini et al., 2004; Martini, 2016). These values are purely indicative and only shown for comparison. Cext gaps are due to a lack of pH data. Asterisks (*) denote $M_w \geq 5.0$ primary shock events: 24 August 2016 ($M_w = 6.0$) and 30 October 2016 ($M_w = 6.5$).

$$\text{TDIC} = \text{Ccarb} + \text{Cext},$$

$$\text{Ccarb} = \text{Ca} + \text{Mg-SO}_4,$$

$$\text{Cext} = \text{TDIC} - \text{Ccarb} = \text{Cinf} + \text{Cdeep}.$$

Ccarb is the amount of carbon derived from the interaction of groundwater with carbonate aquifer rocks, while Cext is carbon derived from processes other than these (i.e., from external sources). This latter component can be expressed as $\text{Cext} = \text{Cinf} + \text{Cdeep}$, where Cinf is the carbon from atmospheric and biogenic CO_2 (infiltrating water) and Cdeep is deep CO_2 from metamorphism, mantle, or magma sources (Chiodini et al., 2000).

In previous studies conducted in the Central Italy, the following thresholds were proposed (Chiodini et al., 2000; Chiodini et al., 2004): $2.0\text{E-}03 \leq \text{Cinf} < 4.0\text{E-}03$ m. The low concentration concerns the waters with carbon mainly from a biogenic source (the background), whereas the high concentration is the threshold for the waters with important contribution of deep carbon (the “cutoff”; that is, the probability that this value is exceeded by Cinf is less than 1%; Chiodini et al., 2004). More recently, $\text{Cinf} = 2.31\text{E-}03 \pm 6.1\text{E-}04$ m has been proposed as representative of the recharge waters of the Apennines (Fronzini et al., 2018).

The easternmost sector of the Apennines has been considered as an area where the probability of finding groundwater with Cext greater than the cutoff is low (Chiodini et al., 2004). Consistent with this notion, the monthly sampling sequence of the S5 to S7 water samples collected in the study area prior to and during the seismic sequence shows a negligible excess of deep CO_2 , that is, $\text{Cext} \approx \text{Ccarb} \approx \text{Cinf}$. In contrast, S1 to S4 waters show an increased input in deep carbon source up to the cutoff value, along with an arsenic-vanadium concentration jump (April 2016; Figures 2 and 3). Three statistic tests performed on S1–S4 springs have verified that the mean Cext detected during the sampling period is statistically different from the mean Cinf of the Apenninic recharging water (Fronzini et al., 2018; Tables 1 and S1–S4).

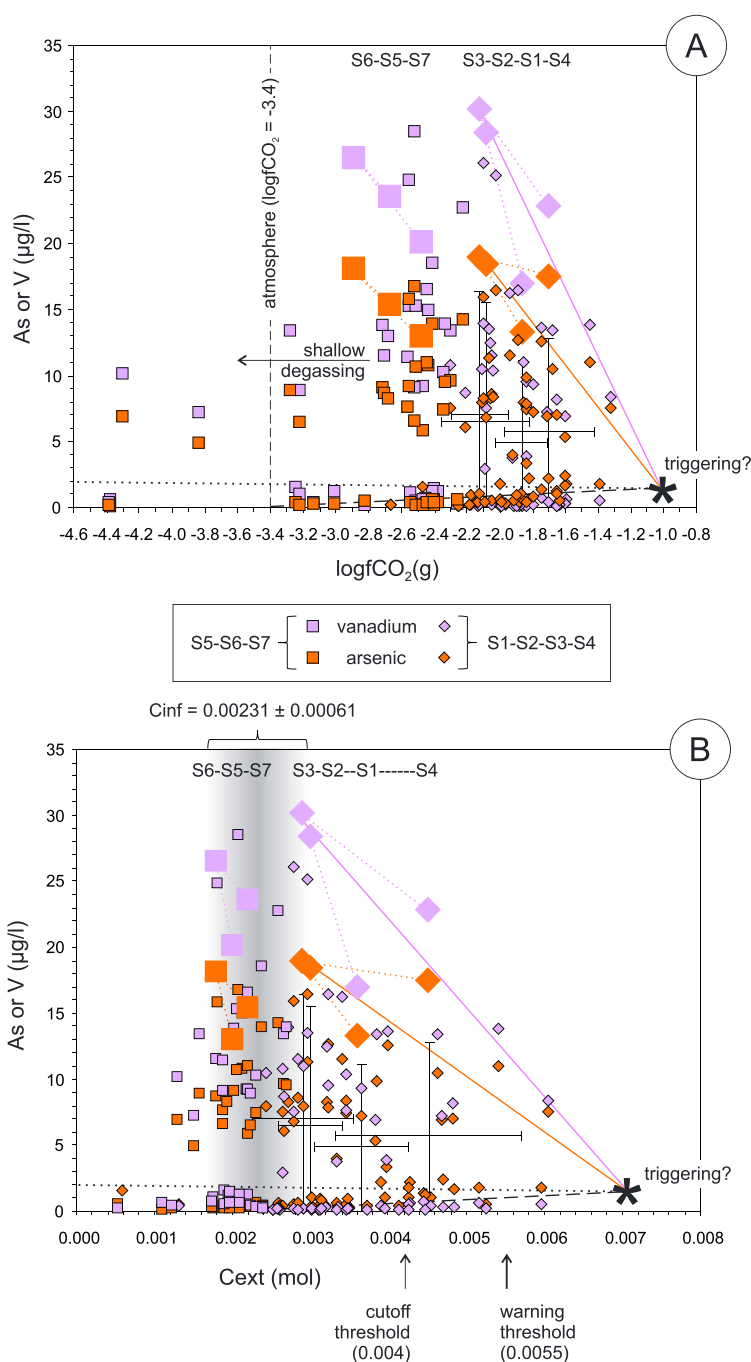


Figure 3. Arsenic (purple) and vanadium (orange) concentrations (µg/L) versus the calculated dissolved CO₂ fugacity as logfCO₂(g) (a) and Cext molality (b). Oxidic-suboxic (Eh ≤ 0: S1, S2, S3, S4; hereafter, S1 to S4) and oxidic (Eh ≥ 0: S5, S6, S7; hereafter S5 to S7) sampled waters are distinguished by diamond and square symbols, respectively. The larger symbols depict the highest As-V concentration detected during the first seismic mainshock (24 August 2016). Unfortunately, it was not possible to calculate the Cext value for this period, due to a lack of pH values. For this reason, the larger symbols were plotted using the averaged Cext values (crosses indicate the mean ± standard deviation of Cext for S1 to S4). The back extrapolation of the trend lines that approximately fit the higher As-V concentrations detected in the S1 to S4 samples (colored solid lines) intersects the CO₂/Cext buildup (dashed black line) at the following supposed desorption triggering values: As and V ≈ 2 µg/L (dotted black line), Cext ≈ 0.007 mol, and logfCO₂ ≈ -1. All sampled water is fresh (total dissolved solid < 1 g/L) and has a Ca-HCO₃ main chemical composition. In comparison to the S5 to S7 spring group (5 < SO₄ < 30 mg/L), the S1-S4 group is more enriched in dissolved sulfate (40 < SO₄ < 180 mg/L), due to interaction with gypsum and anhydrite of the Upper Triassic fm. Moreover, all spring water shows a slight calcite oversaturation. This can be theoretically explained by a shift to the left in the following reaction:

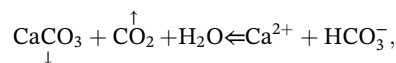
Table 1*Main Input Parameters and Results of the Two-Sample T Tests and Z Test (McDonald, 2014)*

	Mean	Std. dev.	N	Rejection of the null hypothesis H_0 ($H_0 = \text{mean}_{\text{Cinf}} - \text{mean}_{\text{S\#}} = 0$) at $\alpha = 0.05^a$
Cinf	2.31E-03	6.10E-04	83	—
S1	3.65E-03	5.93E-04	16	Yes
S2	3.00E-03	2.88E-03	16	Yes
S3	2.82E-03	5.72E-04	16	Yes
S4	4.52E-03	1.26E-03	15	Yes

Note. Values in molality, N = sample size, Cinf from Frondini et al. (2018). Details are in Tables S1–S4.

^aChecked by the following three tests: Student's T test (equal variance), Welch's T test (unequal variance), and Z test.

Moreover, $\text{Cext} > \text{cutoff}$ is also detected. In particular, spring S4 shows (i) the most significant inverse relation between pH and Cext ; (ii) Cext consistently above the threshold prior to the seismic sequence; (iii) two Cext values above $5.5\text{E-}03$ m, an early warning signal of possible seismic activity in the central Apennines (Martini, 2016), detected prior to As and V increase; and (iv) an abrupt Cext decrease following the seismic sequence, likely related to dilution after fracture opening, as confirmed by the decrease of the TDSs from higher than 400 mg/L down to 181 mg/L (TDS, Table S4-Raiano). The deep origin of the CO_2 along with the highest $\log f\text{CO}_2(\text{g}) = -1.3$ detected in S4 on 21 April 2016 supports the hypothesis of fluid pockets with high CO_2 pressure at crustal depths (Fabrizio et al., 2008). It also supports results from a previous study performed after the 2009 L'Aquila earthquake (Chiodini et al., 2011), that is, $\text{Cext} = 5.3\text{E-}03 \pm 2.9\text{E-}04$ m, $\delta^{13}\text{C}(\text{Cext}) = -8.31 \pm 0.64\text{‰}$. In contrast, the Cext values below or near to the cutoff threshold combined with an alkaline pH close to the water-atmospheric CO_2 -calcite equilibria ($\text{pH} = 8.2$ at $T = 13^\circ\text{C}$) are likely related to shallow CO_2 degassing and calcite precipitation (e.g., S2 water in Figures 3 and 4). Indeed, according to Frondini et al. (2018), the location of the Cext peak values in Figure 2 between the cutoff value and the recent defined limit of $\text{Cext} = 0.03$ m could be induced by these effects. Therefore, the thresholds depicted in Figures 2–4 are purely indicative and necessitate a local redefinition by a systematic inspection of the $\delta^{13}\text{C}$ values.



which depicts calcite precipitation (downward arrow), as supported by travertine deposition in the area (Carrara, 1998; Lombardo et al., 2001), and CO_2 loss at the spring outpouring (upward arrow). As a primary consequence, such combined carbon sinks produce both a pH increase and $\log f\text{CO}_2(\text{g})$ or Cext depletion. These effects are primarily represented by the S5 to S7 spring waters, which show $\log f\text{CO}_2(\text{g})$ values lower than at the atmospheric level (-3.4 ; “shallow degassing” in the A diagram), as well as Cext within the Cinf range (0.00231 ± 0.00061 ; Frondini et al., 2018; B diagram). Cutoff and warning threshold as in Figure 2.

4.2. Desorption

Arsenic and vanadium are redox sensitive elements that can exist between -3 to $+5$ and $+2$ to $+5$ oxidation states, respectively. As($+3$)-As($+5$) and V($+4$)-V($+5$) are the most important species in natural waters. Unfortunately, only aftershock redox potential data are available. These data include $-0.2 < \text{Eh} \leq 0$ volts for S1–S4 (compatible with the presence of dissolved sulfides) and $\text{Eh} \geq 0$ volts for S5–S7 (Table S1). Within these ranges of values, As and V mobility can be significantly reduced due to precipitation as oxides and sulfides, respectively, and/or via adsorption on iron oxide-hydroxide phases (Figure S1, Eh-pH diagram). However, by plotting the concentrations of As versus V detected in the studied groundwater prior to and during primary shocks, a general trend compatible with an oxic-suboxic (Wright et al., 2014) environment is shown in all the sampled springs (Figure 5). A stress-activated oxidation process at the water-rock interface may serve as an explanation for the observed common redox trend (Balk et al., 2009; Grant et al., 2011; Paudel et al., 2018; Singh et al., 2010). Moreover, the combined elemental increase may be the result of desorption from minerals' surface as iron oxide-hydroxides.

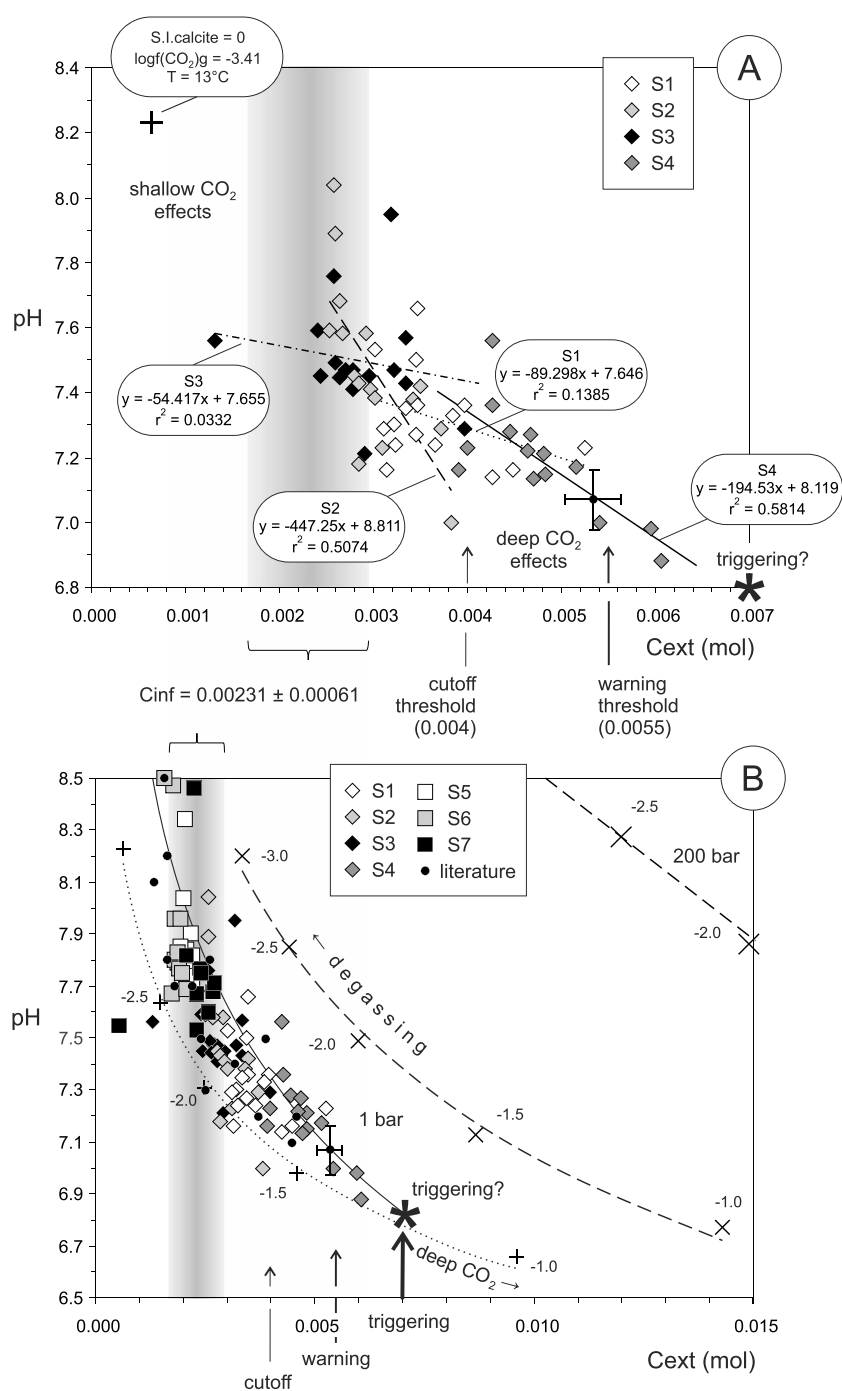


Figure 4. pH ($-\log[H^+]$) versus Cext (molality) calculated from total inorganic carbon. In (a), the linear best fits of water samples S1 to S4 are shown. In (b), all sampled waters, S1 to S4 and S5 to S7, are compared with water-CO₂ equilibria at $T_{\text{average}} = 13^\circ\text{C}$, $P = 10^{-1}$ MPa, and different logfCO₂ values (+numbered and dotted best-fit curve). The black small dots show the composition of the Sulmona basin groundwater, as found in the literature (Conese et al., 2001; Irde, 2008). In both diagrams, the values detected in the S4 spring following the L'Aquila 2009 earthquake are also shown (black small dot with mean $\pm$ standard deviation bars; Chiodini et al., 2011). Cinf (gray field) and cutoff-warning Cext thresholds (arrows) are shown for comparison (see main text for details; Chiodini et al., 2000; Frondini et al., 2018; Martini, 2016) along with the inferred desorption triggering value (Cext = 0.007 mol; Figure 3). In (b), the dashed curve represents the pH-Cext exponential best fit of a high CO₂ water issuing from a deep borehole in the Northern Apennine watershed (Bicocchi et al., 2013). The deep borehole draws fluid from a reservoir in the Upper Triassic rocks (Bicocchi et al., 2013). In this case, the equilibria between dissolved constituents and gases are first calculated at the temperature and pressure values at depth ($T = 120^\circ\text{C}$ and $P = 69$ MPa). Second, shallow degassing is simulated, recalculating the water-gas equilibria by decreasing the logfCO₂ (X numbered and dashed best fit curve) at the same average conditions of the water sampled in this study ($S.I.\text{calcite} = 0$, $T_{\text{average}} = 13^\circ\text{C}$ and $P = 10^{-1}$ MPa). As a comparison, the same calculation at $P = 20$ MPa is also shown (X numbered and dashed best fit line). The solid curve shows that the exponential best fit for the S4 samples extends to higher and lower pH values.

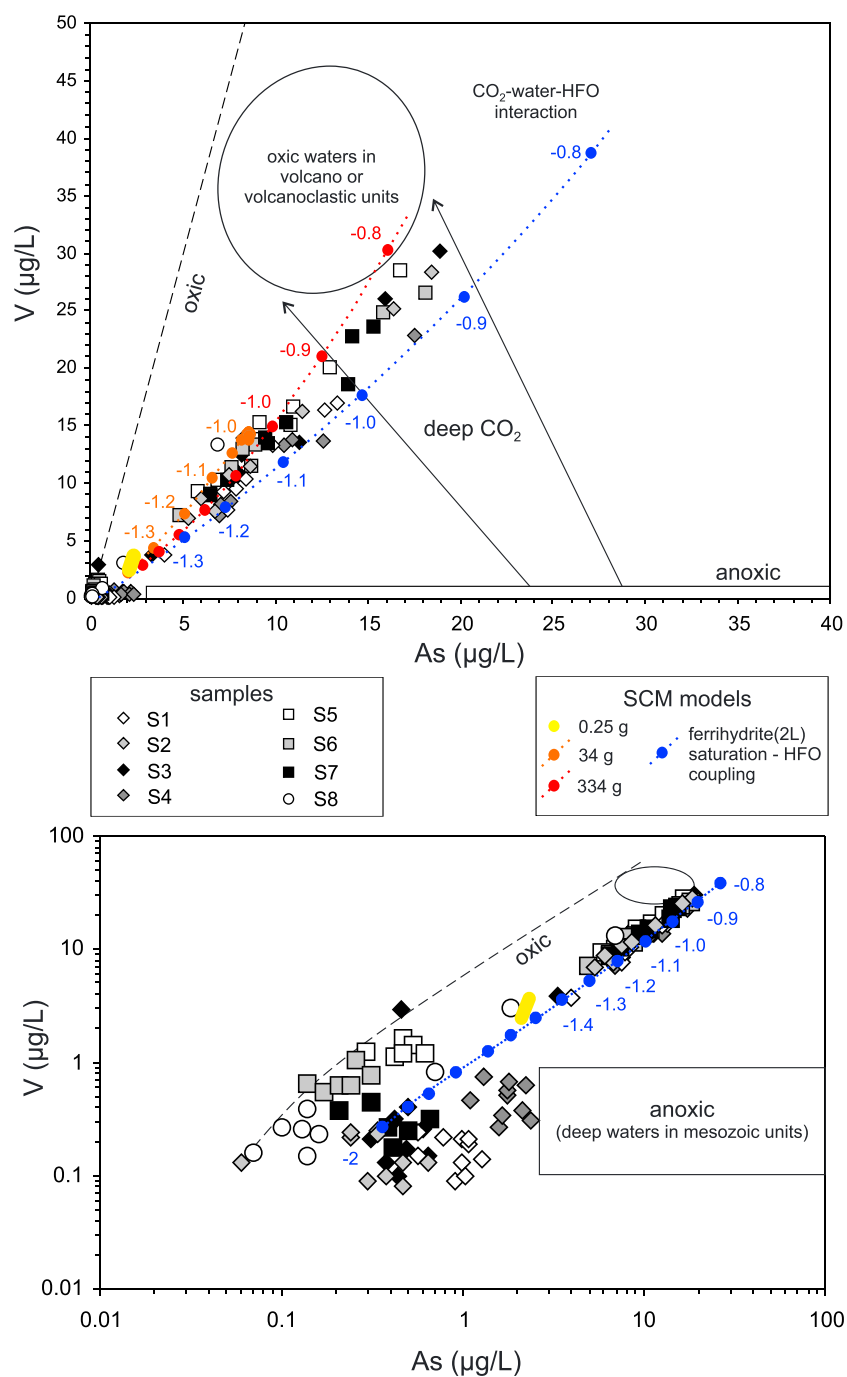


Figure 5. Vanadium and arsenic concentrations in the sampled water. Colored dotted lines show SCM desorption models (see text for explanation) at different HFO amounts or equilibria conditions (key) and $\log f\text{CO}_2$ (numbers and dots). Oxic water fitting (Wright et al., 2014) (dashed black line), oxic water from volcanoclastic units (Sappa et al., 2014; circled field), and anoxic thermal fluids (Boschetti et al., 2005; squared field) are also shown for comparison. SCM = surface complexation modeling; HFO = hydrous ferric oxide.

The V and As concentrations from the interaction between water and surface minerals were calculated via SCM, using PhreeqI computer code (Parkhurst & Appelo, 2013) version 3, applying a double-layer approach, and employing the *minteq.v4.dat* thermodynamic data set. Additional surface complexation constants for dissolved inorganic carbon and iron species from the *wateq4f.dat* data set were also included in the calculations. The desorption process of the adsorbed elements on HFO (HFO, FeOOH) was inferred by first

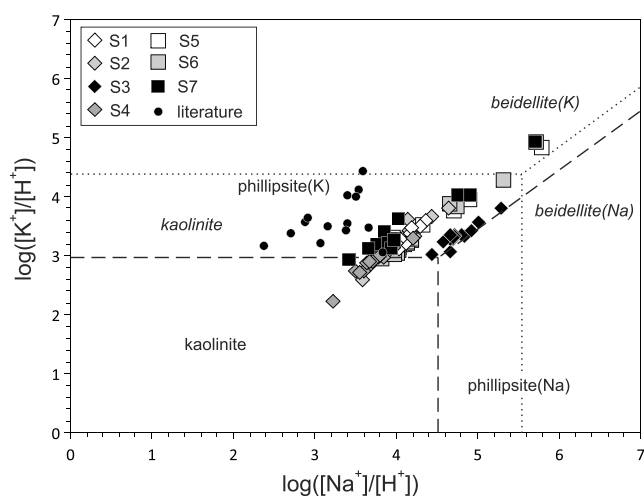


Figure 6. Activity diagrams for the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at $T = 13^\circ\text{C}$ and $P = 10^{-1}$ MPa. Dissolved silica is saturated by cristobalite according to the equilibria calculated by using historical data regarding the S1 spring ($\text{SiO}_2 = 12$ mg/L; Popoli-SPA, 2018). The diagrams are drawn using the Act2 tool of the Geochemist's Workbench code, 7.0.2 release (Bethke, 2008). Lines show the theoretical equilibria between kaolinite and zeolites by using two different thermodynamic databases, thermo.com.v8.r6+.dat (dotted lines and the names of phases in italics; data set enclosed in the software) and gwb_thermodem_lvl2_no-org_06jun17.dat, respectively (dashed lines). Literature data as in Figure 4b. The clustering of the sampled waters is parallel to the zeolites equilibria, in particular for S3, showing the highest As-V concentration during the first mainshock. It is worth noting that cristobalite, kaolinite, and zeolites are the typical weathering products of volcanic ashes and tephra (Bishop et al., 1998).

calculated model paths expand (Figure 5). Furthermore, the greater the CO_2 fugacity, the more the model path matches the real samples. Finally, the reliability of our theory is supported by the following evidence (Figure 5): the highest As-V- CO_2 values of both modeling results and spring water data tend toward the field representing a potential analog site for peak concentrations in the westernmost Apennine sector (Sappa et al., 2014). Indeed, in this latter area, deep CO_2 -bearing groundwater continuously interacts with secondary minerals of the local volcanoclastic deposit (Battistel, 2014; circled area in Figure 5).

Regardless of the interaction with local tephra layers, the similarity between HFO-desorption models and As-V increase in groundwater during seismic events may have an alternative explanation. The accumulation of iron compounds in fault systems and their possible impact on groundwater composition, including radium and radon concentration (Szabo & Zapecza, 1993), has been highlighted several times in the literature (Boullier et al., 2004; Corrigan, 1998; Lipfert et al., 2006; Schuessler et al., 2016; Wang et al., 2017). Locally, the relationship between HFO and groundwater can be explained by an accumulation of amorphous iron hydroxide coatings on fault surfaces, or in fault gouges of the Mesozoic evaporite, rather than as a result of water-rock interaction with tephra layers, which are locally found no deeper than ~ 100 m (Giaccio et al., 2013; Figure 1a). The substantially invariable strontium isotope ratio of the S1 spring (0.70791–0.70794; Figure S2) agrees with an interaction of water with Mesozoic carbonates/sulfates, rather than with Holocene ash layers (0.7083–0.7112; Figure S2; Giaccio et al., 2013). Accordingly, iron oxides can also be derived from the silicoclastic Verrucano unit (Permian-Lower Triassic; Parotto et al., 2003), which overlies the crystalline basement, and also occurs as fragments incorporated in the Upper Triassic sequence during the Alpine orogeny (Boschetti et al., 2017). Consequently, in this latter scenario, deep CO_2 and the As-V anomalies may be related to a deep origin.

The boron data independently support the hypothesis of elemental desorption from secondary minerals. The boron desorption concentration obtainable from SCM can vary significantly due to wide uncertainty in logK values describing strong sites' HFO-borates complexation: from 0.62 in the original *minteq.v4.dat*

equilibrating a local water sample taken during the preseismic event with HFO and then providing an ingress of recharging water in the system in a similar manner to advective transport. In this second step, increasing values of CO_2 fugacity and fluid-calcite equilibria were set ($S.I_{\text{calcite}} = 0$).

The results of the calculated modeling are comparable with the As-V trend depicted by the sampled waters, in particular (i) at high HFO amounts and (ii) if the HFO is connected to the ferrihydrite saturation of the first solution (Figure 5).

From the top (Quaternary alluvial deposits) to the bottom (Paleozoic basement) of the stratigraphic sequence, the adsorbent-desorbent secondary phases (i.e., iron oxide-hydroxides, clay minerals, and zeolites) can theoretically be formed from different siliciclastic sources (Figure 6).

Iron concentration in volcanic ash is highly variable, from lower than 1% as ferrihydrite in soil (andisol; Colombo et al., 2014) to very high amounts in deeper/older deposits (65% to 70% as opaque minerals; Bernoulli et al., 2004). Therefore, since published chemical data primarily concern iron from the unaltered solid fraction, the true concentration of ferrihydrite in local tephra layers is often difficult to determine. However, taking into account the available chemical composition (Galli et al., 2015), porosity (Macedonio & Costa, 2012; 67.5%), and density (Giaccio, 2006; 1.4 g/cm³) of the tephra layers, a minimum HFO concentration of approximately 0.25 g/L, which may correspond to a heavily weathered andisol, can be inferred (Zhu & Anderson, 2002). Using this HFO amount, the desorbed As and V concentrations obtainable from the model are not higher than 2.3 and 3.7 $\mu\text{g/L}$, even if a $\log f(\text{CO}_2)_g = -1$ was entered. If the HFO amount is increased (e.g., supposing that all available iron was ferrihydrite or a similar amorphous phase, i.e., approximately 34 g), the calcu-

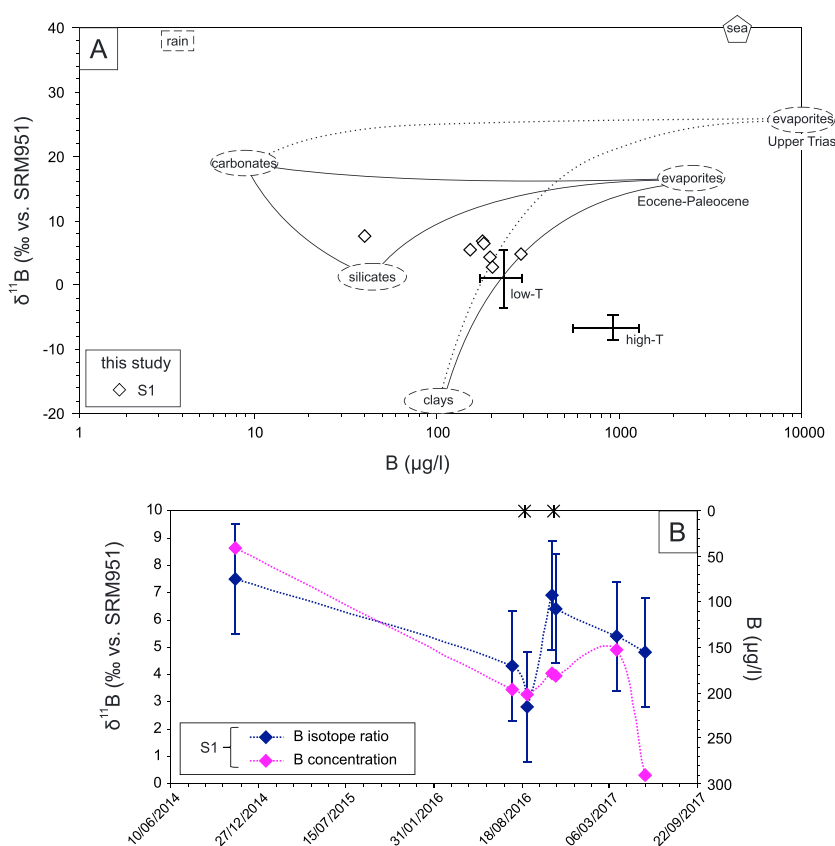


Figure 7. (a) $\delta^{11}\text{B}$ versus boron concentrations in the S1 water collected during the seismic sequence (data in Table S1). Dashed-contoured circles depict different and common boron sources (Barth, 1997; Négrel et al., 2009); solid and dotted lines represent the binary mixing between them. Crosses highlight the mean and standard deviation values detected in hot and cold water from volcanoclastic deposits (Battistel, 2014). (b) Time series of boron concentration and its isotope ratio $\delta^{11}\text{B}$ in S1 spring water. Error bars depict the external reproducibility of the $\delta^{11}\text{B}$ measurements at $\pm 2\text{‰}$ (2σ). Asterisk meaning as in Figure 2.

to 5.63 in the literature (Ranjbar & Jalali, 2014). However, by using the former (lower) value included in the data set, the B concentration increase due to desorption, as inferred by the models, is coherent with that detected in the groundwater samples (Data Set S1). In a similar manner and consistently with the total chromium increase during the seismic event, the Cr concentration in the groundwater desorbed after SCM shows an increment of at least 10 times compared to the initial groundwater concentration (Data Set S1).

It is worth noting that the simultaneous boron concentration increase and boron isotope ratio decrease (from 40 to 290 $\mu\text{g/L}$ and from $\delta^{11}\text{B} = +7.5\text{‰}$ to $\delta^{11}\text{B} = +2.8\text{‰}$, respectively), exhibited by the S1 water samples prior to the seismic events, may be related to desorption from mineral surfaces (Figure 7). This desorption process is supported by the following considerations: (i) clays and iron oxides-(hydroxides) logK values (Ranjbar & Jalali, 2014) and isotope fractionation effects (^{10}B enrichment on the surface of minerals; Lemarchand et al., 2007; Schwarcz et al., 1969) are similar; (ii) similar boron concentration and $\delta^{11}\text{B}$ values were detected in cold groundwater, which interacted with clays and/or iron hydroxides formed in volcanic deposits ($B = 233 \pm 58 \mu\text{g/L}$; $\delta^{11}\text{B} = +0.9 \pm 4.5\text{‰}$; Battistel, 2014). Finally, the hypothesis of boron desorption is in agreement with previous work concerning different boron sources (Barth, 1997; Négrel et al., 2009; Figure 7).

5. Conclusions

In this study, we assessed the possible relationship between deep CO_2 inflow and the anomalies on trace elements such as arsenic (As) and vanadium (V) detected in groundwater before and during the 2016

earthquakes in central Italy. SCM shows that both As and V release can be related to ubiquitous secondary mineral phases as iron oxides and triggered by deep CO₂ dissolved in the water. While the As and V concentration anomalies were significant and have been verified at most of the monitored springs, the possible concomitant boron (B) desorption processes necessitate further analyses to prove that a similar isotopic signature occurred in other groundwater sampling sites. However, the analysis of boron (B) concentration and isotope ratio at one spring provides tentative confirmation that the desorption processes occurred from alteration minerals on volcanoclastic deposits. The combined role of deep CO₂ and elemental desorption processes could open new perspectives in strategies concerning the identification of seismic precursors.

Author Contributions

T. B., M. B., M. P., A. B., and M. D. B. formulated the original hypotheses and designed and developed the research project. M. B., M. D. B., A. B., S. F., and M. P. collected samples, performed research, and participated in the data analysis and data interpretation. T. B. and M. B. performed hydrogeochemical modeling with insights from all authors. All authors discussed the data presented in the manuscript and participated in its writing and in the figure-table preparation. Authors declare no financial conflicts of interests. All data used for this paper are available in Table 1, in Figures S1 and S2, and in two files (Table S1 and Data Set S1; Boschettietal_Supporting_Tables.xlsx and Boschettietal_Supporting_Model_Results.xlsx) associated with the supporting information. Authors declare solely institutional funding from their institutions.

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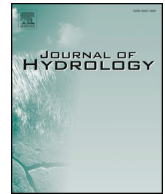
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Research papers

Tracing deep fluid source contribution to groundwater in an active seismic area (central Italy): A combined geothermometric and isotopic ($\delta^{13}\text{C}$) perspective



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ABSTRACT

An understanding of the origin and migration pathways of geofluids in an active seismic area is of paramount importance in terms of societal challenges such as mitigation of seismic hazards. This study investigates the relationship between the stable isotope ratio $^{13}\text{C}/^{12}\text{C}$ of deep CO₂ and geothermometry in selected groundwater samples located close to extensional faults in central Italy. The temperature range is inferred from an equation based on the Na/Li ratio and chemical geothermal modelling: 113–130 °C. Globally, the calculated temperature range agrees with that resulting from deep boreholes in the Northern Apennines. An alternative method is also included to better evaluate the difference in isotopic composition between the aqueous and gaseous $\delta^{13}\text{C}(\text{CO}_2)$ at deep condition. A review of previously published data shows that monitoring of the isotopic composition of the dissolved inorganic carbon (DIC) in springs fed by meteoric origin located in seismically active areas must take into account mass and isotopic balance to correctly evaluate the component, and the role, of deep fluid during seismic events. In particular, the coupled (and corrected) isotope and geothermometric monitoring of the springs could help to distinguish between deep gas or deep fluid contributions to shallow aquifers. The results of this study indicate that faults play a crucial role in controlling the migration of crustal fluids. In addition, they reveal that possible evaluation of potential seismic precursors mandatorily requires a long period of monthly monitoring.

1. Introduction

Geofluids have long been known to influence fault-zone motions and related seismic cycles (Smeraglia et al., 2018, 2016; Ünal-İmer et al., 2016; Uysal et al., 2009; Williams et al., 2017); however, little is known about how and where these fluids originate, and how they migrate towards, along, and away from fault zones during the seismic cycle (Person et al., 2007). The increasing importance of these earthquake-related geofluids in the science of seismic precursors (Barberio et al., 2017; De Luca et al., 2018; King et al., 1995; Onda et al., 2018; Skelton et al., 2014, 2019) makes an understanding of the origin and migration pathways of geofluids of paramount importance in addressing societal challenges such as seismic hazard mitigation.

Fluids with high CO₂ partial pressure are possibly connected with seismic cycles (Skelton et al., 2014; Uysal et al., 2009); therefore, the

stable isotope ratio of dissolved inorganic carbon (DIC) has the potential to be a powerful tool for tracing the hydrogeological processes in seismically active areas (Rosen et al., 2018). For instance, deep pressurised fluids, with CO₂ partial pressure of 68–97 MPa and at temperatures between 120 and 135 °C, were tapped through deep boreholes located in the seismically active Umbria–Marche sector of the Apennines, central Italy (also the area of focus of the current study), at depths of 3.70–4.75 km b.s.l. (Collettini et al., 2008). The $\delta^{13}\text{C}(\text{DIC})$ was used to trace the deep CO₂ in the seismically active area of the Gran Sasso thrust in central Italy (Chiodini et al., 2011), where the relationship between seismic events, hydrothermal anomalies and CO₂-rich deep fluids were also further remarked by Wu et al. (2016). In the surrounding seismogenic sectors, heat anomalies were also inferred in aquifers where CO₂ of endogenic origin dissolves (Chiodini et al., 2013; Di Luccio et al., 2018). Moreover, in some locations of the central

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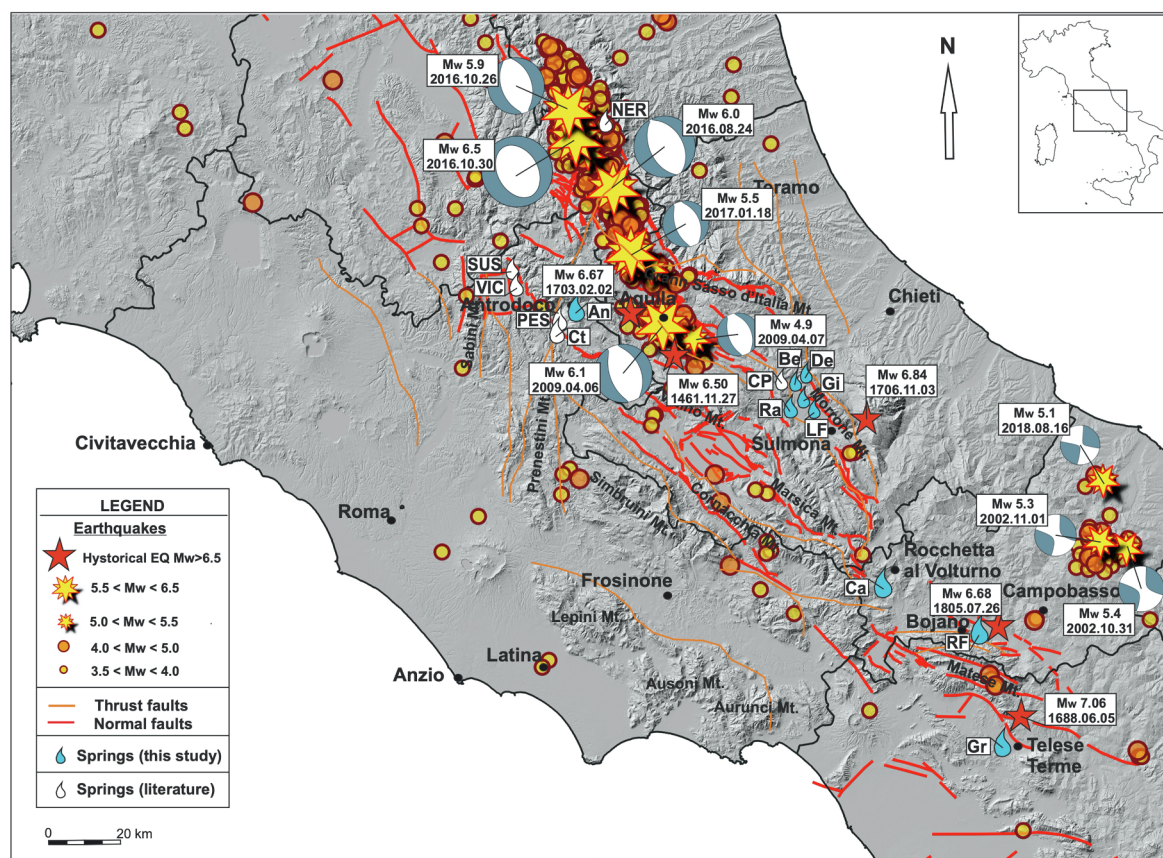


Fig. 1. Map of central Apennines (see location in upper left inset). Seismic data (including focal mechanisms) are from the INGV database (available online at <http://cnt.rm.ingv.it/>) between January 1st, 2000, and June 15th, 2019 ($M_w \geq 3.5$). Historical earthquakes ($M_w > 6.5$) are from INGV historical catalogue (available online at <http://www.mi.ingv.it/terremoti-storici/>). Base digital elevation model is from the ISPRA database SINAnet (available online at <http://www.sinanet.isprambiente.it/it>). Location of the monitoring springs analyzed in this work are displayed by blue drops while those analyzed in other works are displayed by white ones. Faults (red and orange lines, normal and thrust faults respectively) are from the Ithaca database (available online at <http://www.isprambiente.gov.it/en/projects/soil-and-territory/italy-hazards-from-capable-faulting>).

Apennines (central Italy) the heat flow could actually be high, but masked by the rapid and abundant shallow circulation of cold groundwater (Duchi et al., 1991; Giustini et al., 2013).

Our main aim in this work is to track the contribution of deep fluid sources to groundwater in seismically active areas of the central Apennines (central Italy). To achieve this, we analyse groundwater samples from nine selected springs in seismically active areas where upwellings of deep fluids have previously been documented or hypothesised (Fig. 1): the Olevano–Antrodoto thrust area (Petitta et al., 2011), the Sulmona plain (Barberio et al., 2017), and the Matese Mountains (Ascione et al., 2014). In all these areas, no anomalies on stable isotope ratio of oxygen and hydrogen in water molecule, i.e. $\delta^{18}\text{O}$ (H_2O) and $\delta^2\text{H}$ (H_2O), were detected (Barberio et al., 2017; Di Luccio et al., 2018; Petitta et al., 2011; Rosen et al., 2018). In other terms, previous studies showed that all waters could be classified as of meteoric origin and that at the same time the contribution of magmatic/methamorphic fluids (if any) or the isotope fractionations due to water–rock interaction at high temperature seem to be not significant for $\delta^{18}\text{O}$ (H_2O) and $\delta^2\text{H}$ (H_2O) (Clark and Fritz, 1997; McSween et al., 2003; Sheppard, 1986). Differently, the contribution of deep CO_2 gas of magmatic/methamorphic origin to the groundwater of central Italy is well-known and widely documented (Chiodini et al., 2011, 2004, 2013, 2000; Di Luccio et al., 2018; Frondini et al., 2018). However, it is not yet clear whether the contribution of CO_2 occurs only in terms of gas or also by liquid mixing. Therefore, in this study we use and try to combine chemical composition data, the stable isotope ratio $^{13}\text{C}/^{12}\text{C}$ of the DIC, and sodium–lithium geothermometry to evaluate how the

geofluids originated, and the role of heat anomaly on fluid–mineral thermodynamic equilibria and mixing.

2. Geological and hydrogeological settings

The central Apennines are a late Oligocene-to-present fold-thrust belt generated by the eastward rollback of the Adriatic plate under the European plate (Doglioni, 1991; Malinverno and Ryan, 1986). Specifically, the central Apennine accretionary prism developed through folding and thrusting of the passive continental margin of the Adriatic plate. In central Italy, active contraction is presently located to the east of the belt, below the western Adriatic Sea. The stratigraphic horizons where the basal décollement is located can be recognised from seismic reflection profiles (Bally et al., 1986; Billi et al., 2006; Scrocca, 2006) and are mainly represented by Triassic evaporites located in the lower layers of the passive margin sequence. The sole thrust of the Apennines occurs at more than 20 km in the inner sector (west), shallowing to about 10 km towards the foreland. The thrust sheets are mainly composed of Meso-Cenozoic sedimentary succession, as known from deep wells drilled in the Apulian-Adriatic foreland. The succession includes, from bottom to the top: Permian–Triassic phyllites and quartzites, Triassic evaporites and Meso-Cenozoic limestones and dolostones. This succession is duplicated and eastward-imbricated in the Apennines fold-thrust belt, where it is also topped by syn- and post-orogenic siliciclastic marine and continental deposits. The Apennines fold-thrust belt is presently cross-cut by Quaternary seismically active normal faults (Cardello and Tessei, 2013; Galli et al., 2002, 2008). In central Italy, two

major sub-parallel normal fault systems accommodate the late Pleistocene–Holocene deformation: the eastern and western normal fault systems (Barchi et al., 2000; Boncio et al., 2004; Galadini and Galli, 2001; Roberts and Michetti, 2004) that also controlled the formation of intramountain basins (e.g. l'Aquila, Sulmona, San Vittorino and Fucino basins). Extension is currently active in the axial portion of the central Apennines, where it is responsible for earthquakes of up to $M = 7.0$ (Barchi et al., 2000; Boschi et al., 1998) and for extension rates of 2.5–3.5 mm/year (Riguzzi et al., 2012). To the west of this area, the Moho is shallow, at 20–25 km (Ponziani et al., 1995), with high heat-flow values of $< 100 \text{ mW m}^{-2}$ (Della Vedova et al., 2001; Mongelli and Zito, 1991) and high levels of CO_2 degassing (Chiodini et al., 2004). More recently, a re-evaluation of the heat flow in the studied area has inferred even higher heat flow of up to 350 mW m^{-2} (Chiodini et al., 2013; Di Luccio et al., 2018).

In the Apennines, both the Cenozoic clayey syn-orogenic deposits and the Triassic anhydritic evaporites are known as important sealing levels for groundwater, hydrocarbons, and deep endogenic gases such as CO_2 . Carbon-mass balance calculations, hydrogeochemistry with isotopic and hydrological data, identify the presence of a large flux of deep CO_2 centred in the extended sector of the Apennines, with a large area characterised by a flux greater than $0.45 \text{ t d}^{-1} \text{ km}^{-2}$ (Chiodini et al., 2004; Collettini et al., 2008).

The central Apennines belt is characterised by huge carbonate aquifers with high permeability due to fracturing and karst processes. The Meso-Cenozoic carbonate sequences that host the aquifers are often compartmentalised by layers with low permeability (aquitards and aquicludes), composed of siliciclastic continental/marine deposits (Boni et al., 1986; Petitta et al., 2009). At points of contact with the carbonate aquifers, these deposits act as a permeability boundary, preventing underground hydraulic communication and giving rise to the basal springs of the regional groundwater (Fiorillo et al., 2015).

The permeability boundaries between siliciclastic marine and continental deposits and the fractured carbonate aquifers are often represented by normal and thrust faults. Consequently, groundwater frequently undergoes physicochemical changes, which are due to the local upward of mineralising fluids along these tectonic features (Petitta et al., 2011). Groundwater from the carbonate aquifers is subject to these physico-chemical changes upon its movement towards the recent alluvial aquifers. Here, mixing with deep fluids causes groundwater to take on different hydrochemical characteristics. These physicochemical changes may be progressive or fast and localised, depending on the interaction between the tectonic setting and the stratigraphic sequence.

3. Methods

3.1. Sampling and analysis

For this study, nine springs were monitored and sampled during the 2018 non-seismic phase. Five springs – Decontral, Raiano, Bellucci, Le Fonti, Giardino (Table 1) – had been monitored since January 2016, a period matching the hydrogeochemical dataset associated with the 2016–2017 Amatrice–Norcia seismic sequence (central Apennines, Italy) (Barberio et al., 2017). The remaining four springs – Antrodoco, Capovoltorno, Rio Freddo and Grassano (Table 1) – were selected because they are directly fed by regional flow in the carbonate aquifers of the central and southern Apennines and they were monitored as potential seismic precursors.

Data from other springs (e.g. Capopescara (CP), Peschiera (PES), Cotilia (Ct), Vicenna Riara (VIC), Santa Susanna (SUS), and Nerea (NER) (Fig. 1)) have also been considered in this study. The associated databases refer to published works of: Adinolfi Falcone et al. (2008), Giustini et al. (2013), and Rosen et al. (2018).

At the sampling sites, physicochemical parameters (temperature and pH) were measured using a portable digital multiparameter probe (WTW™ MultiLine™ 3420). Carbonate alkalinity was measured by

titration using a portable titrator, HCl 0.02 N as titrant solution, and bromocresol green as dye indicator (Standard Method 2320B) (Clesceri et al., 1999). Following filtration in the field ($0.45 \mu\text{m}$), water aliquots for major and trace cations were acidified at 1% v/v by adding 65% p/p HNO_3 Suprapur® (Merck–Millipore). In the laboratory, major ions were analysed with a Chromeleon Dionex (precision $\pm 2\%$). An ICS 1100 was used for analysing cations, and a Dionex ICS5000 for analysing anions. According to standard methods (Clesceri et al., 1999), the analytical accuracy levels for major ion ionic balance and for minor trace element determination were better than 5%. Concentrations of minor and trace elements were measured using an ICPMS (X Series 2, Thermo Fisher Scientific). The total dissolved solids (TDS) in grams per litre was calculated by summing the concentrations of the primary dissolved constituents and half alkalinity as HCO_3^- , i.e.: $[0.5 \times \text{Alkalinity}] + [\text{other dissolved constituents}]$ (Clesceri et al., 1999).

The stable isotope ratio $^{13}\text{C}/^{12}\text{C}$ of the DIC was determined using water aliquots inferred from previous analyses of the carbonate alkalinity of each specific spring. In the field, the aforementioned water aliquots were injected into 12 ml Na-glass vials (Labco Exetainer®), pre-filled in the laboratory with five droplets of phosphoric acid (ca. 90%) and He gas 6.0 (Spötl, 2005). To limit biological activity and to eliminate the possibility of adding solid particles – especially limestone – to the vials (Dawson, 2017; Li and Liu, 2011), a $0.2 \mu\text{m}$ polyethersulfone (PES) filter was interposed between the syringe and the needle, with the latter then used to puncture the butyl rubber septa of the vials. In the laboratory, the sample vials were stored in a fridge at 4°C until analysis. A GasBench II (Thermo Fisher Scientific), on-line with a Delta Plus XP mass spectrometer (Thermo Finnigan), was used to determine the 'delta value' of the samples' $\delta^{13}\text{C}(\text{DIC})$. These figures were measured and expressed in terms of the 'Vienna–Pee Dee Belemnite (V-PDB)' scale, normalised by assigning the consensus values of -46.6‰ to LSVEC lithium carbonate, $+1.95\text{‰}$ to NBS 19 calcium carbonate (Wieser, 2006), and -5.014‰ to NBS 18. Each sample was analysed in replicate. The accuracy of the method is better than 0.2‰ (2 σ).

3.2. Thermodynamic and isotopic calculations

The mineral-saturation indexes of the water samples were calculated using PHREEQCI and codes from *The Geochemist's Workbench*, which uses *lnl.dat* and *thermo.dat* thermodynamic datasets coupled with Debye–Hückel and B-Dot theory for the activity, mineral saturation indexes and $\text{CO}_2(\text{g})$ partial pressure calculations, respectively (Appelo et al., 2014; Bethke, 2008; Parkhurst and Appelo, 2013). The same codes were also used to calculate the molality ($\text{mol/kg H}_2\text{O}$) concentrations of DIC, Ca and SO_4 employed in the following mass balances (Chiodini et al., 2000):

$$\text{DIC} = \text{C}_{\text{carb}} + \text{C}_{\text{ext}} \quad (1)$$

$$\text{C}_{\text{carb}} = \text{Ca} + \text{Mg} - \text{SO}_4 \quad (2)$$

$$\text{C}_{\text{ext}} = \text{DIC} - \text{C}_{\text{carb}} = \text{C}_{\text{inf}} + \text{C}_{\text{deep}} \quad (3)$$

C_{carb} is the amount of carbon derived from the interaction of groundwater with carbonate aquifer rocks, while C_{ext} is carbon derived from processes other than these (i.e. from external sources). This latter component can be expressed as $\text{C}_{\text{ext}} = \text{C}_{\text{inf}} + \text{C}_{\text{deep}}$, where C_{inf} is the carbon from atmospheric and biogenic CO_2 , i.e. the infiltrating water. $\text{C}_{\text{inf}} = 2.31\text{E-}03 \pm 6.1\text{E-}04 \text{ m}$ has been inferred for the Apennine water recharge (Fronzoni et al., 2018). C_{deep} is deep CO_2 from metamorphic, mantle, or magma sources (Chiodini et al., 2000).

To evaluate the $\delta^{13}\text{C}$ isotope composition of deep CO_2 ($\delta^{13}\text{C}_{\text{ext}}$) in each water sample, the following isotope-mass balance was used (Chiodini et al., 2000):

$$\delta^{13}\text{C}(\text{DIC}) \times \text{DIC} = (\delta^{13}\text{C}_{\text{carb}} \times \text{C}_{\text{carb}}) + (\delta^{13}\text{C}_{\text{ext}} \times \text{C}_{\text{ext}}) \quad (4)$$

The results were compared with those obtained using a subroutine of the NetpathXL code (Parkhurst and Charlton, 2008; Plummer et al.,

Table 1
Physicochemical composition and stable isotope ratio of dissolved inorganic carbon $\delta^{13}\text{C}(\text{DIC})$ of the sampled waters. Minor and trace elements ($\mu\text{g/l}$) are detailed in the [Supplementary File S1](#).

Sample name	Sample code	Sample date	Lat.	Long.	Elevation m a.s.l.	EC $\mu\text{S/cm}$	pH $-\log[\text{H}^+]$	Temp $^{\circ}\text{C}$	Ca mg/l	Mg mg/l	Na mg/l	K mg/l
Le Fonti	LF	5-22-2018	42.118	13.884	313	454	7.614	13.9	60.3	19.7	4.58	1.14
Deontra 1	De	5-22-2018	42.178	13.837	249	828	7.103	13.6	119	32.2	13.1	4.05
Raiano	Ra	5-22-2018	42.108	13.807	285	743	7.071	13.2	118	26.1	8.52	2.30
Bellucci	Be	5-22-2018	42.192	13.847	244	758	7.384	13.0	93.6	19.2	41.4	2.99
Giardino	Gi	5-22-2018	42.163	13.841	253	320	7.793	10.0	44.2	11.8	2.94	0.592
Antrodoco	An	5-22-2018	42.421	13.080	493	1642	6.544	16.9	272	67.1	8.17	2.23
Capovoltumo	Ca	9-7-2018	41.637	14.071	553	494	7.686	11.9	84.4	14.4	1.99	0.629
Grassano	Gr	9-7-2018	41.225	14.514	55	928	7.075	11.9	179	29.3	15.9	2.33
Rio Freddo	RF	9-7-2018	41.473	14.497	514	257	7.873	7.9	49.8	5.95	1.89	0.453

Sample name	Cl mg/l	SO ₄ mg/l	cAlk mg/l	F mg/l	NO ₃ mg/l	TDS mg/l	C.I. %	$\delta^{13}\text{C}(\text{DIC})$ ‰ vs. V-PDB	Chemical classifica- tion	Thermal classification	T _a local annual air temperature*	
											$^{\circ}\text{C}$	Locality
Le Fonti	7.97	8.73	243	0.0775	12.8	237	1.8	-10.2	HCO ₃ -Ca	orthothermal	13.1	Sulmona
Deontra 1	17.8	127	390	0.291	-	508	-1.5	-4.76	HCO ₃ -Ca	orthothermal	13.1	Sulmona
Raiano	10.4	57.2	419	0.147	-	432	0.6	-3.66	HCO ₃ -Ca	orthothermal	13.1	Sulmona
Bellucci	57.2	64.9	346	0.148	-	452	-3.2	-6.06	HCO ₃ -Ca	hypothermal	13.1	Sulmona
Giardino	4.38	9.55	189	0.0539	1.39	169	-2.1	-7.48	HCO ₃ -Ca	hypothermal	13.1	Sulmona
Antrodoco	9.66	448	488	0.904	8.16	1057	-0.3	-0.477	Ca-HCO ₃	orthothermal	12.9	Antrodoco
Capovoltumo	3.01	11.2	253	0.165	0.849	271	0.8	-3.54	HCO ₃ -Ca	hypothermal	12.8	Rocchetta a Voltumo
Grassano	25.0	9.05	575	0.150	1.89	582	-1.8	-1.84	HCO ₃ -Ca	hypothermal	13.5	Grassano
Rio Freddo	4.81	2.10	138	0.363	2.73	152	0.7	-8.70	HCO ₃ -Ca	hypothermal	12.8	San Polo Matrese

E.C.: electrical conductivity cAlk: carbonate alkalinity as HCO₃.

-: not analysed.

TDS: Total Dissolved Solids according to Clesceri (1999).

C.I.: Mean charge imbalance calculated by The Geochemist's Workbench*, version 12 (Bethke, 2008), and NetpathXL (Plummer et al., 1994).

*: Data from <https://it.climate-data.org/info/sources/>

†: Temperature classification according to Schoeller (1962).

1994). Using an inorganic carbon-mass and isotope balance similar to those described in equations from (1) to (4), the subroutine, which originated as a tool for radiocarbon dating adjustment (Plummer et al., 1994), calculated the isotope composition of the $\text{CO}_2(\text{gas})$ or $\text{CO}_2(\text{aq})$ from the $\delta^{13}\text{C}(\text{DIC})$, taking into account both the complete chemical composition of the water samples and all isotopic fractionation factors between aqueous, mineral (calcite) and gas species (Mook, 1976, 1980). Moreover, any error in terms of isotope-mass balance due to chemical analysis can be evaluated by using the charge-balancing option (Plummer et al., 1994).

In both methods, the value of $\delta^{13}\text{C}_{\text{carb}} = 2.2\text{‰}$ was assumed as the isotopic composition of the carbonate aquifer (Di Luccio et al., 2018; Frondini et al., 2018).

4. Results

According to Schoeller (1962) classification and considering the local average annual air temperature (T_a in Table 1), the temperature of Antrodoco and the three springs from the Sulmona basin fall within the orthothermal group ($T_a < T < T_a + 4^\circ\text{C}$). In contrast, the springs in the southern sector of the studied area are hypothermal ($T < T_a$). However, it should be noted that in the Grassano spring, waters with a mean temperature of 21°C (i.e., thermal $T > T_a + 4$) were detected (Corniello and De Riso, 1986). All water samples were fresh ($\text{TDS} < 1\text{ g/l}$), with neutral to slightly basic pH (7.07–7.87) and an HCO_3^- -Ca main chemical composition (Fig. 2a). The Fig. 2a and b also show that the historical chemical composition of the Sulmona springs, in particular Deontra 1 and Raiano, displays chemical variation due to mixing that occurred after the main shocks of earthquakes in 2016–2017 (Boschetti et al., 2019). The exception is the Antrodoco spring sample, which was brackish ($\text{TDS} = 1.05\text{ g/l}$), slightly acidic ($\text{pH} = 6.54$), and showed a predominance of calcium on bicarbonate (Ca-HCO_3) and a relatively high sulphate concentration (448 mg/l) in comparison with the HCO_3^- -Ca springs (from 2.1 mg/l in Rio Freddo to 127 mg/l in Deontra 1). Fluoride and strontium were also higher in the Antrodoco sample (0.9 and 5.2 mg/l, respectively) compared with the other springs (Table 1).

The $\delta^{13}\text{C}_{\text{ext}}$ results, calculated by Chiodini et al.'s (2000, 2004) method and NetpathXL code (Plummer et al., 1994), are similar when the former is compared with the $\delta^{13}\text{C}_{\text{ext}}(\text{CO}_2)\text{aq}$ value obtained by the code (mean difference: $\pm 0.1\text{‰}$) (Table 2). The slight difference, which falls within the analytical error on isotope measurement of $\delta^{13}\text{C}(\text{DIC})$, is mainly due to ion-charge balance correction performed by the code. Moreover, this fact agrees with the assumption in the $\delta^{13}\text{C}_{\text{ext}}$ calculation that no fractionation occurs during input from any source to the solution (Chiodini et al., 2000). Finally, the $\delta^{13}\text{C}_{\text{ext}}(\text{CO}_2)\text{g}$ values are approximately 1‰ more enriched than those for $\delta^{13}\text{C}_{\text{ext}}(\text{CO}_2)\text{aq}$ according to the mean $\text{CO}_2(\text{g})$ - $\text{CO}_2(\text{aq})$ fractionation factor at the sampling temperature (Vogel et al., 1970).

5. Discussion

5.1. $\delta^{13}\text{C}_{\text{ext}}$ and Na/Li geothermometer

The bicarbonate composition of the investigated water samples is mainly due to interaction with calcites and dolomites of the Mesozoic limestones (Fig. 2b). The more peculiar chemical composition of the Antrodoco spring is attributable to a more extensive dissolution of the Triassic sulphate minerals (gypsum-anhydrite of the Burano Formation) (Fig. 2b) (Governa et al., 1989; Petitta et al., 2011). This is confirmed by the fact that this sample showed the highest saturation indexes of gypsum-anhydrite (Table 2). The carbon dioxide partial pressure calculation showed the highest values in the Antrodoco and Grassano springs, having a $\log\text{PCO}_2(\text{g})$ of -0.87 and -1.35 , respectively. The C_{ext} and the relative $\delta^{13}\text{C}_{\text{ext}}$ calculations confirm that these samples had the most enriched values (-1.69‰ for Antrodoco and -4.53‰ for

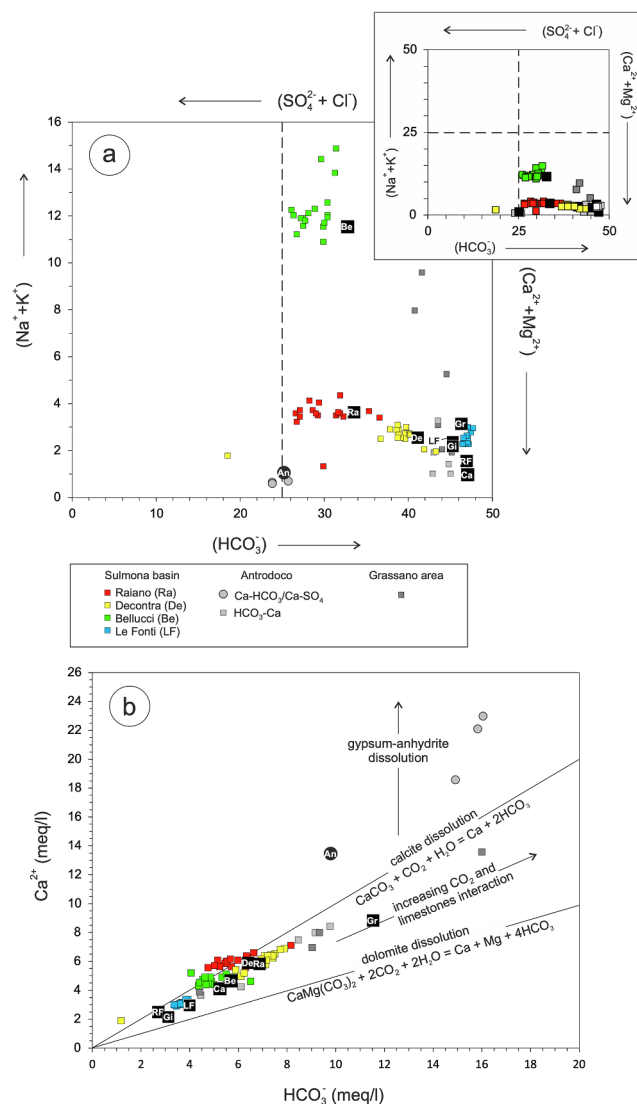


Fig. 2. . Langelier-Ludwig (a) and calcium versus bicarbonate concentration (b) diagrams of the waters sampled in this study (black squares with white codes) compared with data from existing literature: coloured symbols are from the Sulmona basin (Barberio et al., 2017), light grey from the Antrodoco area (Petitta et al., 2011), and dark grey from the Grassano area (Corniello and De Riso, 1986). In both diagrams: dissolved constituents concentrations in equivalent.

Grassano), which are within the hypothetical range of the deeply derived CO_2 (from $+1\text{‰}$ to -5‰) (Chiodini et al., 2004; Frondini et al., 2018). At the opposite end of the scale, Giardino, Rio Freddo and Le Fonti springs showed lowest $\log\text{PCO}_2(\text{g})$ and a range of $\delta^{13}\text{C}_{\text{ext}}$ values similar to those typical of the Apennine infiltrating water (Frondini et al., 2018). According to the $\delta^{13}\text{C}_{\text{ext}}$ versus $1/C_{\text{ext}}$ model described by Chiodini et al. (2011), the other springs showed values of carbon contribution between those of the infiltrating water (affected by biogenic carbon) and the deep source (Fig. 3a). In detail, the groundwater from Sulmona basin (Raiano, Deontra1 and Bellucci) and Capovolturmo fall in the middle of the range. The recalculation of $\delta^{13}\text{C}_{\text{ext}}$ from the $\delta^{13}\text{C}(\text{DIC})$ of the Gran Sasso waters (Adinolfi Falcone et al., 2008) shows that the high-altitude snowmelt and groundwater samples plot between typical atmospheric values $-6.7\text{‰} < \delta^{13}\text{C} < -8.2\text{‰}$ (Coplen et al., 2002) – and those of the Apennine infiltrating waters, respectively (Fig. 3a). An exception is represented by the low-altitude spring of Capopescara, located at the border between the SW Gran Sasso structure and the NE Sulmona basin (Fig. 3a) (Adinolfi Falcone

Table 2

Na/Li geothermometer results (Sanjuan et al., 2014); concentration (molality) and isotope composition of carbon from the deep source, C_{ext} and $\delta^{13}C_{\text{ext}}$ respectively; saturation indexes and carbon dioxide partial pressure from thermodynamic calculation (detailed results and precision measures are presented in the Supplementary File S2).

Sample name	Sample code	Na	Li	Na/Li	*Na/Li geotherm.	molality	$\delta^{13}C_{\text{ext}}$	$\delta^{13}C_{\text{ext}}(CO_2)_{\text{aq}}$	$\delta^{13}C_{\text{ext}}(CO_2)_{\text{g}}$	logPCO ₂ (g)	calcite	dolomite-dis	dolomite-ord	anhydrite	gypsum	fluorite
Le Fonti	LF	1.99E-04	1.40E-07	1.43E+03	13	1.97E-03	-24.24	-23.72	-22.62	-2.312	0.23	-0.44	1.19	-3.07	-2.78	-3.2
Deontra 1	De	5.71E-04	3.04E-06	1.88E+02	101	4.58E-03	-9.29	-9.66	-8.55	-1.612	0.13	-0.73	0.90	-1.76	-1.47	-1.9
Raiano	Ra	3.71E-04	3.63E-06	1.02E+02	138	4.82E-03	-7.82	-7.78	-6.67	-1.549	0.14	-0.80	0.84	-2.09	-1.79	-2.5
Bellucci	Be	1.80E-03	1.74E-06	1.04E+03	24	3.76E-03	-11.43	-12.25	-11.13	-1.944	0.27	-0.57	1.07	-2.11	-1.81	-2.5
Giardino	Gi	1.28E-04	2.27E-07	5.64E+02	47	1.73E-03	-15.83	-16.61	-15.49	-2.616	0.14	-0.77	0.89	-3.14	-2.81	-3.7
Antrodoto	An	3.55E-04	1.75E-06	2.03E+02	96	1.07E-02	-1.69	-1.75	-0.649	-0.870	0.04	-0.91	0.70	-1.04	-0.78	-0.8
Capovoltorno	Ca	8.67E-05	1.67E-07	5.18E+02	51	2.74E-03	-8.96	-8.76	-7.64	-2.296	0.51	-0.20	1.45	-2.86	-2.55	-2.5
Grassano	Gr	6.90E-04	7.50E-06	9.21E+01	146	8.23E-03	-4.58	-4.66	-3.55	-1.347	0.49	-0.24	1.40	-2.80	-2.49	-2.3
Rio Freddo	RF	8.23E-05	2.49E-08	3.30E+03	-12	1.38E-03	-20.29	-20.06	-18.92	-2.758	0.20	-1.04	0.64	-3.74	-3.39	-1.9

*: From Sanjuan et al. (2014), Eq. (7) (for chloride concentrations $< 0.3 \text{ M}$) $T(^{\circ}\text{C}) = \{1074/[\log(\text{Na/Li}) + 0.601]\} - 273.15$.

♣: Calculated by Chiodini et al.'s (2000, 2004) method using $\delta C_{\text{carb}} = 2.2\text{‰}$ for calcite and dolomite minerals (Fronzoni et al., 2018; Di Luccio et al., 2018).

♣: Calculated by NetpathXL (Plummer et al. 1994) using $\delta C_{\text{carb}} = 2.2\text{‰}$ for calcite and dolomite minerals and activating the "ions charge balance" correction function of the code.

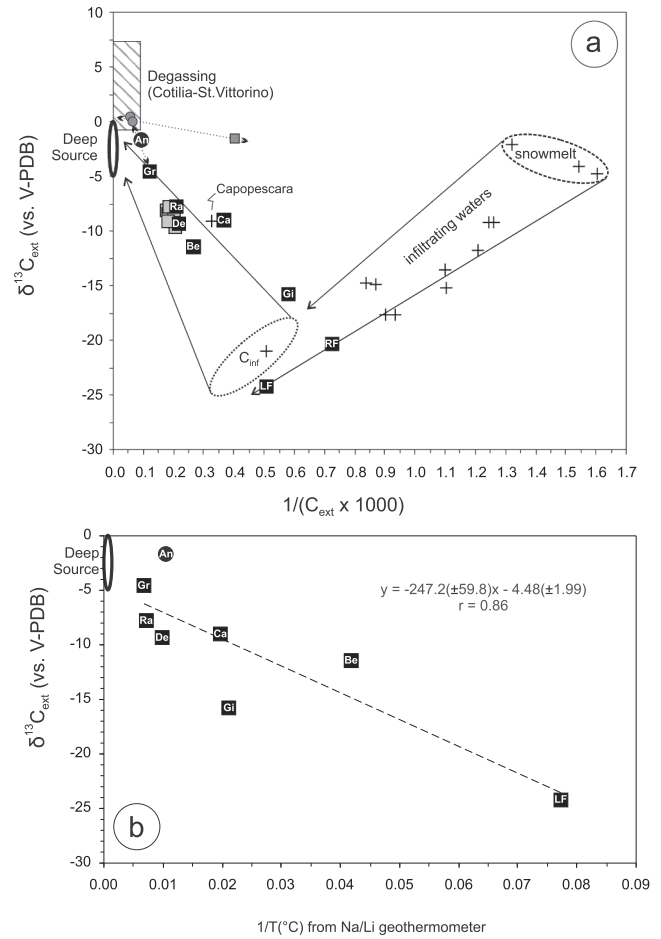


Fig. 3. a) $\delta^{13}C_{\text{ext}}$ versus $1/C_{\text{ext}}$ diagram. C_{inf} area: $\delta^{13}C_{\text{ext}} = -21.6 \pm 2.9\text{‰}$ and $C_{\text{ext}} = 2.31 \pm 0.61 \text{ mmol}$ (Fronzoni et al., 2018); deep source: $\delta^{13}C_{\text{ext}}$ from -5‰ to $+1\text{‰}$ and $1/C_{\text{ext}} = 0$ (Chiodini et al., 2004; Fronzoni et al., 2018). b) $\delta^{13}C_{\text{ext}}$ versus $1/T$, where $T =$ temperature in $^{\circ}\text{C}$ obtained from Na/Li geothermometer (Sanjuan et al., 2014), versus $\delta^{13}C_{\text{ext}}$. The Pearson's coefficient r is statistically significant ($p < 0.01$) taking into account the number of the samples ($N = 8$) and the critical value table ($df = N - 2$, two-tailed test) (Siegle, 2009). In both diagrams, black squares with white codes are water samples from this study. In a): crosses depict groundwater and snowmelt samples from Gran Sasso massif (Adinolfi Falcone et al., 2008); 'Degassing water' field depicts enriched $\delta^{13}C_{\text{ext}}$ value, e.g. in Cotilia springs (Chiodini et al., 2011; Giustini et al., 2013; Petitta et al., 2011); light grey squares represent Raiano spring (Sulmona basin) samples from 14/04/2009 to 19/02/2010 (Chiodini et al., 2011), whereas dark grey circles and square the respectively bicarbonatic and sulphatic waters sampled at Antrodoto (Petitta et al., 2011).

et al., 2008). In Chiodini et al. (2013), a heat flow of only 39 MW m^{-2} was inferred for the latter area, in comparison with a higher heat flow value in the northern Gran Sasso structure (176 MW m^{-2}). These data suggest that the $\delta^{13}C_{\text{ext}}$ anomalies in the Sulmona basin could be the result of a mixing of fluids from different sources. A relationship between $\delta^{13}C_{\text{ext}}$ and the concentration of some dissolved elements suggests a possible contribution, not only of the deep gaseous component, but also of the liquid fraction or a water–mineral re-equilibration due to heat flow. This could be particularly applicable to the samples with the highest $\delta^{13}C_{\text{ext}}$ anomalies. In these samples, the correlation between elements (or their ratio) and the CO_2 from the deep source suggests that the application of chemical geothermometers might be fruitful in terms of inferring the temperature reached by fluids at depth. In the carbonate-evaporite reservoirs of the Apennine, the sodium/lithium Na/Li (Minissale and Duchi, 1988) and sulphate/fluoride SO_4/F (Chiodini et al., 1995; Marini et al., 1986) have been shown to be the most

reliable geothermometric equations. In the first case, Minissale and Duchi (1988) applied the Na/Li equation put forward by Fouillac and Michard (1981) to spring waters from the northern Apennines. Application of an updated Na/Li equation by Sanjuan et al. (2014), specifically for the chloride concentration of the waters considered in this study ($Cl < 0.3$ M), gave temperatures of 96 °C (Antrodoco) and 146 °C (Grassano) (Table 2) and showed a significant correlation with the $\delta^{13}C_{ext}$ (Fig. 3b). Indeed, the Pearson's coefficient r is statistically significant ($p < 0.01$) taking into account the number of the samples ($N = 8$) and the critical value table ($df = N - 2$, two-tailed test) (Siegle, 2009). Moreover, an ANOVA test on the slope and linearity of the normal probability plot also confirms that the regression is statistically significant (OriginLab, 2017) (Supplementary File S3).

Two water samples from the Sulmona Basin – Decontra 1 and Raiano – showed inferred temperatures of 101 °C and 138 °C, respectively (Table 2). However, their scattered chemical composition (Fig. 2), the $\delta^{13}C_{ext}$ mixed source (Fig. 3a) and the local low heat-flow rates suggest that the geothermometric results of the groundwater from Sulmona should be considered prudently. Statistical analysis of 32 samples collected to date at Raiano spring (excluding three outliers – two from before the seismic sequence, and the 06/12/2016 sample, which suffered dilution after the main earthquake shock) shows that the temperatures calculated from the Na/Li ratio were significantly drawn from a normally distributed population (OriginLab, 2017), with $T(Na/Li)_{mean} = 126 \pm 12$ °C (1 σ) (Supplementary File S4). Lower (similar to local air) or negative temperature values were obtained for the three water samples with $\delta^{13}C_{ext}$ similar to the $\delta^{13}C_{inf}$ of the Apennine infiltrating waters (Giardino, Rio Freddo and Le Fonti springs) (Fig. 3b). The application of the SO_4/F equation, specifically for water samples within the low-temperature range (50–150 °C; Chiodini et al., 1995), gave negative results for Antrodoco and Grassano and $T = 46$ °C for Rio Freddo. According to Blasco et al. (2018), the unproductive results of the SO_4/F geothermometric approach could be due to the anhydrite and fluorite undersaturation of the studied waters.

5.2. – Geothermal modelling and recalculation of the $\delta^{13}C_{ext}$

During the upwelling of fluid, its composition could be altered by CO_2 degassing, carbonate precipitation, and mixing with shallow waters. The use of geothermal modelling provides a more reliable approach to reconstructing fluid composition at depth and to estimating reservoir temperature (Battistel et al., 2014). This is mainly because it considers the entire chemical analysis of the involved fluid, rather than just a portion (e.g., elements ratio), thus avoiding some of the restricting assumptions on geothermometric equations based on an elements couple (Bethke, 2008).

In this study, we tried to restore the deep fluid composition of the samples with the highest C_{ext} and $\delta^{13}C_{ext}$ values by recalculating equilibria between water and typical carbonate-evaporite minerals and increasing both temperature and CO_2 , thus also attempting to restore the flashed gas. The results obtained from geothermal modelling are close to those determined by the Na/Li geothermometer, with $\log PCO_2 = 1.1 \pm 0.3$ calculated at the saturated vapour pressure (Fig. 4). Finally, the $\delta^{13}C_{ext}$ was recalculated using Netpath code (Plummer et al., 1994) at the mean temperatures obtained by Na/Li and geothermal modelling ($T_{Antrodoco} = 113$ °C; $T_{Grassano} = 130$ °C). Considering the temperatures measured in the Antrodoco 1 borehole (up to 60 °C at 3 km) (Trumpy and Manzella, 2017), the temperature inferred for that spring should correspond to a depth of approximately 5.6 km. The CO_2 partial pressure, alkalinity and the pH were recalculated at the mean temperatures and a total pressure of $P = 100$ MPa using PHREEQC code and the *phreeqc.dat* thermodynamic dataset, which use the Peng–Robinson equation of state for calculating the solubility of gases at high pressures (Parkhurst and Appelo, 2013). The $\delta^{13}C_{ext}(CO_2)_g$ at the deep temperature and alkalinity values obtained by NetpathXL code were + 0.13‰ and –1.28‰ for Antrodoco and

Grassano, respectively (Table 3). These latter values are enriched at + 0.8‰ and + 2.3‰ compared to the $\delta^{13}C_{ext}(CO_2)_g$ values obtained by the same code at sampling conditions. In the Burano formation at Antrodoco, the followings values for carbonate minerals were detected: $\delta^{13}C_{dolomite} = +2.7$ ‰ and $\delta^{13}C_{calcite} = +1.6$ ‰ (Masi et al., 1995). The central value between the two carbonates is close to the mean value employed for limestones in central Italy used for the $\delta^{13}C_{ext}$ calculation (i.e., $\delta^{13}C_{carb} = +2.2$ ‰) (Di Luccio et al., 2018; Frondini et al., 2018). NetpathXL code permits a differentiation of the isotope composition of both calcite and dolomite in order to obtain a more accurate evaluation of the deep $\delta^{13}C(CO_2)$. The obtained $\delta^{13}C_{ext}(CO_2)_g = +0.095$ ‰ for Antrodoco is slightly higher than the aforementioned value, i.e. $\delta^{13}C_{ext}(CO_2)_g = +0.13$ ‰. However, this difference is negligible in the light of the accuracy of the $\delta^{13}C(DIC)$ analytical method. A similar approach has been employed to infer deep $\delta^{13}C_{ext}(CO_2)_g$ values at Raiano. The geochemical modelling applied to that sample produced a temperature of $T = 129$ °C (Supplementary File S4), which is within the historical mean obtained by the Na/Li geothermometer ($T = 126 \pm 12$ °C; Supplementary File S5). At that temperature, the carbon dioxide partial pressure at the saturated vapour pressure is $\log PCO_2(g) = 0.82$, whereas it is approximately 1.3 at the total pressure of 100 MPa (Table 3). The mean temperature of $T = 127$ °C for that spring could be compatible with a fluid from a depth of approximately 7 km that is within a complex thrust zone where late Triassic evaporites (Anidriti di Burano formation) are tectonically interbedded with late Permian–Triassic quartzites and phyllites (Verrucano formation) (Romano et al., 2013; Santilano et al., 2019). The recalculated $\delta^{13}C_{ext}(CO_2)_g = -3.36$ ‰ is significantly different from the value at sampling condition; i.e. $\delta^{13}C_{ext}(CO_2)_g = -6.67$ ‰ (Table 2). However, the values inferred for Antrodoco and Grassano are closer to the $\delta^{13}C_{ext}$ values of 0‰ and –1.5‰, as recently calculated for the deep source end-member in the central Apennine area (Chiodini et al., 2013; Di Luccio et al., 2018).

5.3. – Waters sampled during the 2016–2017 central Italy seismic sequence

After testing the above-described method with chemical and isotopic $\delta^{13}C(DIC)$ data from our dataset referring to the non-seismic sequence (2018, see Table 1), we also applied the same method to the chemical and isotopic data collected by Rosen et al. (2018) during the seismic sequence in Amatrice–Norcia during 2016–2017 in order to evaluate possible geochemical anomalies related to the seismic cycle.

The chemical and isotope compositions of four springs were studied during the seismic sequence that occurred in central Italy between August 2016 and January 2017 (Rosen et al., 2018). In that study, the authors reported that the postmainshock $\delta^{13}C(DIC)$ value range of the waters was from –5‰ to –3‰, placing it within the range of mantle-derived CO_2 in the central Apennines; i.e. –5‰ to –1‰ (Chiodini et al., 2004, 2000). However, they did not perform the necessary isotope-mass balance to determine the $\delta^{13}C_{ext}$. Indeed, even higher $\delta^{13}C(DIC)$ values (up to + 2.2‰) were measured in the PES springs during periods of non-seismic alarm (Civita and Fiorucci, 2010). In Fig. 5, we plotted the recalculated $\delta^{13}C_{ext}$ and C_{ext} parameters from the chemical and isotope values published by Rosen et al. (2018) (Supplementary File S6). In that manuscript, the most enriched $\delta^{13}C(DIC)$ values were detected in PES and SUS springs. In terms of the recalculated $\delta^{13}C_{ext}$, these samples are clustered between the ‘deep’ and ‘ C_{inf} ’ sources (Fig. 5a), which are similar to the so-called ‘group B’ water samples of Chiodini et al. (2011). However, despite the addition of deeply derived CO_2 , the highest $\delta^{13}C_{ext}$ detected in a PES spring on 31 October 2016 (i.e. one day after the main shock on 30 October 2016) was not higher than –6‰. It should be also noted that during the seismic sequence the PES spring samples also showed a linear path when $\delta^{13}C_{ext}$ is plotted against the temperatures inferred by the Na/Li geothermometer (Fig. 5b). This fact testifies the addition of a liquid deep source, which is characteristic of the St. Vittorino plain (Petitta

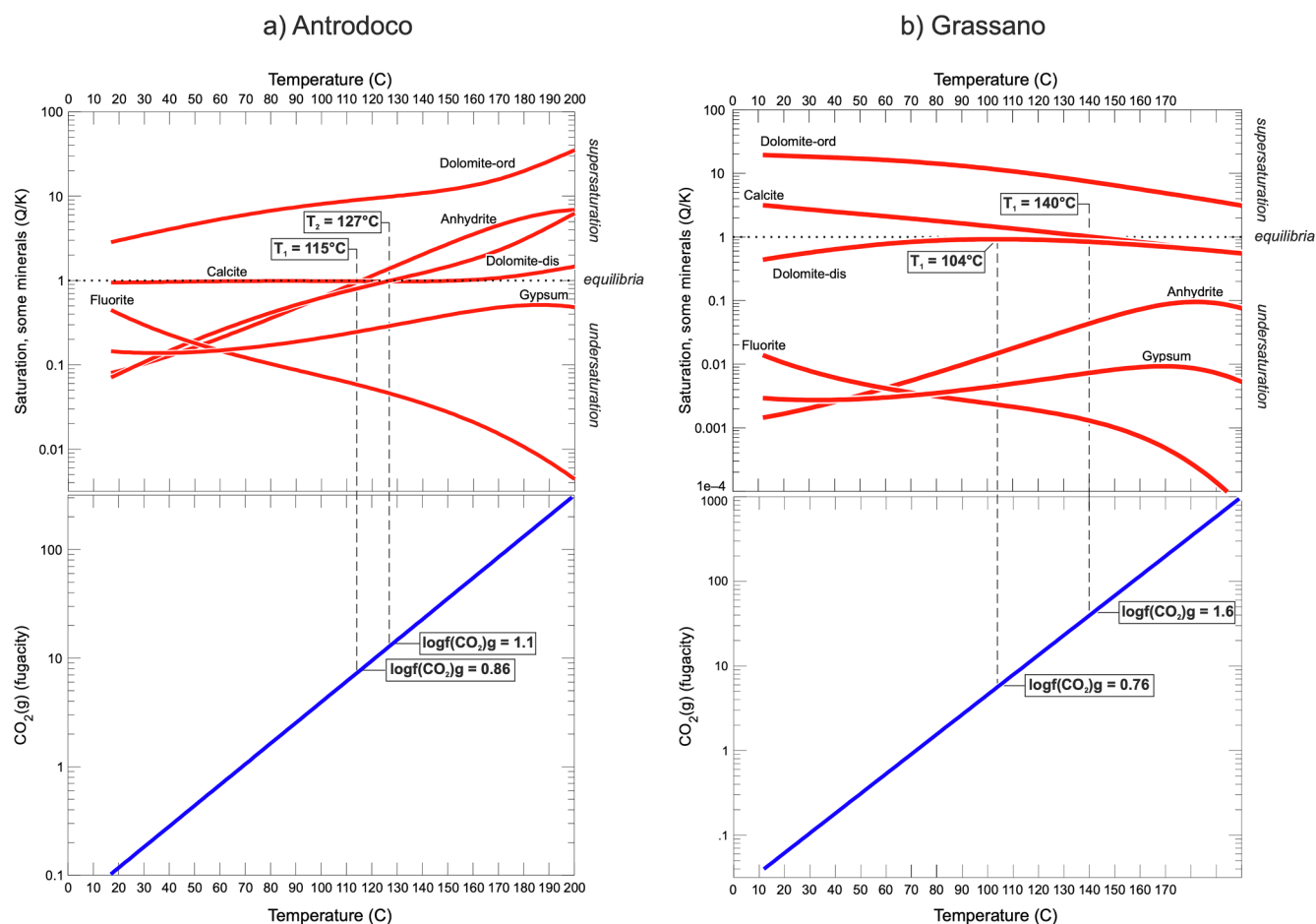


Fig. 4. Antrodoco and Grassano geothermal modelling calculated using the React tool of *The Geochemist's Workbench* (Bethke, 2008) and thermo.dat thermodynamic dataset. Red lines and blue lines depict the variation mineral saturation indexes and partial pressure of carbon dioxide at increasing temperature, respectively.

Table 3

Recalculation of some parameters, at depth conditions, for the three samples that showed the most enriched $\delta^{13}\text{C}_{\text{ext}}$ (Table 2). The physico-chemical conditions at $P = 100$ MPa were recalculated using PHREEQC code and phreeqc.dat, which use the Peng–Robinson equation of state for calculating the solubility of gases at high pressure (Parkhurst and Appelo, 2013). Mean temperature derived from Na/Li equation at $\text{Cl} < 0.3$ M (Sanjuan et al., 2014) and geothermal modelling. $\delta^{13}\text{C}_{\text{ext}}(\text{CO}_2)_g$ derived from NetpathXL code (Plummer et al., 1994), assuming $\delta^{13}\text{C}_{\text{carb}} = +2.2\text{‰}$ for both calcite and dolomite (Di Luccio et al., 2018; Frondini et al., 2018).

Sample	ID	Mean T °C	vsp at mean T			total P = 100 MPa		
			pH	logPCO ₂	$\delta^{13}\text{C}_{\text{ext}}$ (CO ₂) _g	pH	logPCO ₂	$\delta^{13}\text{C}_{\text{ext}}$ (CO ₂) _g
Antrodoco	An	113	5.2	1.0	0.130	4.9	1.5	0.226
Grassano	Gr	130	5.5	1.2	−1.28	4.9	1.8	−1.11
Raiano	Ra	128	5.7	0.87	−3.36	5.1	1.3	−3.08

vsp = vapour saturated pressure.

et al., 2011). Indeed, deep fluid with a lithium concentration up to 200 $\mu\text{g/l}$ has been measured in that area (Cotilia Thermal Spring) (Civita and Fiorucci, 2010). This also agree with the abrupt changes at PES spring of the calculated Na/Li temperature and $\delta^{13}\text{C}_{\text{ext}}$ during the seismic sequences of the 2016–2017 (Fig. 6a). In contrast, SUS samples depicted $\delta^{13}\text{C}_{\text{ext}}$ variation at an almost constant Na/Li ratio, probably due to an ingress of only the gas phase (and no liquid) from the deep source. However, the mixing between deep and shallow sources at PES springs is supposed to be quite normal, presumably constant, but with

variable proportions. This hypothesis is supported by the historical concentration data regarding sodium and lithium detected in that spring (Barbieri et al., 2017; Civita and Fiorucci, 2010) (Fig. 6b), which confirm that mixing also occurred during periods without earthquake warnings. Rather, the anomalous Na/Li ratio detected on 31 October 2016 (Fig. 5b) could be due to: i) an increased contribution from the shallow source after a post-seismic permeability change (Charmoille et al., 2005); ii) a change of mineralisation potentially affecting the character of a fault slip in response to earthquakes (Bense et al., 2013); or iii) a combination of both of these phenomena.

6. Conclusions

The chemical composition and stable isotope ratio $^{13}\text{C}/^{12}\text{C}$ of the DIC of nine selected springs from the central Apennines show a correlation between the temperatures inferred by geothermometers and the isotopic composition of the deep CO₂ gas of magmatic/methamorphic origin (the so-called C_{ext}), which is dissolved in water as CO₂(aq). The shallow groundwater end-member of the mixing is characterized by a biogenic signature of the dissolved carbon dioxide, which is typical of infiltrating waters (the so-called C_{inf}). The sodium–lithium geothermometric equation allows direct verification of this correlation. Among the studied spring-water samples, those from the Olevano–Antrodoco and the Matese fault systems showed the most promising results for studying deep fluids involved in seismic swarms. In the Sulmona basin, the Raiano spring showed the most enriched values in term of $\delta^{13}\text{C}_{\text{ext}}$ and the related deep temperature. The inferred range of temperature (113–130 °C) and the mean CO₂ partial pressure calculated at depth (logPCO₂ = 1.1 $\pm$ 0.3) for these three springs are comparable with

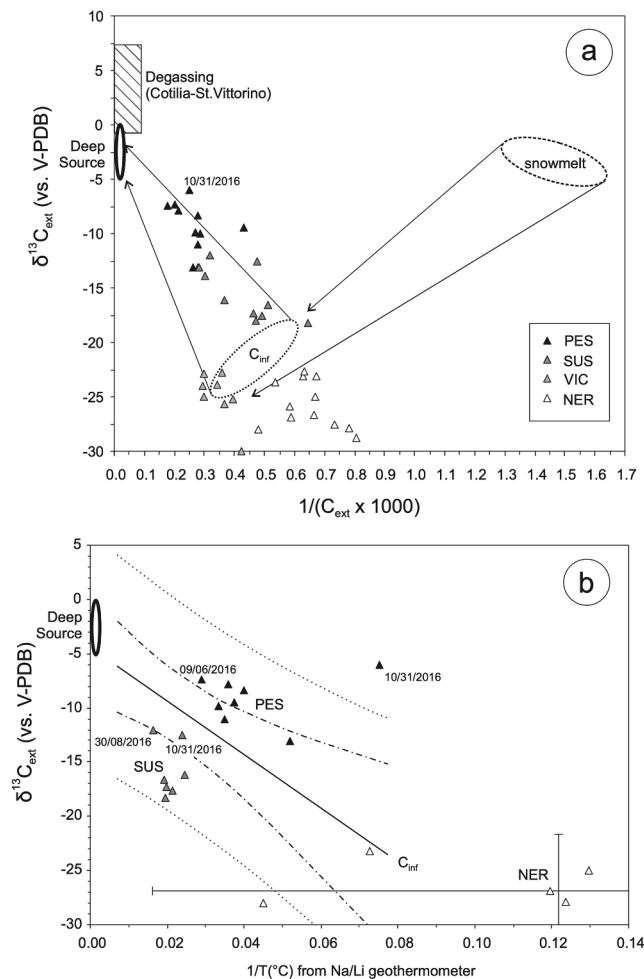


Fig. 5. Recalculated $\delta^{13}C_{ext}$ (‰ vs. V-PDB), C_{ext} (mol) and Na/Li geothermometrical temperature ($^{\circ}C$) parameters of the NER, PES, SUS and VIC springs collected during the 2016–2017 central Italy seismic sequence (Rosen et al., 2018) (Supplementary File S6). In a): $\delta^{13}C_{ext}$ versus $1/C_{ext}$ diagram (fields as in Fig. 3); in b): $\delta^{13}C_{ext}$ versus $1/T$, where T = temperature in $^{\circ}C$ obtained from Na/Li geothermometer (Sanjuan et al., 2014). In b), the solid line depicts the linear best-fit shown in Fig. 3b, along with its confidence (dotted-dashed curves) and prediction (dotted curves) intervals, calculated at 95% confidence level (OriginLab, 2017). The error bar depicts the variations of the two parameters in the NER waters.

figures obtained from deep boreholes in the northern Apennines (Collettini et al., 2008). The observed correlation between $\delta^{13}C_{ext}$ and Na/Li temperature was also verified in samples collected during a seismic sequence and recalculated from Rosen et al. (2018). Therefore, in terms of the endogenic CO_2 flow and the seismic cycle of the study area, we can infer from our results that the monthly samples performed in our study are useful for distinguishing between springs which receive deep CO_2 contributions only and those having a mix of gas plus liquid phases. The combined results of $\delta^{13}C_{ext}$ and Na/Li ratio data demonstrate that mixing between deep and shallow fluids occurs in some seismic area of central Italy. The resulting fluids seem to be in equilibrium with the aquifer minerals at temperature not higher than $150^{\circ}C$. The temperature range detected in the studied groundwater is not higher enough to produce a ^{18}O -enrichment in the water molecule due to interaction with minerals (e.g. Giggensbach, 1992). This could explain the reason why no significant $\delta^{18}O(H_2O)$ variations were detected during seismic swarms (Barberio et al., 2017; Rosen et al., 2018). As deep CO_2 input during pre-seismic crustal dilatancy seems to be one of the driving factors for the hydrochemical changes of groundwater observed before strong earthquakes in various localities (including

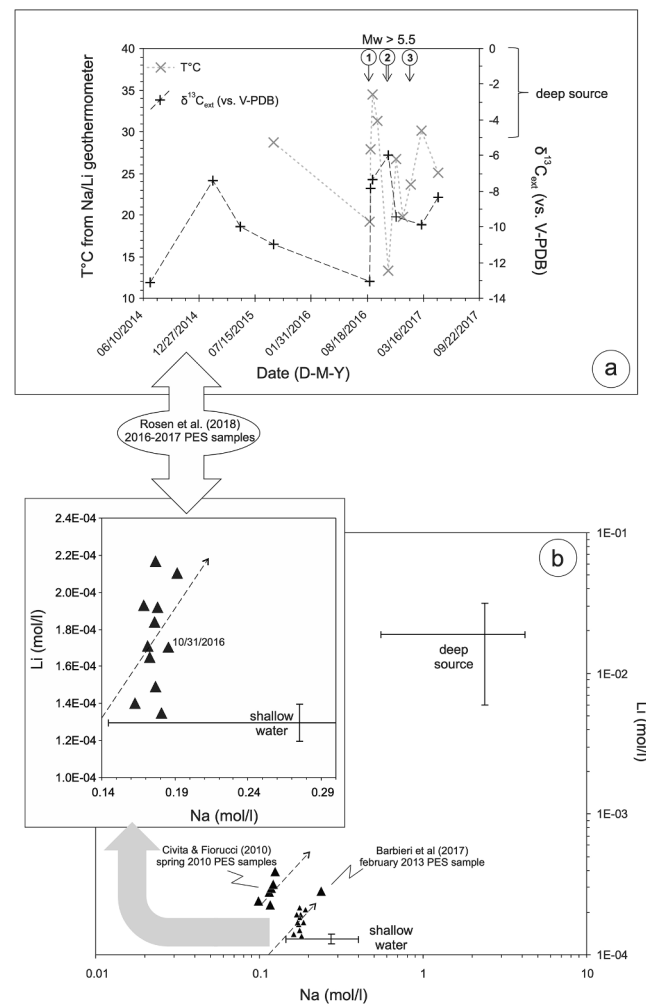


Fig. 6. a) Time series for Na/Li geothermometrical temperature ($^{\circ}C$) and $\delta^{13}C_{ext}$ (‰ vs. V-PDB) during the 2016–2017 central Italy seismic sequence as recalculated from chemical and isotope of Rosen et al. (2018); vertical arrows depict the main seismic events: ①: 08/24/2016, ②: from 10/26/2016 to 10/30/2016, ③: 01/18/2017. b) Historical sodium versus lithium concentration (mol/l) of the PES spring (Peschiera–Velino river valley, central Italy) (Barbieri et al., 2017; Civita and Fiorucci, 2010; Rosen et al., 2018). The variation in the concentration of the two elements at 'deep source' (Barbieri et al., 2017; Civita and Fiorucci, 2010; Tassi et al., 2012) and 'shallow water' (Barbieri et al., 2017) are depicted by error bars. These two components represent the main end-members (along with meteoric recharge, approximately at the origin of the axes) involved in the mixing that produces the PES-spring variation (Barbieri et al., 2017; Civita and Fiorucci, 2010).

Apennines and Italy), our results identify a useful method to be adopted for selecting springs to monitor and identify of possible hydrogeochemical precursors of earthquakes. However, the combined and complex response of Na/Li and C_{ext} variations during an earthquake sequence necessarily requires an historical chemical and isotope dataset to allow for a complete and in-depth understanding of the complex hydrogeological and geochemical processes involved, with the ultimate aim of select and verify the possible hydrogeochemical precursors of earthquakes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jhydrol.2019.124495>.

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Optimization of dissolved Radon monitoring in groundwater to contribute to the evaluation of the seismic activity: an experience in central-southern Italy

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Abstract

Anomalies in Radon (^{222}Rn) concentrations prior to earthquakes have been widely documented in seismogenic areas worldwide, but questions about their predictability remain largely unanswered. Even if it is not universally accepted, the analysis of the high-resolution time series of Rn (^{222}Rn) concentrations in groundwater, air and soil has been proposed as a suitable method to identify seismic precursors. This study, which is aimed at identifying potential gas-geochemical precursors to nearby earthquakes, analyses groundwater Rn concentrations, which were continuously measured between April 2017 and December 2019. We conducted a detailed time series analysis of dissolved Rn in two springs emerging along two active fault zones in the inner sector of the central-southern Apennines (i.e. the Matese and Morrone fault zones) in Italy. We used a simple statistical method to identify seismic precursor anomalies in Rn concentrations. Anomalies are commonly assumed as values exceeding $\pm 2\sigma$. Furthermore, we calculated the strain radius (for which a gas-geochemical precursor was expected) and the epicentral distance (from both our monitoring stations) of each seismic event of $M_w \geq 3.5$ that occurred in the monitoring area. Results from our ongoing research are promising and show significant correlations between seismic signals and Rn concentrations. However, longer time series data that include more energetic earthquakes are needed to shed light on the behaviour of this gas in relation to crustal deformation processes.

Keywords Radon · Earthquakes · Precursors · Geochemistry · Groundwater · Springs

1 Introduction

Studies about earthquake-induced natural processes have always fascinated scientists all over the world. To date, scientific research has produced several results [1–4], which in most cases are represented by the detection of geophysical or geochemical anomalies in acquired long time series data. These anomalies have been highlighted in different geoscience disciplines and concern variations in: foreshock sequences [5], ratios of seismic wave velocities V_p/V_s [6], electromagnetic fields [7], surface deformations [8], groundwater flow and chemistry [9–14] and gas emissions [15–18]. In particular, Radon (^{222}Rn) has been widely

investigated over the last few decades as a potential seismic precursor candidate [10, 19–21].

However, despite these studies, there are still several significant gaps in adopting Rn as an earthquake precursor. According to a previous study [22], there are many reasons for poor understanding of possible precursor activity, such as inadequate statistical evidence, the lack of long-term measurements and the difficulty in distinguishing between seasonal variations and anomalies at the same magnitude. Acquiring a solid understanding of the chemical and physical processes occurring in the Earth's upper crust requires a substantial number of measurements. ^{222}Rn is an endogenous natural noble gas with

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a radioactive half-life of 3.82 days produced by α -decay from Radium (^{226}Ra). It is highly soluble in water, and the behaviour of Rn in groundwater is influenced by the geological nature of the substratum. The concentration of Rn in soil depends strongly on chemical, physical and geological factors, such as grain size, porosity and permeability along with seasonal variations, including temperature and atmospheric pressure [23, 24]. The migration of Rn is driven by rock permeability, which increases with the presence of fractures, structural discontinuities and karst cavities [25, 26]. Both mechanisms of Rn transport (diffusion and advection) depend on rock porosity and permeability, which at the same time vary as a function of the stress field [27]. Due to changes in crustal stress/strain and variations in pore pressure that occur before earthquakes, anomalies in Rn concentrations have been traced and analysed in seismogenic areas worldwide [28, 29]. This evidence is associated with changes in water–rock interactions, which is commonly explained as the strong ability of gas migration promoted by the creation of highly permeable zones, such as microcracks and fractures.

Since 2014, with the aim of establishing new hydrogeological, hydrogeochemical, and gas-geochemical monitoring sites, a few pilot sites for the research of seismic precursors have been installed in the central–southern Apennines (Italy), where they have been continuously monitored and updated [12–14, 30, 31]. This study presents the results obtained from the investigation of Rn gas concentrations in groundwater that were continuously measured in two springs fed by regional carbonate aquifers in Italy. The aim of this paper is to evaluate whether the high-frequency monitoring of Rn dissolved in groundwater can be correlated with regional seismic activity, hence contributing to the identification of potential seismic precursors. Furthermore, the creation and development of regional monitoring networks comprising a large number of sensors for the measurement of dissolved Rn will allow a better understanding of the behaviour of this gas in relation to seismic activity and hydrogeological factors.

2 Geological and hydrogeological settings

The central-southern Apennine chain is an east-verging fold-thrust belt related to the west-dipping subduction of the Apulian lithosphere [32], which was developed during the Neogene and Quaternary periods. This mountain chain is characterized by NE-verging thrust faults, which dissected the tectonic edifice into several thick tectonic sheets. The post-orogenic crustal extensional regime has progressively cut across these thrust sheets from the Messinian-Pliocene onwards [33, 34] (Fig. 1). In particular,

systems of NW-striking normal faults have created half-graben intramountain basins mostly filled by Pliocene-Quaternary continental deposits [35]. At present, the extensional regime is strongly seismogenic along the axis of the central Apennines, while the compressional regime is active along the eastern margin of the Apennines and beneath the western Adriatic Sea [36–38] (Fig. 1).

The Apennine belt is characterized by huge fractured aquifers hosted by Meso-Cenozoic carbonate sequences. Due to the fold–thrust belt structure, the groundwater flowpath of the fractured aquifers is controlled at their base by the geometry of tectonic and stratigraphic contacts with low-permeability layers (aquicludes), such as pre- and syn-orogenic basinal and flysch clayey series [39]. The aquifer systems are characterized by high transmissivity, which is mostly due to fractures and karst cavities. Significant flow through springs is usually both stable and huge.

In this work, we performed continuous monitoring of Rn in two springs: the Giardino spring (SG) and the Rio Freddo spring (SRF) located at Lat. 42.162819° and Long. 13.841160° and at Lat. 41.472902° and Long. 14.496860°, respectively; the springs are fed by two regional carbonate aquifers: Mt. Morrone and the Matese Mts (Fig. 2A). In the northern sector, the Mt. Morrone aquifer is bounded by the thrust zone between the Gran Sasso carbonate unit and the Mt. Morrone carbonate unit. In the eastern sector, it is bounded by the thrust zone between the Mt. Morrone unit and the Laga siliciclastic unit, while in the western sector, it is bounded by the Mt. Morrone active extensional fault [40]. The SG (Fig. 2A) is a main discharge outlet of the Mt. Morrone aquifer and is characterized by steady flow and chemical regimes with a high discharge rate of approximately 1 m³/s [12, 31]. Its waters are predominantly tapped by the local drinking water company (ACA Pescara). This spring is located at the north-western boundary of the aquifer at the intersection with the Mt. Morrone normal fault (striking NW–SE by approximately 25 km and dipping towards the SW: Fig. 2A). This fault triggered pre-historical earthquakes up to M_w 6.5 or stronger. The current rate of extension in this area assessed through GPS measurements is 3–4 mm/a [8].

The wide karst area of the Matese Mts aquifer crops out in the median sector of the Apennine chain and presents high slopes and elevations up to 2050 m [41]. Carbonate sequences are represented by limestone and limestone-dolostone (late Triassic-Miocene) series with a thickness ranging between 2500 and 3000 m. Along the northern and eastern sectors, the Matese massif (hanging wall) is tectonically bounded by a thrust fault onto younger low-permeability argillaceous complexes and flysch sequences (footwall). Along the southern and

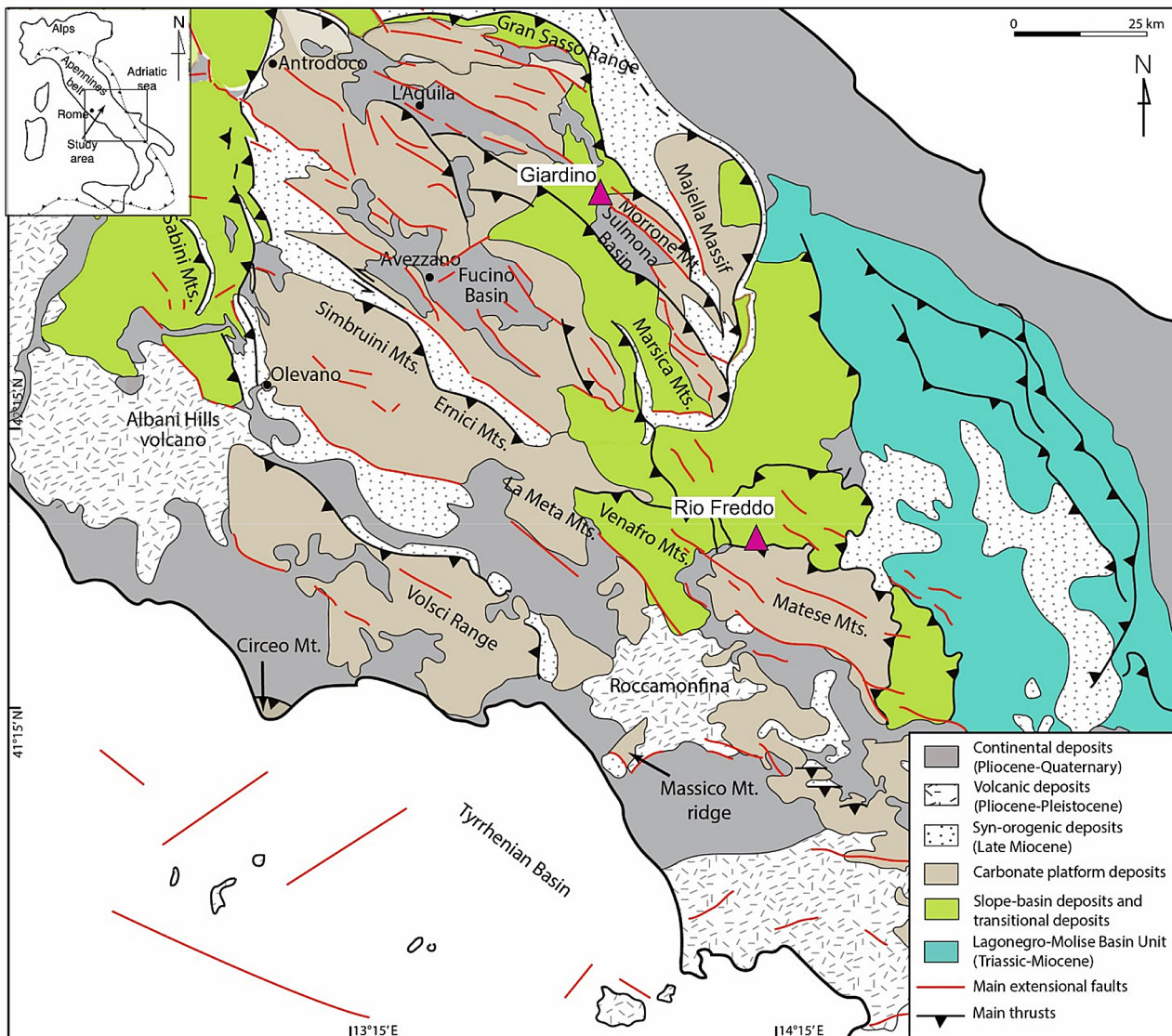


Fig. 1 Regional geological map of central-southern Apennines, Italy. Modified from [34]

western sectors, the massif is bounded by normal faults, and it is covered by recent Quaternary deposits of the Volturno river plain. Three main groups of springs are fed along the northern side of the massif near the village of Bojano [42]. These springs are fed by the karst system of the north-central sector of the Matese massif and have a total mean discharge of about $2.8 \text{ m}^3/\text{s}$. Most of them are tapped by A.S.R. Molise Acque for drinking purposes. The SRF (Fig. 2A) is located east of the village of Bojano along debris deposits that cover the fault between the limestone and flysch sequences [43]. The Matese area is a region characterized by high seismicity with a NE–SW extension rate of $2.0 \pm 0.2 \text{ mm/a}$ estimated via GPS data [44].

3 Materials and methods

To investigate the relationship between Rn gas in ground-water and seismic activity, Rn concentrations were continuously measured between April 2017 and December 2019 in the SG and between June 2018 and December 2019 in the SRF. To strip gas from the water, the study used an AlphaGUARD probe (Model PQ2000PRO: see Fig. 2B, C) with high-capacity storage equipped with a RAM 7 module. The gas was subsequently sent to the detector for measurements through a low-flow pump. Moreover, in addition to Rn water concentrations, the device simultaneously recorded ambient temperature, relative humidity, and atmospheric pressure thanks to additional sensors. The AlphaGUARD detector consists

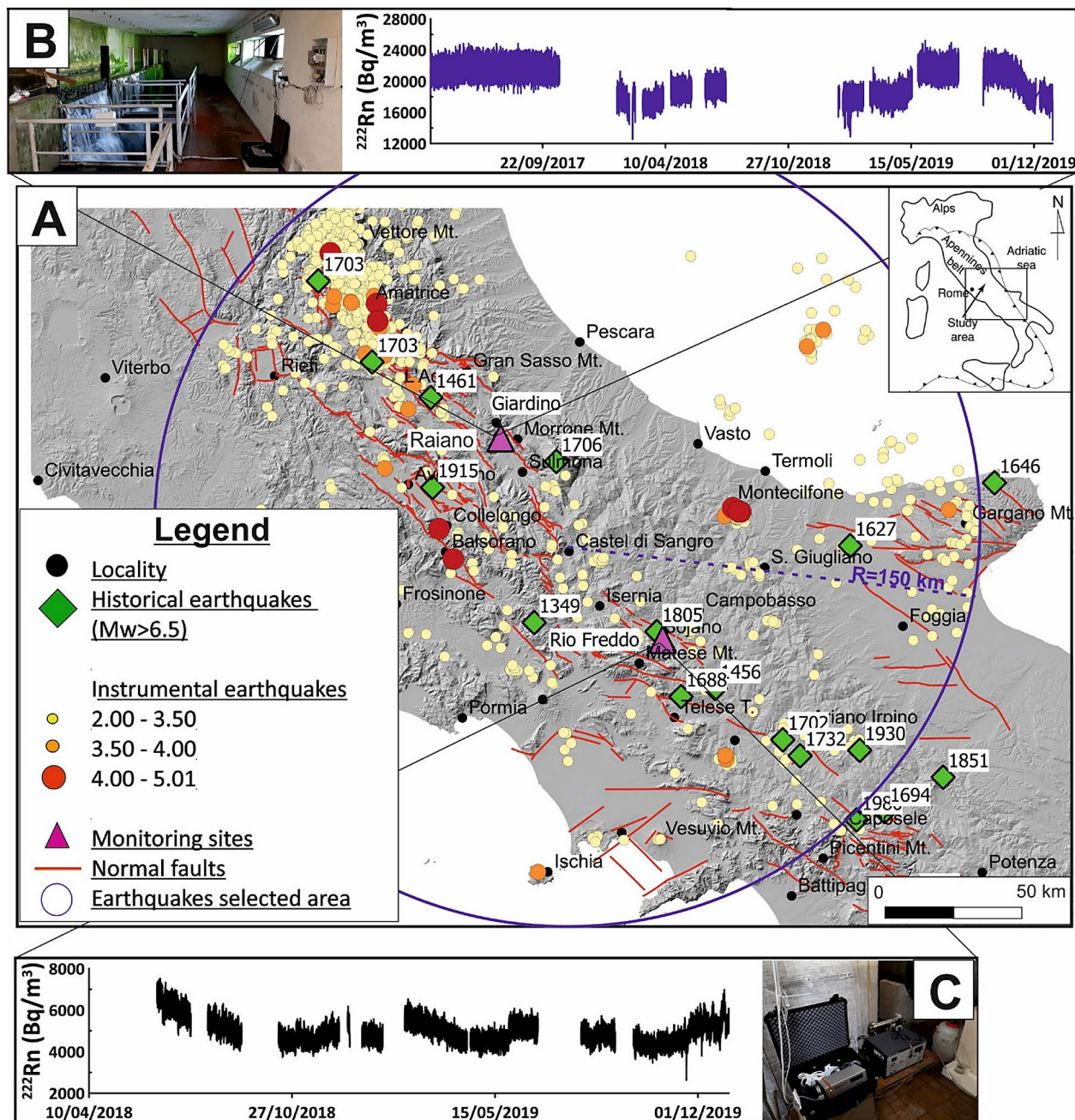


Fig. 2 **A** Map of central-southern Apennines, Italy. Location of springs is displayed with cyan triangular symbols. Earthquakes (1 April 2017–31 December 2019) occurred in the study area are displayed with circles of different size and colour depending of their magnitude. Historical earthquakes ($M_w \geq 6.5$) are shown with green rhombuses. Seismic data are from the INGV database (available

online at <http://terremoti.ingv.it/>). **B** AlphaGUARD probe (left) and time series (1 April 2017–31 December 2019) of Rn concentrations (right) at SG. **C** AlphaGUARD probe (right) and time series (1 June 2018–31 December 2019) of Rn concentrations (left) detected at SRF

of a pulse ionization chamber associated with an alpha spectrometer that recognizes the specific pulses caused by Rn. The probe guarantees a fast and precise response to different concentrations and maintenance-free operation, owing to its long-term stable calibration (sensitivity 1 CPM at 20 Bq/m^3 ; error of 3%) and is suitable for the

continuous measurement of Rn concentrations between 2–2,000,000 Bq/m^3 . The automatic data-sampling frequency was set to every 10 min. The two instruments were installed in the surplus flow at the exit of the two collected springs. To identify potential seismic precursors, these springs were also sampled monthly together with

other selected springs [12, 14] to determine their chemical–physical parameters, major ions, trace elements and stable water isotopes.

4 Results

The Rn concentrations in the groundwater were measured between April 2017 and December 2019 in the SG (Fig. 2B) and between June 2018 and December 2019 in the SRF (Fig. 2C). The waters of the SG and SRF are mainly enriched in bicarbonate and calcium ions (Ca-HCO₃ facies) due to carbonate dissolution. In terms of chemical–physical parameters (e.g. pH, temperature and electrical conductivity), both springs are characterized by a slightly basic pH of 7.85, temperatures ranging from 7.8 to 11.9 °C, and limited mineralization defined by electrical conductivity values of 315 and 263 µS/cm for the SG and the SRF, respectively. Both Rn time series included missing data that corresponded to periods of probe maintenance or periods of low water flow when the probe emerged, thus measuring atmospheric Rn concentration. Acquisition disturbances were also caused during monthly data download operations. The Rn concentration maximum values were 25,216 and 7520 Bq/m³, while the minimum ones were 12,416 and 2624 Bq/m³ for the SG and SRF, respectively. In the time series shown in Fig. 2B, C, the dissolved Rn concentrations appear to be variable around the average values of 20,068.83 and 5038.3 Bq/m³, respectively. However, it is possible to observe seasonal variations or rapid changes in Rn content commonly linked to the hydrogeological and hydrological cycles [22].

Figure 2A shows the background seismicity of the study area (available online: <http://terremoti.ingv.it/>), which was recorded in the same period of the gas-geochemical monitoring. Earthquakes that occurred in an area with a radius of 150 km centred on Castel di Sangro (Lat. 41.783991°, Long. 14.108032°) were selected. This locality is the mid-point between the two monitoring stations (i.e. the SG and SRF in Fig. 2A). The M_w 5.1 Montecilfone earthquake, which occurred in Molise on August 16, 2018, was the main seismic event during the monitoring period (2017–2019).

5 Time series processing and interpretation

This study conducted some simple data processing to identify potential anomalies in Rn concentrations related to seismic activity. In particular, some simple elaborations were adopted, which were similar to those that allowed other researchers to identify significant evidence of correlations between gas anomalies and seismic activity in tectonically active areas [2, 21, 45, 46]. The frequency of Rn activity for both springs is described by the typical Gaussian distribution (Fig. 3). Hence, the recorded fluctuations (whether temporal, diurnal or seasonal) are within the range included in $M \pm 2\sigma$, where M and σ are the mean and standard deviations of the time series, respectively, [47]. Instead, anomalies in Rn concentrations are defined as significant deviations from the mean value; specifically, it is commonly assumed that signals related to earthquakes fall outside the so-called 2- σ confidence interval [48].

Based on these studies, the mean values and the standard deviations of Rn activity, which are useful for

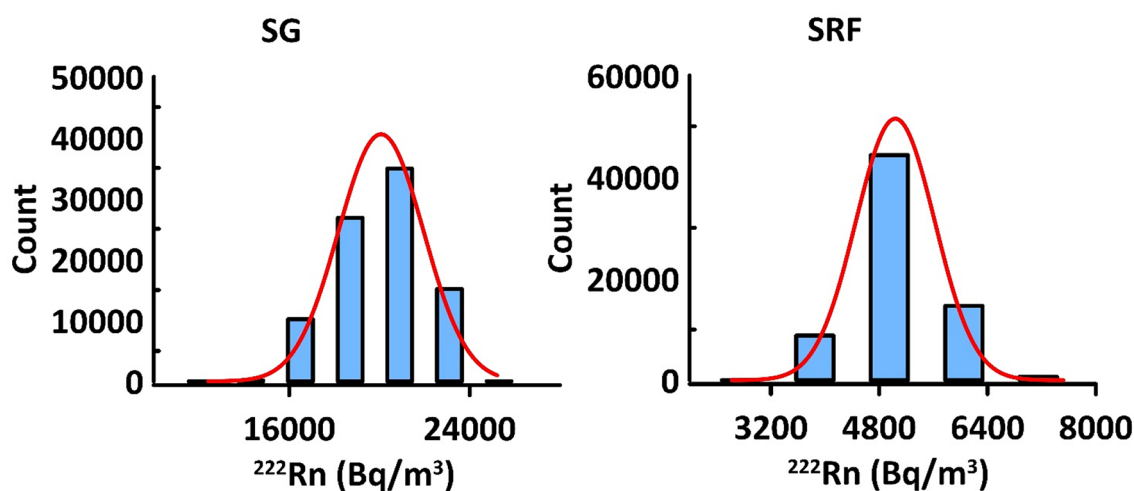


Fig. 3 On the X-axis, the Rn activity is shown (Bq/m³); on the Y-axis the count is displayed. The frequency of Rn activity for both springs (SG on the left and SRF on the right) is described by the typical

Gaussian distribution, represented as the symmetric “bell curve” shape with a red line

the detection of outliers, have been calculated for the SG (SG0, Fig. 4) and for the SRF (Fig. 5). The acquired time series are shown in Figs. 4 and 5 with three-hour moving averages, which were adopted to eliminate data noise. The mean values and the $\pm\sigma$ and $\pm 2\sigma$ thresholds are also displayed in graphs by solid and dashed lines, respectively. These graphs also show seismic events of $M_w \geq 3.5$ (taken from the previously described database).

In Fig. 4, SG0 represents the entire SG time series recorded between April 2017 and December 2019. Since this series is uneven, the sequence has been separated into four sections (SG1–SG4 in Fig. 4) to improve the accuracy of the processing. No intervals exceeding the $\pm 2\sigma$ thresholds in relation to the seismicity of the study area are observed. However, decomposing the SRF time series is not necessary, as the data show a relatively limited variation from the mean value of about 5000 Bq/

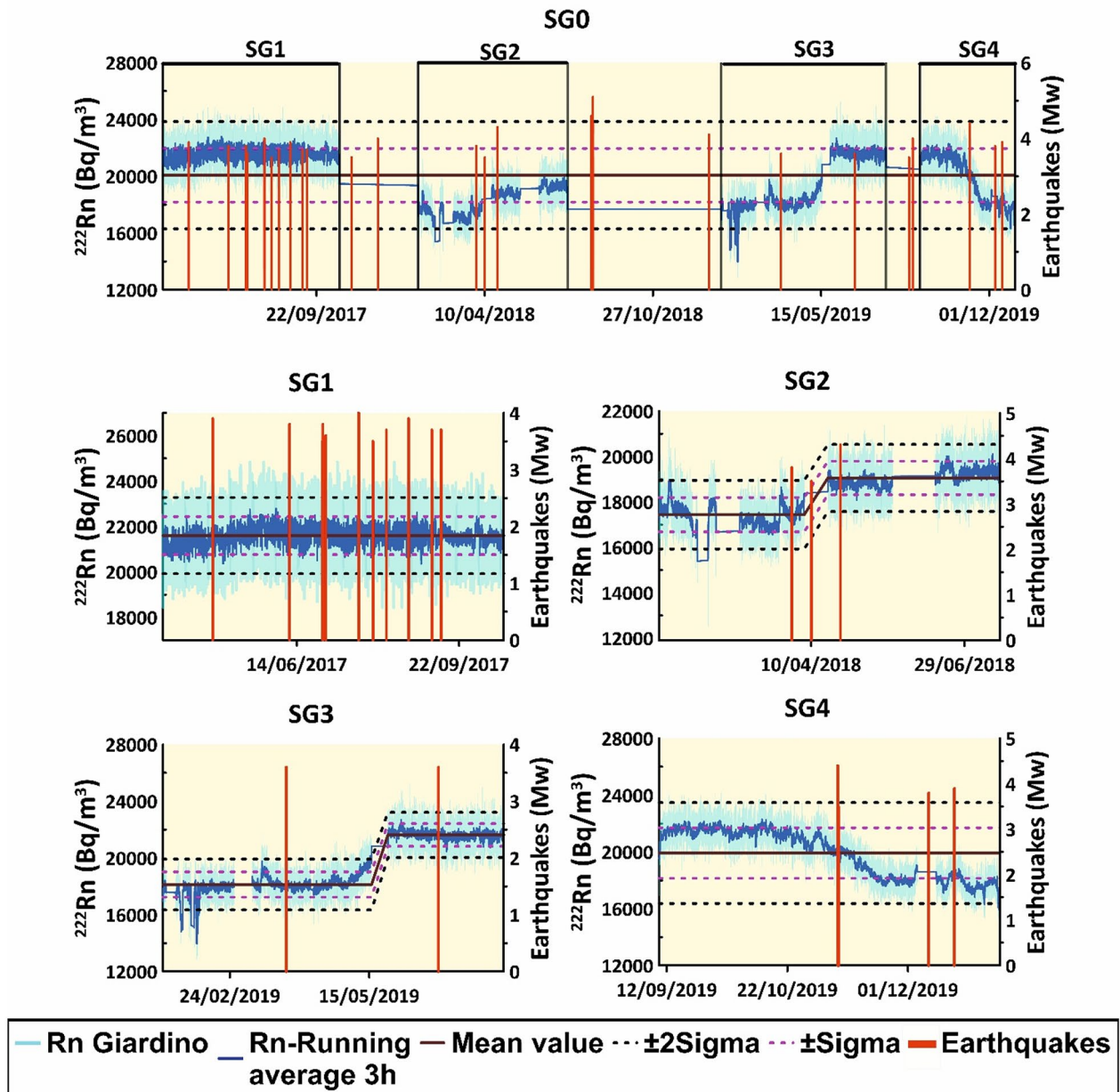


Fig. 4 Time series (1 April 2017–31 December 2019) of Rn concentrations recorded at SG (SG0). SG1, SG2, SG3, and SG4 are the four segments into which the sequence was divided. Rn activity is displayed with cyan lines, while its moving averages of 3 h are shown

with blue lines. Mean values and the $\pm\sigma$ and $\pm 2\sigma$ thresholds are displayed with solid lines and with dashed ones, respectively. Seismic events with $M_w \geq 3.5$ (from the INGV database, available online at <http://terremoti.ingv.it/>) are shown with red bars

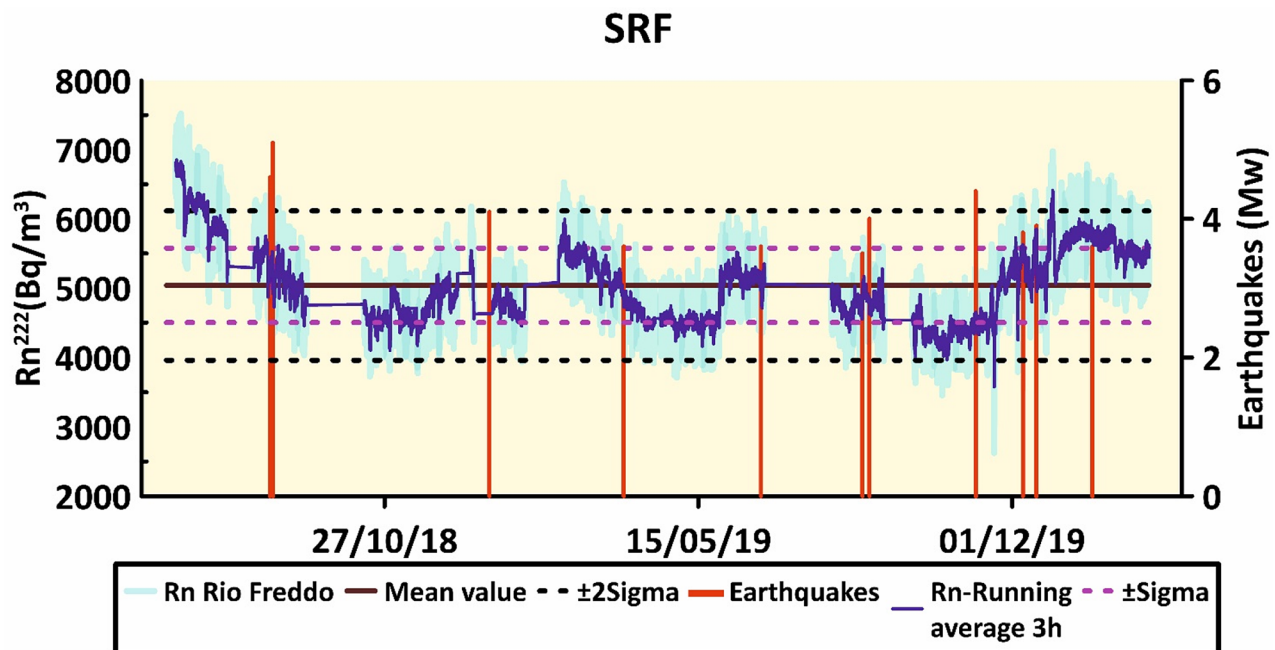


Fig. 5 Time series (1 June 2018–31 December 2019) of Rn concentrations recorded at RFS. Rn activity is displayed with cyan line, while its moving averages of 3 h are shown with blue line. Mean value and the $\pm\sigma$ and $\pm2\sigma$ thresholds are displayed with solid line

and with dashed ones, respectively. Seismic events with $M_w \geq 3.5$ (from the INGV database, available online at <http://terremoti.ingv.it/>) are shown with red bars

m^3 (Fig. 5). Additionally, in this case, as for the SG, there are no intervals exceeding the $\pm2\sigma$ thresholds in relation to seismic activity. The values exceeding $\pm2\sigma$ are due to different conditions: (1) at the SG, they are related to sensor emersions above the water surface (Fig. 4), while (2) at the SRF, they are represented by the initial values of the time series that are presumably attributable to another condition (before the start of monitoring), whose course is not known (Fig. 5).

Additionally, a different data processing procedure was considered. According to Dobrovolsky et al. [49], two parameters must be treated together to calculate the strain radius (R in km) of the effective precursory manifestation zone: the magnitude of the earthquake (M_w) and the distance between the epicentre and the measuring site (D in km). In this way, these authors defined a relationship to identify the interactions between gas-geochemical and seismic signals using the following empirical equation:

$$R = 10^{0.43 \times M} \quad (1)$$

where R is the strain radius of the precursory manifestation zone and M is the moment magnitude (M_w).

The conceptual basis of Eq. (1) is that an approximately circular region around the epicentre of the earthquake should undergo elastic crustal deformation prior

to earthquakes [50]. Therefore, precursory signals were expected for events where $R \geq D$. Considering two earthquakes of the same magnitude, a closer seismic event affects the Rn activity in the monitoring site more significantly than a distant one.

Equation (1) was applied to $M_w \geq 3.5$ earthquakes that occurred at the two study sites (between April 2017 and December 2019). Epicentral distances from the two sites were also determined (Fig. 6). This processing allowed the identification of five seismic events for the SG and six seismic events for the SRF, in which a possible Rn response was expected in terms of geochemical precursor signals.

The response could not be verified for three of the five seismic events identified at the SG due to the lack of Rn data, while no interaction was observed for the four Montecilfone seismic events at the SRF. The non-interaction between the gas content and the Montecilfone earthquakes has a geodynamic explanation; these seismic events occurred in a different plate (i.e. in the Adria plate subducting towards the SW beneath the Apennines) from the Apennine belt where the monitoring sites are located [51]. Therefore, it is not surprising that the Montecilfone seismic sequence did not cause anomalies in the inner sector of the Apennines.

Overall, three seismic events produced expected Rn activity responses as presented in Fig. 7. Specifically, the M_w 3.8 L'Aquila earthquake, which occurred on March 31st,

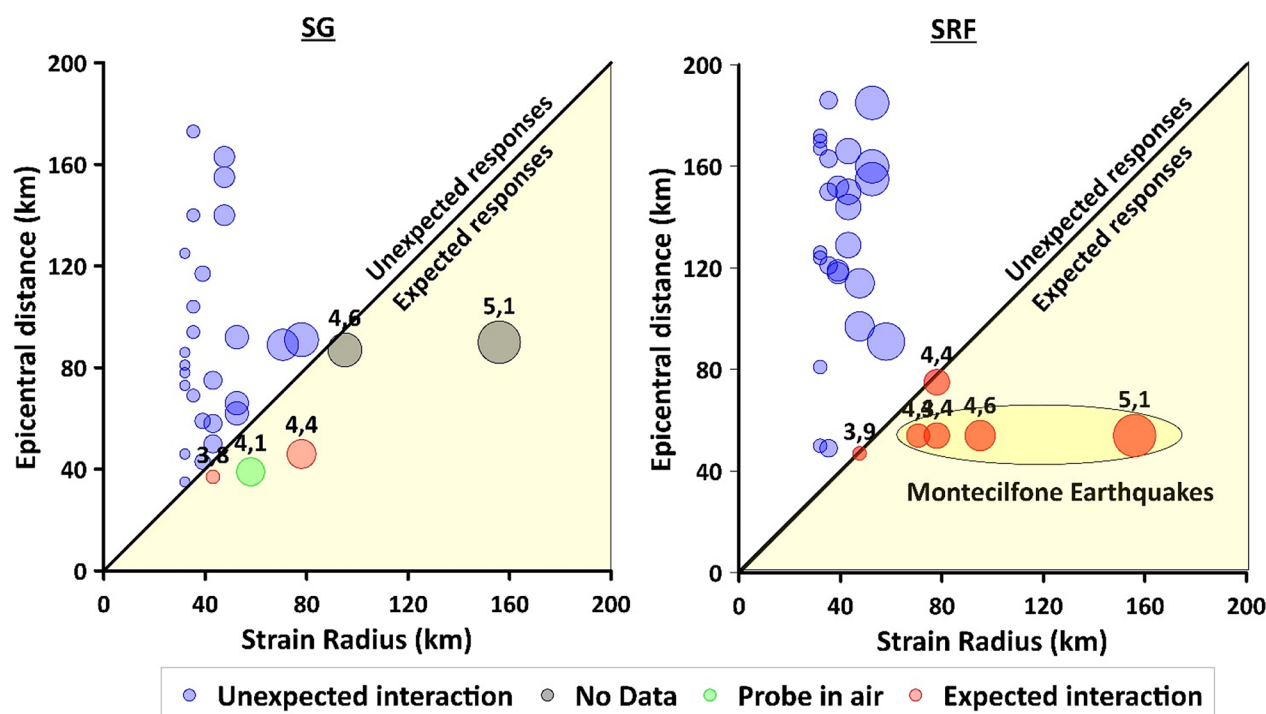


Fig. 6 Seismic events with $M_w \geq 3.5$ in the R - D plane, where R is the strain radius of the precursory manifestation zone, and D is the epicentral distance (km) from the two springs [49, 50]. Earthquakes, for which an interaction between gas-geochemical and seismic signals was supposed, fall into the “expected responses” area (the

label indicates the M_w earthquake). Only red circles are taken into consideration due to lack of R_n data, sensor emersions, and unexpected interactions that are displayed with black, green and blue circles, respectively

2018, was detected at the SG; the M_w 4.4 Balsorano earthquake, which occurred on 7 November 2019, produced responses at both springs; and the M_w 3.9 San Leucio del Sannio earthquake, which occurred on 16 December 2019, produced a response at the SRF. These two latter events present comparable R and D values at the SRF. For this reason, they fall on the straight line (Fig. 6, SRF) that separates the expected interaction area ($R \geq D$) from the unexpected interaction area ($R < D$). Specifically, an increase in R_n concentration (which lasted for about 12 h) of $\approx 1200 \text{ Bq/m}^3$ (7% with respect to the average value) and another one of $\approx 1500 \text{ Bq/m}^3$ (8% with respect to the average value) were observed at the SG seven and 11 days before the L'Aquila and the Balsorano earthquakes, respectively (the black arrow in the SG, Fig. 7A, B). For the latter earthquake, a decrease of approximately 2000 Bq/m^3 (after the peak) was also observed. Another increase in R_n concentration of $\approx 500 \text{ Bq/m}^3$ (10% with respect to the average value, which lasted about six hours) was recorded at the SRF about 17 days before the Balsorano earthquake (the black arrow on the left in the SRF, Fig. 7C). A different R_n behaviour was identified at the SRF before the San Leucio del Sannio earthquake. The preparation phase of this seismic event is illustrated by a clear increasing trend

during the month of November of $\approx 1000 \text{ Bq/m}^3$ (20% with respect to the average value: the black arrow at the SRF on the right, Fig. 7). In all the observed cases, it can be inferred that changes in the strain field before seismic activity may have affected gas and fluid migration, causing an increase in R_n content ranging from 7 to 20% with respect to (background) pre-anomaly values. Therefore, the recorded pre-seismic signals could be explained as the result of dilation and/or contraction of fracture systems that led to changes in the gas flow behaviour; however, it is believed that a more accurate analysis of time lags between the R_n signals and the occurrence of earthquakes is necessary, as the identified interactions are too limited in number to clarify this aspect. Additionally, processes of dilation and/or contraction are expected to drive some changes in the chemical content of groundwater, whose intensity would be inversely correlated with the groundwater resource volume in the corresponding aquifers due to different dilution rates. Furthermore, some transient and evident perturbations in R_n concentrations before the San Leucio del Sannio earthquake were detected, but these were attributed to the users' field interventions. The sampling frequency of 10 min allowed the acquisition of accurate data through which it was possible to measure

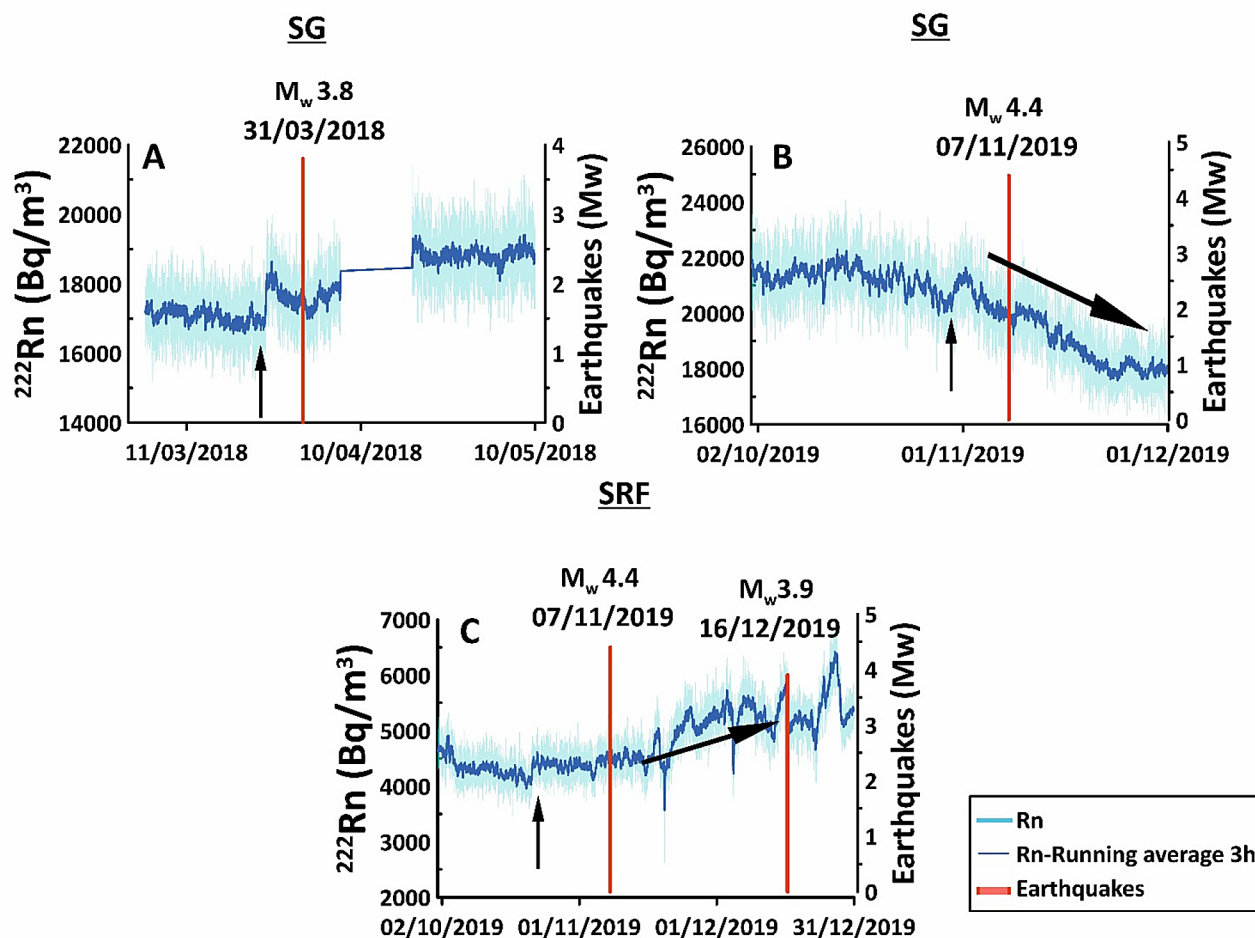


Fig. 7 Time series of Rn concentrations in relation to seismic activity. The seismic events that produced expected Rn activity responses are shown with red bars. **A** M_w 3.8 L'Aquila earthquake occurred on March 31st, 2018, detected at SG; **B** M_w 4.4 Balsorano earthquake occurred on 7 November 2019, detected at SG; **C** M_w

3.9 San Leucio del Sannio earthquake occurred on 16 December 2019 and M_w 4.4 Balsorano earthquake occurred on 7 November 2019, both recorded at SRF. The black arrows show the identified anomalies

the duration of the anomalies until the signals returned to stable background values.

Considering the anomalies recorded on the Rn time series at the two sites, the correlation between the selected events (for which a response was expected) and the hydrogeochemical time series acquired in the SG and SRF areas was investigated. Indeed, the monthly sampling of some selected springs in the two areas made it possible to detect some anomalies in springs with deeper input [12, 14]. Box-and-whiskers statistical analyses performed on the hydrogeochemical data of these springs revealed anomalous values (outliers) in Li, V, Cr and Cs concentrations in the Raiano spring (Fig. 2A) before the Balsorano earthquake, for which anomalies in Rn content were recorded at both stations (i.e. the SG and SRF in Fig. 7).

The recorded variations and trends identified in the hydrogeochemical time series of the Rn-monitored SG and

SRF did not show clear relationships with seismic events. Nevertheless, a potential response could exist that is represented by the behaviour of some elements and ions, such as Cl, SO_4 and Fe, and parameters such as electrical conductivity and temperature at the SG, where limited changes were recorded. Moreover, the sampling frequency of the water chemistry (every month) did not allow comparisons with the Rn time series (one measurement every 10 min). Therefore, the availability of longer time series data is essential for the correct evaluation of the variations in the acquired series.

6 Conclusions

The properties of Rn as an extremely mobile and nonreactive gas makes it an ideal tracer in water with the potential use in the short-term forecast of earthquakes. When used

in conjunction with other chemical and physical parameters, its prediction significance is greatly enhanced. This study performed continuous monitoring of dissolved Rn in two springs (the SG and the SRF) in central–southern Italy. This monitoring was and remains aimed at identifying potential gas-geochemical precursors to nearby earthquakes. Despite the absence of intermediate–strong seismic events during the monitoring period, some preliminary results can be drawn from the ongoing research:

- The first three years of gas-geochemical monitoring (April 2017 to December 2019) highlighted a good stability of Rn concentrations in two springs fed by regional carbonate aquifers in central–southern Italy.
- Significant Rn increases recorded before three small seismic events ($M_w < 4$) confirm that the preliminary results achieved are promising and are in line with the international known approaches and results [10, 18, 21, 45]. Indeed, significant Rn anomalies were found for all monitored seismic events that were expected to influence the Rn concentration in groundwater based on the strain radius (R in km) of the effective precursory manifestation zone.
- Specifically, the M_w 4.4 Balsorano earthquake, which occurred on 7 November 2019, produced significant responses in Rn concentrations in both springs as well as hydrogeochemical anomalies before this seismic event in concentrations of Li, V, Cr and Cs that were recorded at the nearby Raiano spring.
- The hydrogeochemical time series acquired at SG and SRF showed no significant relationship to seismic events. The difference between the sampling frequencies of the gas-geochemical and hydrogeochemical monitoring did not allow comparisons to be made between the recorded Rn anomalies and the geochemical time series.
- On the basis of the above-mentioned results, we are confident that the expansion of the monitoring network through the installation of additional sensors for the measurement of dissolved Rn in water will allow geoscientists to shed light on the behaviour of this gas in relation to crustal deformation processes, depending on the earthquake's magnitude and epicentral distance.

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Code availability Office, QGIS, Grapher.

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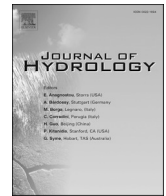
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Research papers

HydroQuakes, central Apennines, Italy: Towards a hydrogeochemical monitoring network for seismic precursors and the hydro-seismo-sensitivity of boron

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ABSTRACT

Hydrogeochemical changes before $M_w \geq \sim 5.0$ earthquakes are hoped to be applicable as seismic precursors. It is now necessary to pass from single experiences to structured networks, systematically monitoring large seismic areas for long periods. Our aim is to provide a pilot methodological experience for how such networks could be realized and the types of results they could deliver. We present the method and some initial results to document the method's applicability. In 2017, we started the HydroQuakes project in seismically active central Italy, with the Sulmona and Matese areas selected as the two monitoring nodes. Each node includes 5–6 monitored springs, and for each spring, we performed laboratory analyses of major and trace elements and some isotopes. We installed in situ probes for continuous monitoring. Between December 2017 and January 2020, the most energetic earthquakes were three events with M_w of 3.9, 4.1, and 4.4. They were not preceded by significant hydrogeochemical anomalies, except for the M_w 4.1 event. Despite its low M_w , this earthquake occurred over a large normal fault at a great depth in the crust (~ 17 km) and was preceded by weak but detectable hydrogeochemical anomalies of boron and $\delta^{11}\text{B}$ that were similar but milder than the hydrogeochemical anomalies before the 2016 M_w 6.0 earthquake in the central Apennines. This and previous evidence show the B and $\delta^{11}\text{B}$ hydro-seismo-sensitivity and indicates that pre-seismic hydrogeochemical anomalies could arise mostly before $M_w \geq \sim 5.0$ earthquakes, with weak exceptions occurring in specific conditions such as long and deep faults.

1. Introduction and background

The science of hydrogeochemical precursors of intermediate and strong earthquakes is characterized by many single instances and accounts, both recent and historical (Scholz et al., 1973; Linde et al., 1988; Roeloffs, 1988). Indeed, the hydrological effects that occur during the seismic cycle (particularly during strong earthquakes) have long been observed and documented as they are among the most outstanding coseismic phenomena and can be observed over great distances (i.e. up to hundreds of kilometers from the epicenter; Wakita, 1975; Muir-Wood and King, 1993; Manga et al., 2003; Ingebritsen and Manga, 2014, 2019; Shi et al., 2015; Hosono et al., 2018, 2020a; Cucci, 2019; Barberio et al., 2020a; Mastroiello et al., 2020; Sun et al., 2020). Examples include the

formation and/or disappearance of springs and variations in their discharge, changes in the water levels of boreholes, co- and post-seismic increases or decreases of streamflow, and variations in the chemical and physical attributes of groundwater (Wang and Manga, 2010; Amoruso et al., 2011; Ingebritsen and Manga, 2014; Barberio et al., 2017, 2020a; Fidani et al., 2017; Hosono et al., 2020b; Singh and Mukherjee, 2020).

Most (but not all) of these hydrological phenomena are known to often be co- or post-seismic (e.g. Jonsson et al., 2003; Yan et al., 2014; Petitta et al., 2018; Rosen et al., 2018; Kawabata et al., 2020; Hosono and Masaki, 2020; Ide et al., 2020; Kim et al., 2020; Lutzky et al., 2020; Nakagawa et al., 2020; Barberio et al., 2020a; Sato et al., 2020). Recently, however, geochemical changes in groundwater prior to intermediate and/or strong (usually $M_w \geq \sim 5.0$) earthquakes have started

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to be both a concrete hope and a big scientific and technological challenge for geoscientists working in the field of seismic precursors (Roeloffs, 1988; Wakita, 1996; Biagi et al., 2000; Hartman and Levy, 2005; Orihara et al., 2015; Paudel et al., 2018; Kopylova and Boldina, 2019; Hwang et al., 2020; Kim et al., 2020; Shi et al., 2020). Significant recent instances of pre-seismic hydrogeochemical anomalies were recorded in Japan (Igarashi et al., 1995; Tsunogai and Wakita, 1995), Turkey (Inan et al., 2012), Iceland (Claesson et al., 2004; Skelton et al., 2014, 2019;

Andr n et al., 2016), and Italy (Barberio et al., 2017; De Luca et al., 2018; Boschetti et al., 2019; Barbieri et al., 2020).

The aforementioned instances from different seismic sites show that pre-seismic hydrogeochemical anomalies are potentially suitable as seismic precursors. A critical evaluation to groundwater-related precursors of earthquakes (see Paudel et al., 2018 for a review) claims, however, that they have never produced statistically significant prediction schemes (Jordan et al., 2011). To one day reach the goal of

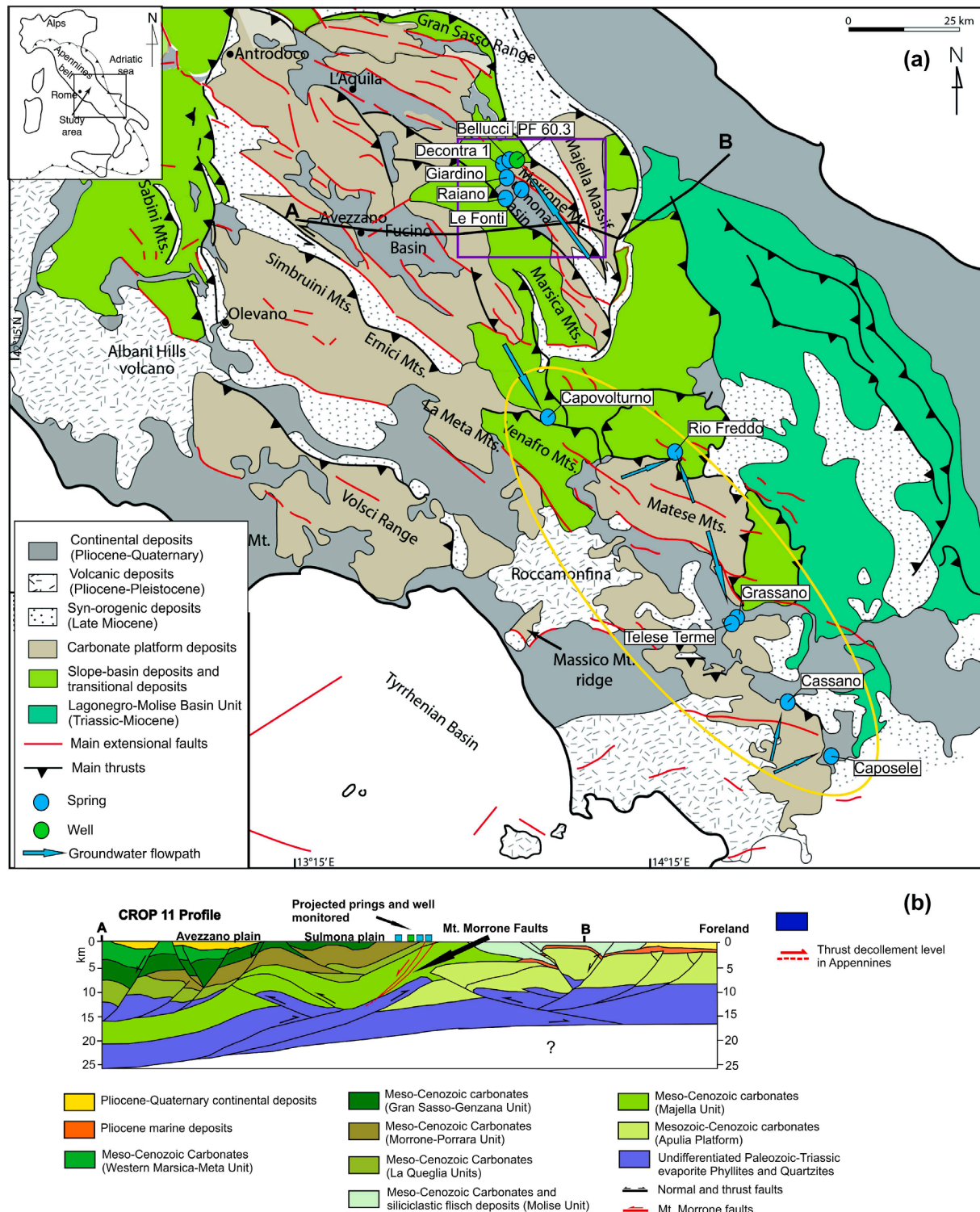


Fig. 1. (a) Geological map of the study area (central Apennines, Italy; modified after Barberio et al., 2020b; Curzi et al., 2020) and regional geological cross-section through the central Apennines (modified after Patacca et al., 2008).

forecasting major earthquakes through statistically significant prediction schemes, it is now necessary to pass from single experiences (see previous instances) to structured networks, systematically monitoring large seismic areas for long periods. The aim of this paper is to provide a pilot methodological experience (i.e. the HydroQuakes project) for how such networks could be realized and the types of results they could deliver. The objective is mostly methodological from a more than two years perspective, with some initial results about earthquakes and hydrogeochemical anomalies being presented primarily to document the applicability of the methods.

The identification of hydrogeochemical precursors of earthquakes usually faces four main problems: earthquake size (is there an earthquake magnitude threshold for the manifestation of potential precursors?); timing (how long before the earthquakes do the precursors manifest themselves?); distance (at what distance from the epicenter do the precursors manifest themselves?); and site-specificity (how specific to the region are these precursors?). The novel message from this work is that these problems can be solved through the building of national structured networks, systematically monitoring large seismic areas for long periods.

Moreover, we emphasize that building a hydrogeochemical monitoring network and further improving it could be useful not only for the identification of seismic precursors, but potentially also for other relevant scientific and societal issues, such as volcanic precursors in groundwater (Sato et al., 1992; Armienta and De la Cruz-Reyna, 1995),

water quality and pollution (Pebesma and de Kwaadsteniet, 1997), leakage from CO₂ geological storage (Zheng et al., 2009; Lions et al., 2014), induced seismicity (Ellsworth, 2013; Impropa et al., 1915), climate change (Green et al., 2011; Fiorillo et al., 2014) and precursors to offshore seismicity and volcanicity (Cuffaro et al., 2019; Billi et al., 2020).

2. Geological and seismotectonic setting

The Sulmona and Matese areas (Figs. 1 and 2), which are the two hydrogeochemical monitoring nodes for the HydroQuakes project (Figs. 3 and 4), are located in the central Apennines fold-thrust belt. The carbonate-bearing thrust sheets overthrust towards the east onto Mio-Pliocene clayey and sandy flysch deposits from foreland or piggy-back basins progressively formed towards the east (Doglioni, 1991; Billi et al., 2006; Patacca et al., 2008).

The Triassic anhydritic evaporites at the base of the Meso-Cenozoic carbonates, as well as the Messinian evaporites and Mio-Pliocene clayey syn-orogenic deposits on top of the carbonates, are known as important sealing levels (aquicludes) for groundwater (Chiodini et al., 1995, 2004; Casero and Bigi, 2013; Barberio et al., 2017). Furthermore, the fractured Meso-Cenozoic carbonates forming the thrust sheets of the Apennines belt form the bulk of most aquifers in the central Apennines (Boni et al., 1986; Petitta et al., 2009, 2015).

The occurrence of clayey deposits in the subsurface stratigraphy of

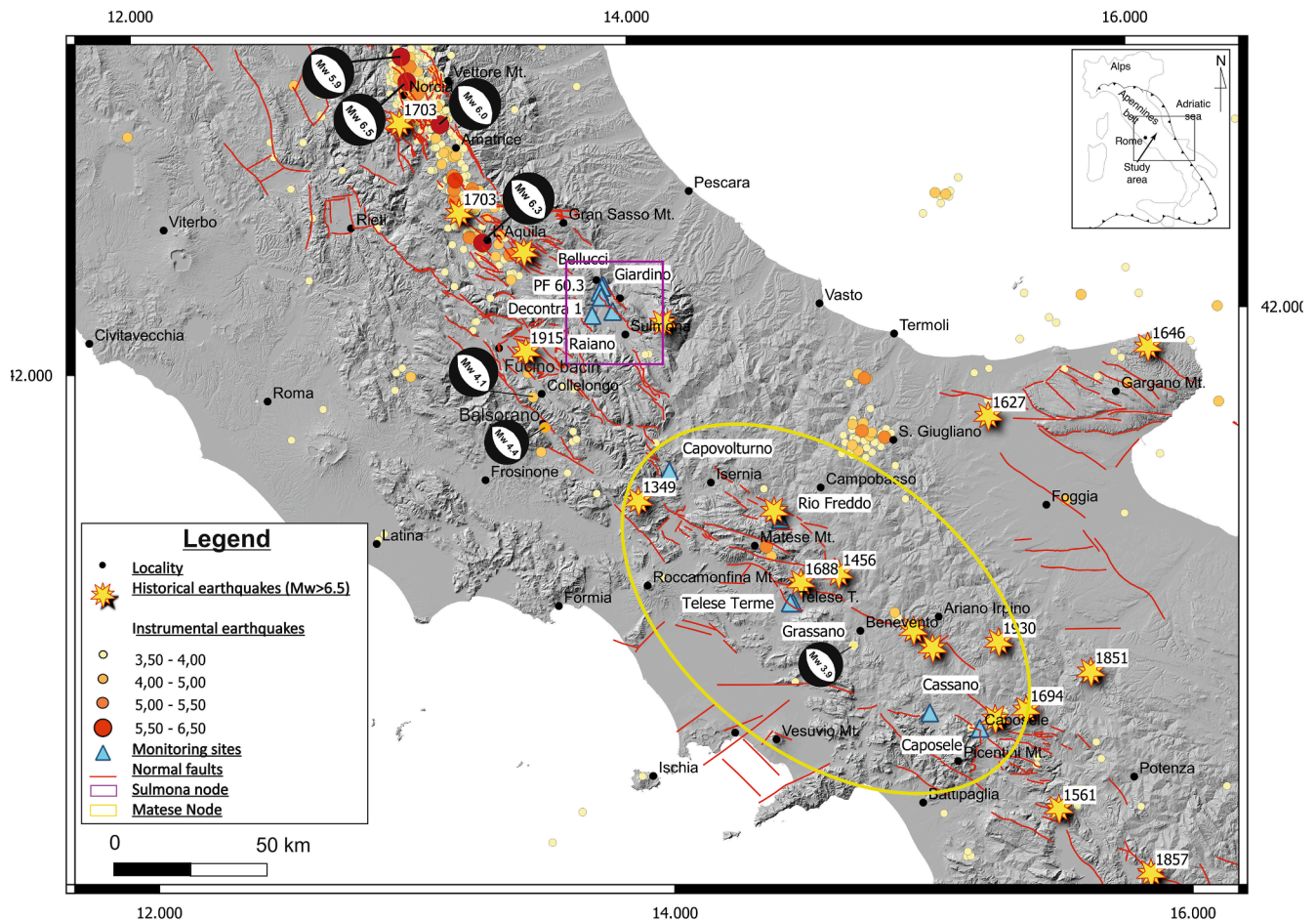


Fig. 2. Study sites. Map of Central Apennines, Italy (see location in upper right inset). Active faults (all extensional) are from the Ithaca database (available online at <http://www.isprambiente.gov.it/en/projects/soil-and-territory/italy-hazards-from-capable-faulting>). Base digital elevation model is from the ISPRA database SINAnet (available online at <http://www.sinanet.isprambiente.it/it>). Locations of monitored springs are displayed with blue triangles. Yellow stars represent the main historical earthquakes occurred in the area. Other earthquake epicenters are from the INGV database (available online at <http://cnt.rm.ingv.it/events>). The purple square and the yellow ellipsis are the Sulmona and Matese nodes of HydroQuakes, respectively.

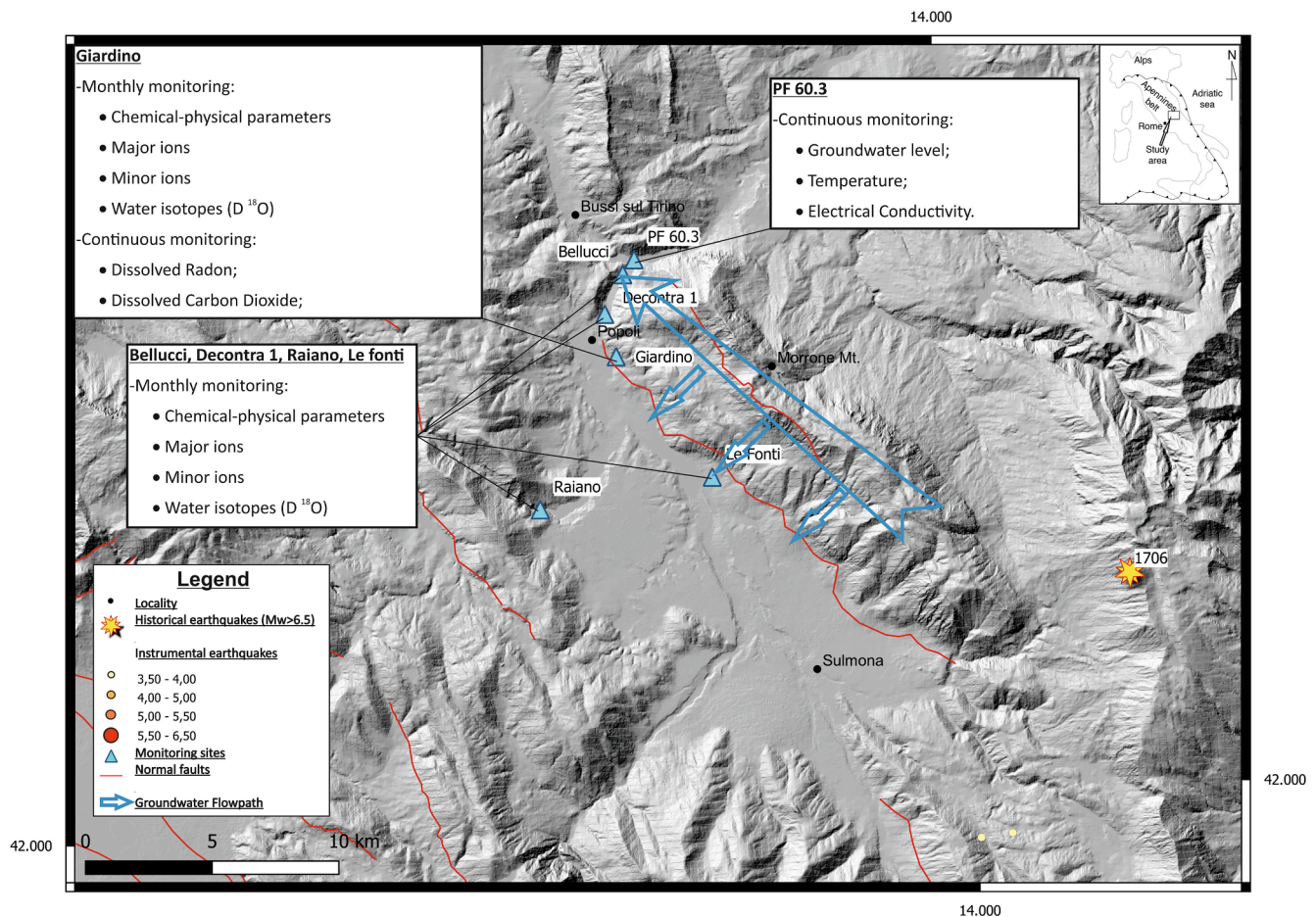


Fig. 3. Sulmona node area (see location in upper right inset and in Table S1). Active faults (all extensional) are from the Ithaca database (available online at <http://www.isprambiente.gov.it/en/projects/soil-and-territory/italy-hazards-from-capable-faulting>). Base digital elevation model is from the ISPRA database SINANet (available online at <http://www.sinanet.isprambiente.it/it>). Locations of monitored springs are displayed with blue triangles. Yellow stars represent the main historical earthquakes occurred in the area. Other earthquake epicenters are from the INGV database (available online at <http://cnt.rm.ingv.it/events>). In insets, instrumentation installed in each spring and further information concerning the hydrogeochemical monitoring are reported.

the central Apennines is relevant to the hydrogeochemical precursors of earthquakes. Indeed, some trace elements, such as As, B, Cr, Fe, Li, Sr, and V, are adsorbed in clay minerals (especially illite) and their mobility depends on groundwater acidity, which in turn depends on CO_2 fugacity. This latter is a gas typically released from the deep crust of the central Apennines and carried in an aqueous solution upwards during (pre-)seismic dilation phases (Chiodini et al., 1995, 1999, 2011, 2020; Miller et al., 2004; Barberio et al., 2017; Boschetti et al., 2019; Martinelli et al., 2020).

Post-orogenic extensional tectonics has progressively affected the Apennines from west to east between late Miocene and present times and it is currently active with many $Mw \geq 6.0$ normal fault earthquakes having occurred along the axial region of the Apennines belt (Cavinato and Celles, 1999; Pauselli et al., 2006; Galli et al., 2008). Normal faults, in particular, generated the largest historical and recent earthquakes (up to $Mw \sim 7.0$) in the central Apennines, including the 1915 Avezzano (Mw 7.0), 1980 Irpinia (Mw 6.9), 2009 L'Aquila (Mw 6.3), and 2016 Amatrice-Norcia (Mw 6.0 and 6.5) earthquakes (Galadini and Galli, 1999; 2000; Galli et al., 2008, 2009; Chiaraluce, 2012; Trippetta et al., 2019).

In particular, on January 13th, 1915, one of the largest and most destructive earthquakes (i.e. the aforementioned 1915 Avezzano Mw 7.0 earthquake) in Italy claimed 30,000 victims (Cucci et al., 2018). This earthquake was a normal faulting event (Serva et al., 1988; Westaway et al., 1989; Blumetti et al., 1993; Michetti et al., 1996) generated along the Fucino fault, a NW-striking SE-dipping tectonic structure (DISS

Working Group, 2018) ~ 28 km long. The fault is located along the mountainous slope that borders the Fucino basin towards the east (Figs. 1 and 2).

The Fucino normal fault is observed and drawn on the CROP 11 deep seismic profile as a surface dipping by about 55° towards the east and reaching a maximum depth of about 17 km beneath the Fucino basin and its western boundary (Patacca et al., 2008). The Fucino basin is close to the Sulmona and Matese monitoring nodes described in this paper (Fig. 2). On January 1st, 2019, an Mw 4.1 normal fault earthquake (epicenter: Lat. $41.88^\circ N$, Long. $13.55^\circ E$) occurred that was probably on this fault (Cavinato and Parotto, 2019) at a depth of ~ 17 km below the Collelongo village. The related focal mechanism shows a direction of maximum extension-oriented NE-SW (<http://terremoti.ingv.it>).

On November 7th, 2019, an Mw 4.4 normal fault earthquake (epicenter: Lat. $41.78^\circ N$, Long. $13.60^\circ E$) occurred beneath the Balsorano village (16 km deep), which is only about 8 km to the south of Collelongo in the southern-central part of the Roveto Valley (<http://terremoti.ingv.it>). The epicenter of this earthquake was near the superficial expression of the Roveto Valley fault (Smeraglia et al., 2018). The related focal mechanism shows a direction of maximum extension-oriented NE-SW over normal fault surfaces striking NW-SE in a similar way to the previous event in the Collelongo area and to the most recent earthquakes in the central Apennines.

Moreover, in November 2019, a seismic sequence started with epicenters in the Benevento area close to the Matese node. The maximum magnitude was reached on December 16th, 2019, with an Mw 3.9

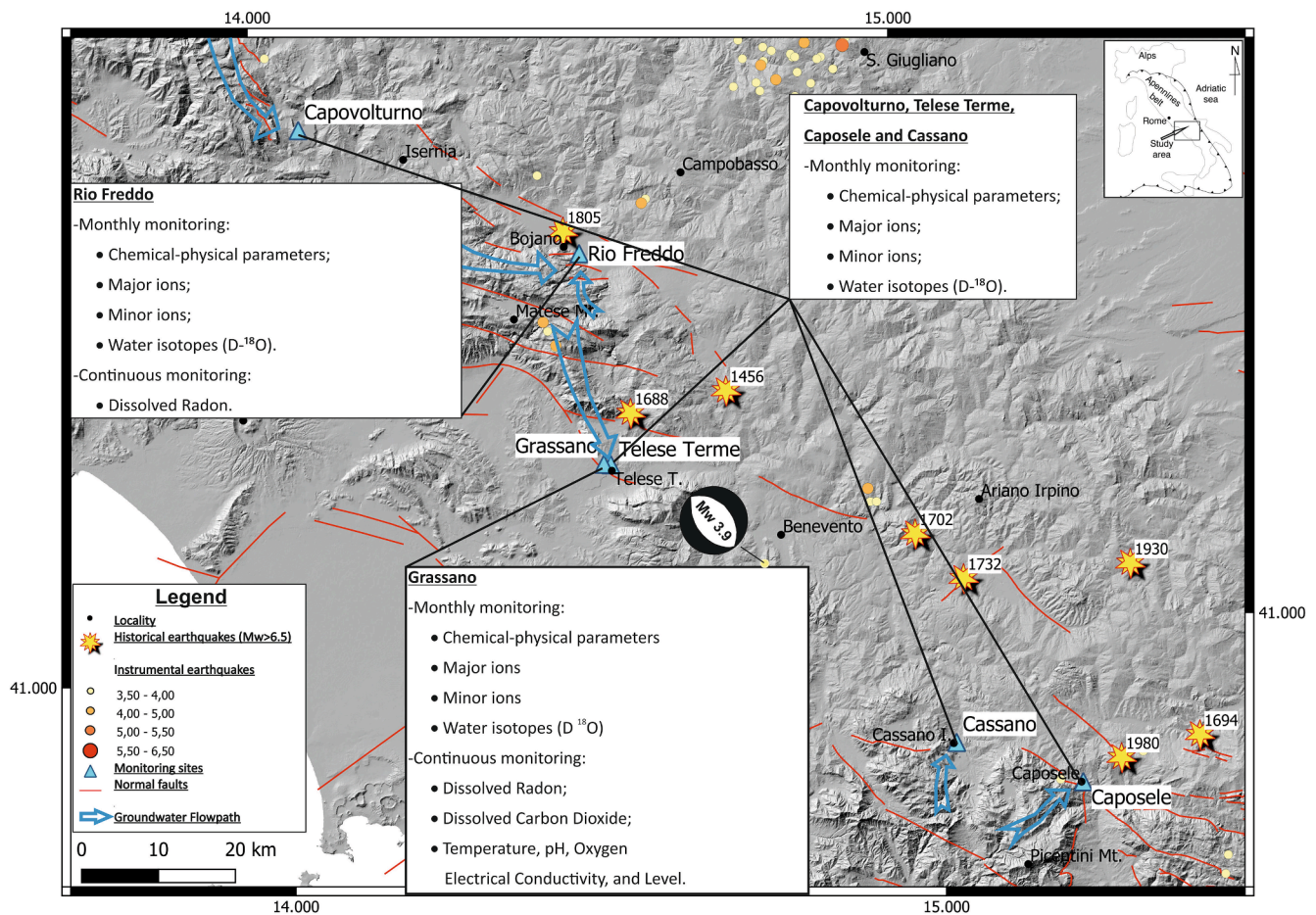


Fig. 4. Matese node area (see location in upper right inset and Tables S1 and S2). Active faults (all extensional) are from the Ithaca database (available online at <http://www.isprambiente.gov.it/en/projects/soil-and-territory/italy-hazards-from-capable-faulting>). Base digital elevation model is from the ISPRA database SINAnet (available online at <http://www.sinanet.isprambiente.it/it>). Locations of monitored springs are displayed with blue triangles. Yellow stars represent the main historical earthquakes occurred in the area. Other earthquake epicenters are from the INGV database (available online at <http://cnt.rm.ingv.it/events>). In insets, instrumentation installed in each spring and further information concerning the hydrogeochemical monitoring are reported.

earthquake (11 km deep; epicenter: Lat. 41.08°N, Long. 14.74°E) located 2 km to the west of San Leucio del Sannio village (<http://terremoti.ingv.it>). These three earthquakes, hereafter named the Collelongo (January 1st, 2019, M_w 4.1), Balsorano (November 7th, 2019, M_w 4.4), and San Leucio del Sannio (December 16th, 2019, M_w 3.9) earthquakes, are studied in this paper together with hydrogeochemical data from the HydroQuakes stations.

Moreover, a seismic sequence occurred between April and August 2018, 3 km SE of Montecilfone (epicenter: Lat. 41.87°N, Long. 14.88°E) at a depth of about 20 km. The two Montecilfone mainshocks (M_w 5.1 and 4.3) are shown below in the diagrams comparing the chemical and seismic time series in the study area. The Montecilfone earthquake epicenters fall within the 150 km in diameter selection circle (centered in Bojano) that we used in this paper for the seismic data selection (see [Supplementary Material](#)). In our opinion, however, the Montecilfone earthquakes (and the related sequence) should be disregarded for what concerns the potential seismic precursors in the HydroQuakes nodes as the related hypocenter falls in a different plate (i.e. the Adria plate subducting beneath the Apennines belt) from the Apennines fold-thrust belt where the HydroQuakes project is located.

3. Hydrogeological setting

The central Apennines (Figs. 1 and 2) are characterized by large fractured aquifers hosted by Meso-Cenozoic carbonate sequences (thrust sheets). These are often compartmentalized and sealed by low-

permeability clay- or evaporite-rich layers (aquicludes), such as syn-orogenic siliciclastic marine deposits or Messinian evaporites (Boni et al., 1986; Petitta et al., 2009). Fault zones with associated clay-rich gouge zones (Smeraglia et al., 2016, 2017) may also locally hinder groundwater flow and determine high hydraulic gradients, where karstic processes are limited. Nevertheless, their hydrogeological role can be different where the groundwater flow has the same direction of the faults; in this latter case, faults have a limited and local effect on hydrogeological setting.

The intermountain basins and the river valleys are filled with thick Plio-Pleistocene (mainly post-orogenic) continental deposits forming aquitards for the underlying carbonate aquifers (Boni et al., 1986; Petitta et al., 2009; Barberio et al., 2017). In the recharge areas of the carbonate aquifers, the infiltration is very high (up to 1,000 mm/a, 70–80% of rainfall) and is driven mostly by fractures and secondarily by dissolution features (Petitta et al., 2011, 2015; Barberio et al., 2017). In central Apennines, groundwater flow systems develop, in places, in hierarchical patterns. For instance, the Gran Sasso aquifer, which is one of the largest hydrogeological structure in central Apennines, shows a divergent groundwater flow from the aquifer core toward its boundaries, with a very clear vertical hierarchy (Worthington, 1991) affecting spring discharge and showing overflow and base flow with different proportionality related to decreasing altitudes. Most springs have very high discharge rates (0.5–1 m³/s on average, up to 18 m³/s) and steady regimes, especially on the study area, representing the final destination of the regional base flow (Boni et al., 1986; Petitta et al., 2009, 2011,

2015; Fiorillo et al., 2015; Barberio et al., 2017). The regional base flows are the main targets of this study.

The Sulmona area (Fig. 3) is located between the Gran Sasso and the Mt. Morrone carbonate aquifers. Regional groundwater flows converge to feed a few base-flow springs in the Sulmona plain with discharges between less than $0.01 \text{ m}^3/\text{s}$ and $>1 \text{ m}^3/\text{s}$. The carbonate aquifers host regional groundwater flow and feed springs located at ridge piedmonts that frequently correspond to active normal faults. The Mt. Morrone carbonate aquifer is confined by low-permeability layers isolating the carbonate deep aquifer from local shallow aquifers in the Sulmona plain. In this area, groundwater is mainly of the calcium bicarbonate type due to the carbonate dissolution, but it is occasionally mixed with deep sulphate-calcium-bicarbonate waters. This deep contribution is increased by active faults and related deep rock deformation (Miccadei et al., 1992; Salvati, 2002; Petitta et al., 2011, 2015; Desiderio et al., 2012; Fiorillo et al., 2015; Carucci et al., 2012; Barberio et al., 2017, 2018).

The Matese massif (Fig. 4) is an important carbonate aquifer formed by a Meso-Cenozoic (mainly Cretaceous) carbonate succession that is about 2,000 m thick. Syn-orogenic terrigenous Miocene deposits also crop out in the Matese area and are mostly located around the massif (Celico, 1978). The Matese massif is bounded at the edges by flysch deposits that come into contact with the massif itself through normal and thrust faults. The tectono-karstic depressions located in the central sector of the massif divide this unit into eastern and western sectors. Within these two tectonic-karstic sectors, numerous springs occur, such as the Bojano (about $4.6 \text{ m}^3/\text{s}$) and Grassano (about $4.7 \text{ m}^3/\text{s}$) springs (Celico, 1978). In this area, groundwater is mainly of the calcium bicarbonate type.

The Mt. Picentini (Fig. 4) are included in the Matese node and form a karstic system over an area of about 600 km^2 in the central Apennines. Outcropping rocks belong to a calcareous-dolomitic succession of the Trias-Miocene time and have a thickness of over 2,500 m, are very fractured and faulted, and are frequently reduced to fault breccia. These rocks are, in places, covered by pyroclastic deposits that have thicknesses from some decimeters to some meters and whose presence influences the infiltration processes in the karst substrate. The calcareous-dolomitic series is bordered by less permeable sequences consisting of clayey and flysch sequences (Ietto, 1965; ISPRA, 2009). Some main faults limit the groundwater flow, subdividing the karst system of the Mt. Picentini into various sub-units (Celico and Civita, 1976; Celico, 1978; Coppola et al., 1989).

4. Methods

Within the framework of the HydroQuakes project, we adopted a series of methods mainly aimed at hydrogeochemical monitoring for the identification of potential precursors to earthquakes. Our initial strategy was inspired by previous works on the same subject. In particular, since 2002, there has been a hydrogeochemical monitoring system in Húsa-vík, northern Iceland, which has the main aim of identifying potential precursors to earthquakes. This system presently consists of a monitoring borehole that is 100 m deep. Since 2002, significant hydrogeochemical changes have been identified before at least three large earthquakes ($M_w > 5.5$) occurred off northern Iceland in 2002, 2012, and 2013 (Claesson et al., 2004, 2007; Skelton et al., 2014, 2019; Andrn et al., 2016). We took advantage of this previous experience to develop our monitoring nodes for the HydroQuakes project.

In the HydroQuakes project, two main monitoring nodes (Matese and Sulmona; Fig. 2) and a total of eleven springs (six in the Matese node and five in the Sulmona node; Figs. 3 and 4 and Tables S1 and S2) have been selected and periodically (monthly) sampled. Some of these springs are continuously monitored through in-situ-installed probes (Tables S1 and S2, and Fig. S2). A borehole is also monitored through an in situ probe for the piezometric level, temperature, and electric conductivity (Tables S1 and S2), and not for the groundwater chemical composition.

The methods adopted for the HydroQuakes project are fully described in the Supplementary Material together with the used instruments and software (Tables S1 and Figs. S2 and S3) and the data (Tables S3–S12). As our main aim is methodological with some initial results shown to corroborate the method's relevance, in the Supplementary Material, we explain all methods used in the HydroQuakes project, although not all related results are addressed and interpreted in this paper. Moreover, as we have observed a high variability of element concentrations for the Telese Terme spring (Matese node; Table S1), likely due to the high mineralization of this spring and related seasonal variability, we do not discuss the data here that are nonetheless all reported in Tables S3–S6.

5. Results

5.1. Coefficients of variation

The coefficient of variation corresponds to the ratio between the standard deviation (σ) and the absolute value of the mean ($|\mu|$) of results from the physical-chemical measurements and analyses realized in situ and on the groundwater samples collected during the considered period. The coefficient of variation (Tables S8 and S9) can help identify the most variable elements (i.e. their concentrations in groundwater) and the related anomalous concentrations over the time series (e.g. Barberio et al., 2017). Obviously, an element's variability over time could depend on reasons different from the seismic ones, and the coefficient of variation alone cannot identify seismic precursors. For this reason, a time series of element concentrations must be studied in parallel with a time series of seismic data (see the following sections), and other causes of element concentration variability, such as pollution or seasonality, must be ruled out by proper studies and analyses (see the methodological section in Supplementary Material).

Figs. 5(a), S5, and S6 show that the coefficients of variation of the monitored springs are low (i.e. less than 0.6) for most elements, with the exception of B, which is characterized by coefficients of variation exceeding 0.8 in the springs of Rio Freddo and Caposele. To better understand these coefficients, we compared them (Fig. 5) with the coefficients of variation of the same attributes (i.e. the same elements, isotopes, and parameters) for the springs of the Sulmona area during the period January 2016–March 2017 (Fig. 5b; Barberio et al., 2017). During this latter period, the central Apennines were hit by a strong seismic sequence with two $M_w \geq 6.0$ earthquakes. The M_w 6.0 Amatrice and M_w 6.5 Norcia earthquakes occurred on August 24th, 2016 and October 30th, 2016, respectively (Tinti et al., 2016; Smeraglia et al., 2017).

In other words, with Fig. 5, we propose a comparison of chemical-physical variations of groundwater in the central Apennines between low seismicity (2017–2020; Fig. 5a) and high seismicity (2016–2017; Fig. 5b) times (“peacetime vs. wartime”). The coefficient of variation of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ is, in both cases, close to zero. In the high seismicity case (i.e. the Sulmona node during 2016–2017), the high variability of As, V, Cr, Fe, and B (Fig. 5b) was interpreted as being connected with pre- and co-seismic hydrogeochemical changes (Barberio et al., 2017; Boschetti et al., 2019). In contrast, in the low seismicity case (Matese and Sulmona nodes during 2017–2020), all parameters were characterized by markedly lower coefficients of variation (Fig. 5a), except for B, which as previously described reaches higher values (>0.8). This exception is addressed in the next sections.

5.2. Time series of chemical-physical parameters

Fig. 6 shows the values for the chemical-physical parameters (Table S4) measured during the monitoring time window (December 2017–January 2020) against the background seismicity of the area. No evident temporal correlations between background seismicity and the chemical-physical parameters occurred. The temporal variability of

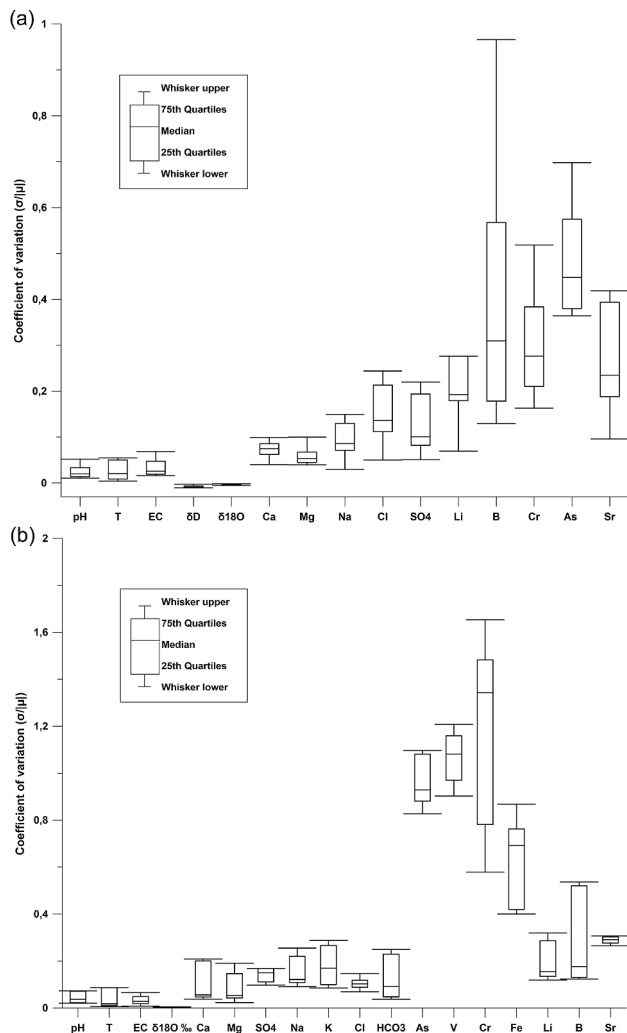


Fig. 5. (a) Coefficient of variation for selected chemical element concentrations and physical-chemical parameters measured in the Sulmona and Matese nodes between November 2017 and January 2020. (b) Coefficient variation for chemical element concentrations and physical-chemical parameters measured in the Sulmona area between January 2016 and March 2017 (Barberio et al., 2017).

these chemical-physical parameters is very limited, as demonstrated by the related statistical coefficients of variation (Figs. S5 and S6). Moreover, ~98% of the monthly values of the chemical-physical parameters did not exceed the $\pm 2\sigma$ value (i.e. twice the standard deviation) of the entire population (Tables S4, S10, and S11).

5.3. Time series of major chemical elements

Fig. 7 shows the time series of the selected major elements (i.e. their groundwater concentration) that are potentially relevant to the science of hydrogeochemical precursors (e.g. Claesson et al., 2004; Skelton et al., 2008, 2014, 2019; Inan et al., 2012). All the data is in Table S4. The groundwater concentrations of the major elements during the monitoring time window (December 2017–January 2020) are shown against the background seismicity of the area

Fig. 7 shows no evident temporal correlation between background seismicity and the major chemical elements. The temporal variability of all the major chemical elements is very limited, as demonstrated by the related statistical coefficients of variation (Figs. S5 and S6). Moreover, ~97% of the monthly values of the major element concentrations did not exceed the $\pm 2\sigma$ value of the entire population (Tables S5, S10, and

S11).

5.4. Time series of trace chemical elements

Fig. 8 shows the time series of the selected trace elements (i.e. their groundwater concentration) relevant to the science of hydrogeochemical precursors (e.g. Claesson et al., 2004; Skelton et al., 2008; Barberio et al., 2017). All the analyzed trace elements are reported in Table S6. Trace elements are shown during the monitoring time window (December 2017–January 2020) against the background seismicity of the area. Fig. 8 shows no evident temporal correlation between background seismicity and the trace element concentrations, except for a weak increase in B concentration before the Collelongo earthquake. Except for B and As, the temporal variability of the trace chemical elements is very limited, as demonstrated by the statistical coefficients of variation (Figs. S5 and S6). Moreover, ~98% of the monthly values of the trace element concentrations did not exceed the $\pm 2\sigma$ value of the entire population (Tables S6, S10, and S11).

5.5. Isotopes of H_2O (δ^2H and $\delta^{18}O$)

Fig. 9 shows the values of $\delta^2H_{H_2O}$ and $\delta^{18}O_{H_2O}$ during the monitoring time window (December 2017–January 2020) against the background seismicity of the area. No evident temporal correlation between background seismicity and the isotopes of H_2O is shown. The temporal variability of δ^2H and $\delta^{18}O$ is close to zero, as demonstrated by the related statistical coefficients of variation (Figs. S5 and S6).

5.6. Isotopes of B and Sr ($\delta^{11}B$ and $^{87}Sr/^{86}Sr$)

As the Mw 4.1 Collelongo earthquake occurred on a large fault (i.e. capable of Mw 7.0 earthquakes; see the geological and seismotectonic setting section for further details) at deep levels in the crust (i.e. earthquake hypocenter at ~17 km depth), we studied the role and behavior of B and Sr and the related isotopes in pre- and post-seismic times, as done previously for the 2016 Mw 6.0 Amatrice earthquake in the central Apennines (Boschetti et al., 2019). Therefore, following the principles and results presented in Boschetti et al. (2019), we analyzed the B and Sr isotopes ($\delta^{11}B$ and $^{87}Sr/^{86}Sr$) in the groundwater samples collected immediately before and after the Collelongo earthquake that occurred on January 1st, 2019. We performed these isotope analyses on samples from the Grassano and Decontra springs as these springs showed a variability in the concentrations of the analyzed elements (B and Sr), particularly B. Fig. 10 shows a slight decrease in $\delta^{11}B$ before the earthquake and a subsequent increase after the seismic event (Fig. 10a), while $^{87}Sr/^{86}Sr$ did not significantly change prior to the seismic event or after it (Fig. 10b).

6. Discussion

6.1. General noncorrelation between hydrogeochemistry and low seismicity

During the two years of monitoring, we recorded the background values of the groundwater from the springs monitored in the HydroQuakes project. Except for the hydrothermal Telesse Terme spring, all monitored springs showed mostly stable values during the year, with most of the elemental concentrations within the $\pm 2\sigma$ interval (Figs. 6–8 and Tables S4–S7). This evidence confirms that the groundwater of the two nodes is characterized by a negligible influence from seasonal recharge water and from its interaction with surface waters (Barberio et al., 2017; Fiorillo et al., 2019).

Therefore, the two nodes of the HydroQuakes project were appropriately chosen from a hydrogeochemical point of view as the related springs are characterized by stable background regimes, over which the possible anomalies connected with transient phenomena like

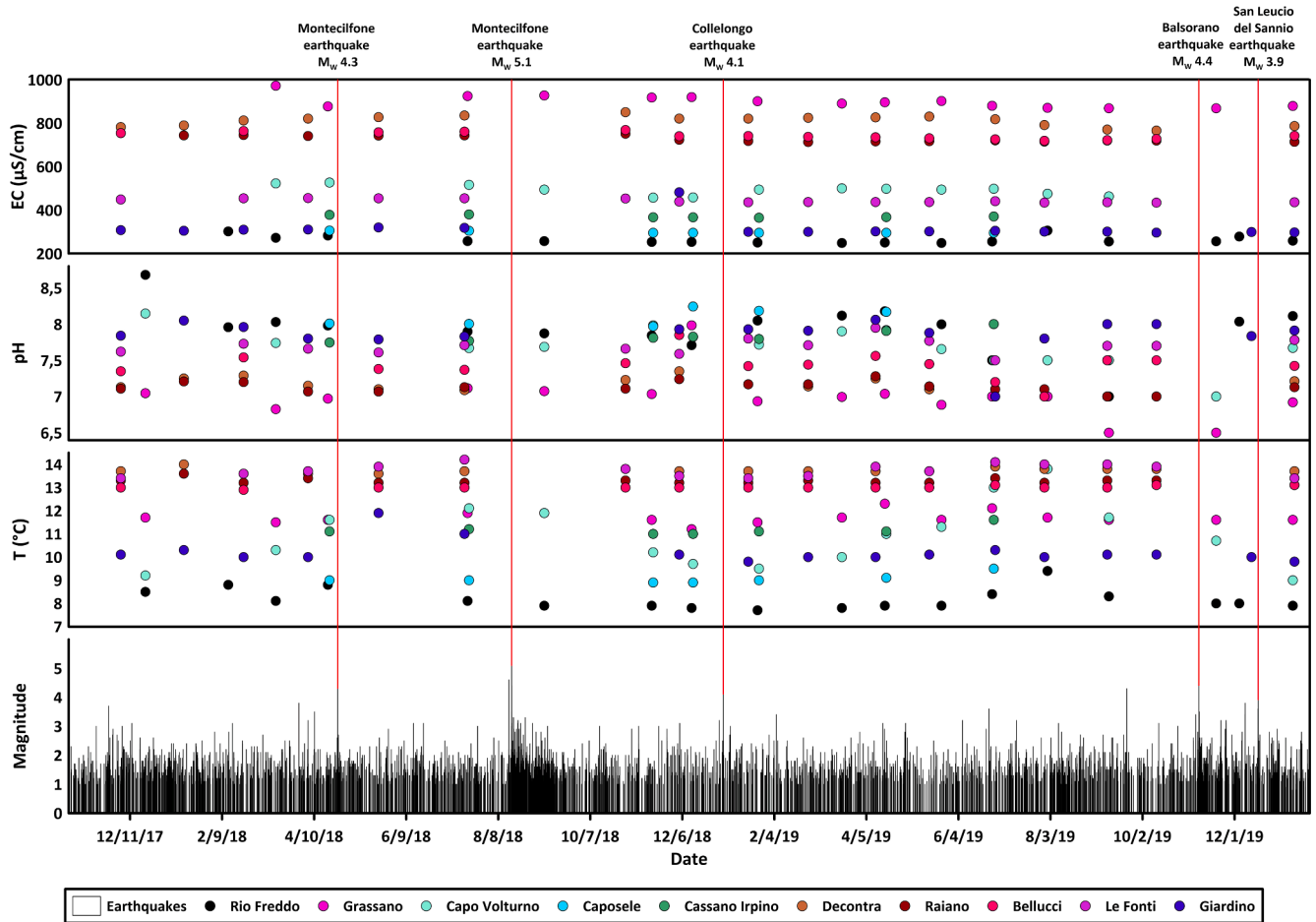


Fig. 6. Time series of chemical-physical parameters and earthquake magnitude (November 1st, 2017–January 31st, 2020). Each plot includes chemical-physical parameters from the Sulmona and Matese nodes (Table S4). Seismic data are from the INGV database (available online at <http://terremoti.ingv.it>).

earthquakes could be easily identifiable (e.g. Skelton et al., 2008; Barberio et al., 2017). Moreover, the values of the isotopes of the water molecule (Fig. 9) were stable over time, as can also be observed in Fig. 5 (a), where the variation coefficients of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$ are close to zero. This indicates that the recharge area of the monitored springs did not change during the two years of monitoring and that the groundwater flow was not affected by seasonal isotope change in recharge. This additional evidence supports the hydrogeochemical stability of the selected springs.

Our time series show that the earthquakes that occurred in the study area were not substantially preceded by hydrogeochemical anomalies. Indeed, as mentioned above, most of the elemental concentrations fell within the $\pm 2\sigma$ interval (Figs. 6–8 and Tables S4–S7) and have low coefficients of variation (Fig. 5a and Tables S8 and S9). The substantial lack of pre-seismic anomalies during the study period is consistent with the fact that these anomalies can arise only with medium and strong earthquakes ($M_w \geq 5.0$). This notion aligns well with previous studies carried out in various seismic areas around the world. Indeed, all the hydrogeochemical seismic precursors that have been recognized so far have been substantially recorded for earthquakes with $M_w \geq 5.0$ (Igarashi et al., 1995; Tsunogai and Wakita, 1995; Claesson et al., 2004, 2007; Inan et al., 2012; Skelton et al., 2014, 2019; Barberio et al., 2017; Boschetti et al., 2019).

This result, if further validated by future hydrogeochemical and seismic observations, may indirectly corroborate the suitability and usefulness of the hydrogeochemical precursors of earthquakes. If such precursors were, in fact, common even for low intensity earthquakes ($M_w \leq 4.0$), then their usefulness would be greatly reduced. In the next

section, we discuss a possible exception to this behavior that, for its peculiar tectonic setting (i.e. dimensions of the causative fault and depth of the earthquake hypocenter), may indirectly confirm what we discussed above.

6.2. The case of the Collelongo Earthquake: Boron as a potential seismic precursor

In November 2018, at both the Grassano and Deontra springs, we recorded an increase in B concentration and a corresponding slight decrease in the $\delta^{11}\text{B}$ value at Grassano (Fig. 10a). The following month, the concentration of B began to decrease again, returning to the pre-earthquake value immediately after the seismic event, whereas the $\delta^{11}\text{B}$ showed a slight increase, once again more evident at Grassano spring. These results show that the increase in the concentration of B was simultaneous with the decrease of the $\delta^{11}\text{B}$ isotope before the seismic event, as previously observed in the Sulmona area prior to the 2016–2017 Amatrice-Norcia seismic sequence with two $M_w \geq 6.0$ mainshocks (Barberio et al., 2017; Boschetti et al., 2019).

Boschetti et al. (2019) showed that the B and $\delta^{11}\text{B}$ opposite trends were due to the desorption of B from mineral surfaces such as clays (e.g. Barth, 1997; Négrel et al., 2009) at deep crustal levels during pre-seismic dilation phases, when CO_2 -rich fluids ascend and interact with the surrounding rocks. The opposite B and $\delta^{11}\text{B}$ concentration trends were particularly evident in the Grassano spring (rather than in the Deontra spring), where a marked pre-seismic increase of B concentration was observed (Fig. 10a).

Our explanation for the pre-seismic trends of B and $\delta^{11}\text{B}$ (Fig. 10a) is

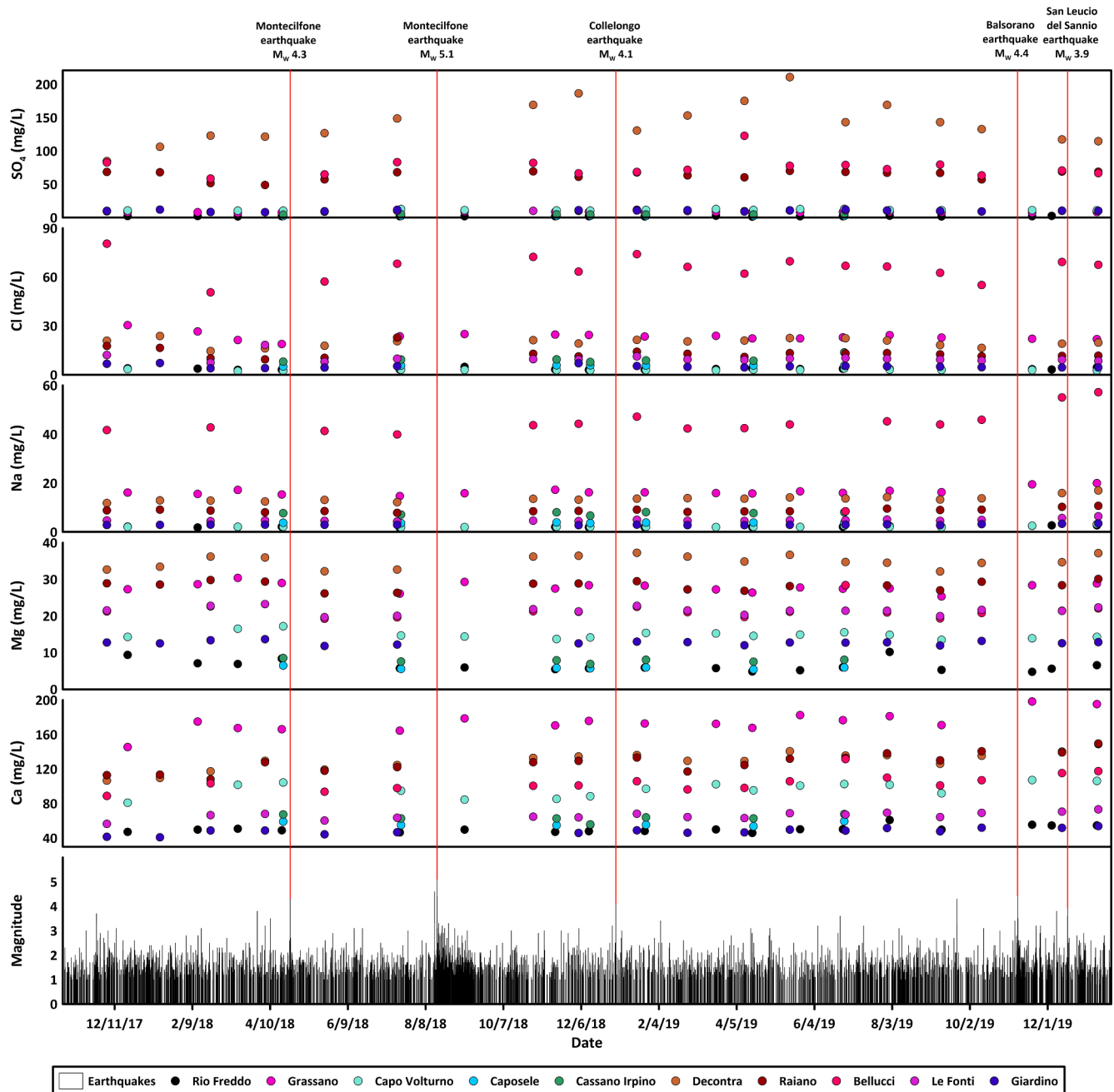


Fig. 7. Time series of major elements concentration (mg/L) and earthquake magnitude (November 1st, 2017–January 31st, 2020). Each plot includes geochemical data from the Sulmona and Matese nodes (Table S5). Seismic data are from the INGV database (available online at <http://terremoti.ingv.it>).

in line with those of Barberio et al. (2017) and Boschetti et al. (2019). These trends are likely linked to the pre-seismic dilation, which led to the release of deep CO_2 and its partial dissolution in the circulating groundwater (Boschetti et al., 2019; Barbieri et al., 2020; see also Chiodini et al., 2011). In turn, the adsorbed CO_2 could have allowed the desorption of trace elements like B from minerals and substances present in the Apennine subsurface, including clays (Boschetti et al., 2019).

In contrast to the general conclusion of previous papers (e.g. Igarashi et al., 1995; Tsunogai and Wakita, 1995; Claesson et al., 2004, 2007; Inan et al., 2012; Skelton et al., 2014, 2019; Barberio et al., 2017), this process was activated by an earthquake with low magnitude (Collelongo earthquake, Mw 4.1). This earthquake is a particular case, however, as it occurred on a very large Apennine fault (the fault that generated the 1915 Mw 7.0 Avezzano earthquake) at depths of about 17 km (Cavinato and Parotto, 2019). Therefore, we believe that, although the coseismic

rupture was rather small and weakly energetic (Mw 4.1), the pre-seismic dilation phase may have activated and released deep fluids, including CO_2 . This consequently led to the aforementioned desorption process, which ultimately caused B and $\delta^{11}\text{B}$ variations in the waters of the Deontra and Grassano springs two months before the earthquake.

The large size of the causative fault where the low magnitude earthquake occurred and its deep hypocenter (17 km deep) supports our hypothesis of a pre-seismic deep fluid upward mobilization. This hypothesis is also corroborated by the detection of B variations in both nodes (Matese and Sulmona) of the HydroQuakes project, which are about 75 km distant. Moreover, this result suggests that B may be one of the most sensitive hydrogeochemical precursors of earthquakes, at least in the central Apennines (Boschetti et al., 2019).

Taking into account the external reproducibility of isotope analyses ($\pm 2\sigma$), the results obtained for both $\delta^{11}\text{B}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ before and after

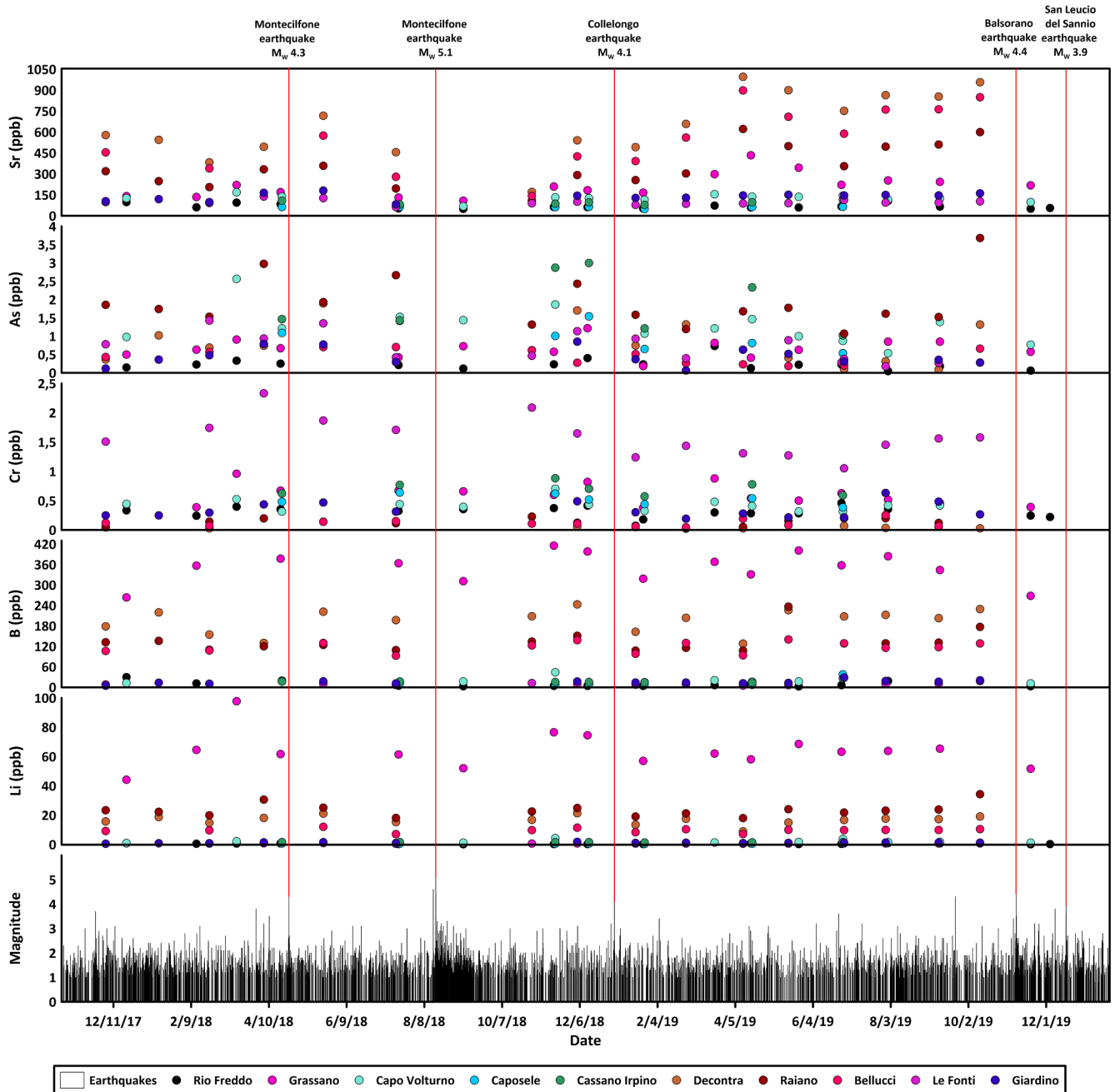


Fig. 8. Time series of trace elements concentration and earthquake magnitude (November 1st, 2017–January 31st, 2020). Each plot includes geochemical data from the Sulmona and Matese nodes (Table S6). Seismic data are from the INGV database (available online at <http://terremoti.ingv.it>).

the Collelongo earthquake showed negligible differences (Fig. 10b). However, it should be noted that boron isotope values are lower than expected for interaction with a Mesozoic carbonate/evaporite aquifer (Fig. 10). Despite a marked decrease in Sr concentration occurred at Decontra prior to the seismic phase, the isotopic signature of Sr prior to and during the coseismic phase of the Collelongo earthquake remained substantially unaltered and with a path similar to Grassano spring. Therefore, the fluid circuit did not change, but there may have been a change in the degree of water–rock interaction, probably as consequence of an increase in the deep CO_2 influx (e.g., Miller et al., 2004; Barbieri et al., 2020; Chiodini et al., 2011, 2020; Martinelli et al., 2020).

Thermodynamic and B isotopic calculations (see Supplementary Material) help us understand the plausible geochemical processes behind the observed pre-seismic B and $\delta^{11}\text{B}$ changes. Scatterplots of Fig. 11(a) and 11(b) show $\delta^{11}\text{B}$ values against B concentrations and

temperature at a depth inferred by Na/Li molar ratio (Sanjuan et al., 2014; Barbieri et al., 2020), respectively. These plots reveal that, in the water samples of this study, these variables are controlled by different processes. It should be also noted that the least square fittings are statistically significant (Fig. 11a and b), and the regression extrapolation points towards high B concentration/ ^{11}B -depleted water samples interacting with silicates (Battistel, 2014; Paternoster, 2019).

Furthermore, B concentration at the sample sites shows a general increase with the C_{ext} parameter, i.e. the deep source of inorganic CO_2 (Barbieri et al., 2020; Table S12). This evidence agrees with the well-known contribution of deep crustal fluids in the spring waters of central Italy located in seismically active areas (Chiodini et al., 1999, 2011, 2020; Collettini et al., 2008; Barbieri et al., 2020). The $\delta^{11}\text{B}$ values of meteoric water circulating in carbonate–evaporite formations of marine origin would be similar to the range of the latter, i.e. +18.2‰

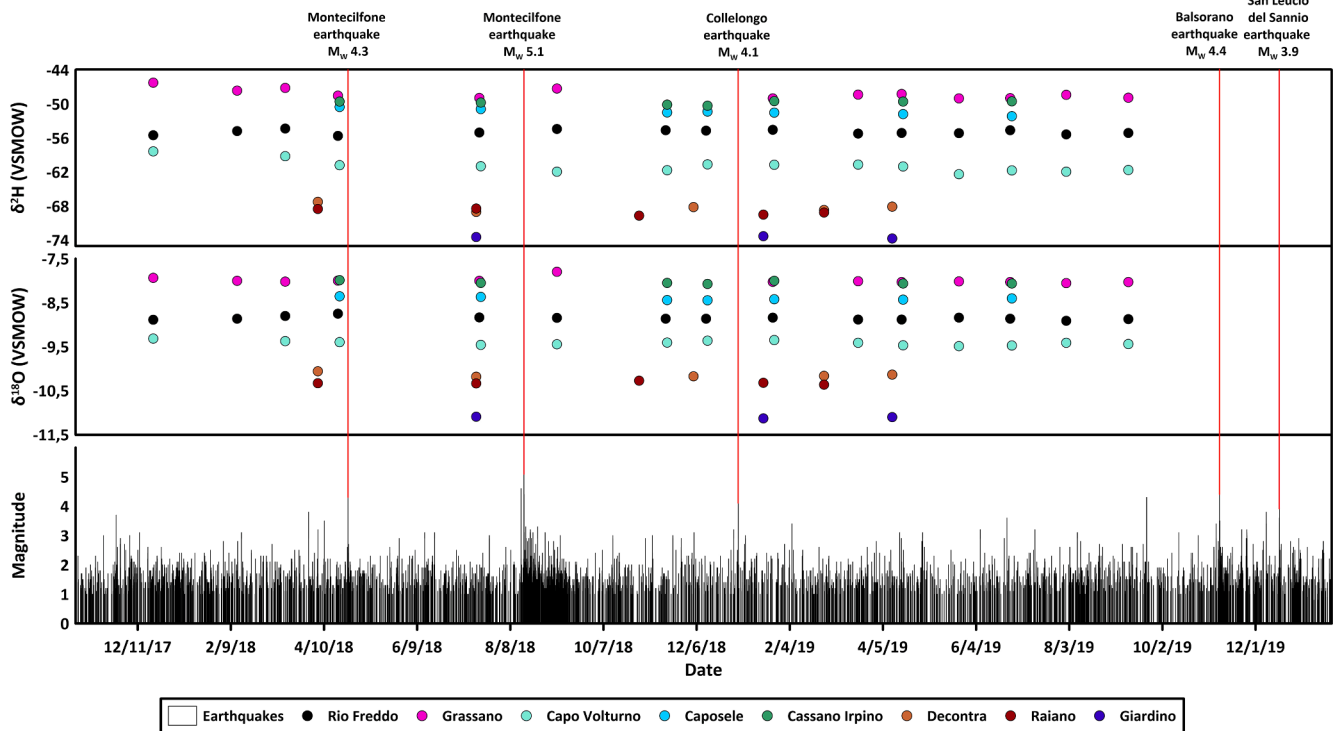


Fig. 9. Time series of $\delta^{18}\text{O}$, δD , and earthquake magnitude (November 1st, 2017–January 31st, 2020). Each plot includes $\delta^{18}\text{O}$ and δD from the Sulmona and Matese nodes (Table S7). Seismic data are from the INGV database (available online at <http://terremoti.ingv.it>).

to $+31.7\%$ (e.g. Swihart et al., 1986; Paris et al., 2010). Lower and lower $\delta^{11}\text{B}$ values, as represented in Fig. 11(b), could indicate the additional contribution of B from different processes, such as adsorption/desorption at low temperatures (Pennisi et al., 2006; Lemarchand et al., 2015; Boschetti et al., 2019) or interaction with ^{11}B -depleted silicates at high temperatures (Fig. 11b).

Locally, Miocene limestone values of $+5.67 \pm 0.44\%$ for $\delta^{11}\text{B}$ were also detected in the studied area (e.g. Majella Massif, Tonarini et al., 2003). These values are very similar to the groundwater values detected in this study; however, the almost constant Sr isotope ratio detected in the springs (Fig. 10b) seems to confirm that groundwater flow occurred mainly within the Mesozoic evaporite formations of the Apennines, i.e. $^{87}\text{Sr}/^{86}\text{Sr} = 0.7078 \pm 0.0001$ (Boschetti et al., 2005); however, values up to 0.7091 ± 0.0008 were detected in shallow groundwater and surface waters interacting with Mesozoic carbonates (Boschetti et al., 2005; Nisi et al., 2008). $\delta^{11}\text{B}$ values of $8.4 \pm 1.1\%$ and $^{87}\text{Sr}/^{86}\text{Sr} = 0.70804 \pm 0.00002$ were reported for three groundwaters flowing in Mesozoic carbonate in the Venturina system (Tuscany; Pennisi et al., 2006). Moreover, in groundwater with a normal pH range of $6.5 \div 8.5$ and dominated by exchange reactions, the range of measured $\delta^{11}\text{B}$ is explained by a solid–liquid fractionation factor of approximately $12 \div 15\%$ (Gaillardet and Lemarchand, 2017; Saldi et al., 2018). Therefore, it cannot be excluded that the dissolved B in the studied waters may derive not only from clays (Boschetti et al., 2019), but also from desorption of previously precipitated inorganic carbonates with $\delta^{11}\text{B}$ values in the range of the marine ones (e.g. Paris et al., 2010).

The regression analysis and sample distribution in Fig. 11(b) also indicates that B in the water samples is potentially controlled by temperature. A regression analysis of B concentration versus temperature inferred by the Na–Li geothermometer and extended to all the samples is shown in Table S12.

At higher temperatures, the deep magmatic/metamorphic fluid contribution becomes more and more important. As demonstrated in our previous study (Barbieri et al., 2020), water from the Cotilia Spa spring (San Vittorino plain, central Apennines, Lat. $42^\circ 22' 36.35''\text{N}$ Long

$12^\circ 59' 52.55''\text{E}$) is a potential CO_2 -rich deep fluid end-member of central Italy (for the chemical-physical parameters of the Cotilia Spa spring see Barbieri et al., 2017; Civita and Fiorucci, 2010). On that site, the temperature inferred by $\Delta^{13}\text{C}(\text{CO}_2\text{--CH}_4)$ fractionation factors is 403°C (Beaudoin and Therrien, 2009; Giustini et al., 2013; Fig. 11b). By considering this temperature value and $\delta^{11}\text{B} = -2.65\%$ as measured in this study, the Cotilia Spa sample falls just between the composition of deep tourmaline-equilibrated fluids at 300°C and 600°C (Tonarini et al., 1998; Fig. 11b). In the central Apennines, the temperature values detected or inferred from deep borehole fluids are generally between 120°C and 350°C (Zuppi et al., 1974; Chiodini and Cioni, 1989; Governa et al., 1989; Collettini et al., 2008). Therefore, the temperature inferred by boron and carbon isotope fractionation factors could be considered as the highest one, compatible with those fixed for equilibria reactions in a metamorphic environment (Collettini et al., 2008). The linear regression between the $\delta^{11}\text{B}$ and Na/Li geothermometric temperature values calculated for the monthly monitored samples along with the water sample from Cotilia Spa is statistically significant (Fig. 11b). Moreover, the regression slope is comparable with that of the theoretical composition of waters at different temperatures derived from the $\Delta^{11}\text{B}$ (silicates–fluids) fractionation factor (Gaillardet and Lemarchand, 2017). At lower temperatures and shallow depths, clay–water adsorption/desorption (if any) could occur, too. Most probably, as testified in our previous study (Boschetti et al., 2019), this effect could be plausibly more pronounced and relevant at higher magnitude seismic events, during or prior to which CO_2 migration could trigger the desorption of more B and other elements such as As and V (Barbieri et al., 2017).

7. Conclusions

Consistent with previous recent works on hydrogeochemical precursors, the HydroQuakes project's data and results confirm that hydrogeochemical anomalies prior to earthquakes are to be expected mainly for $M_w \geq 5.0$ events. An important exception to this notion is,

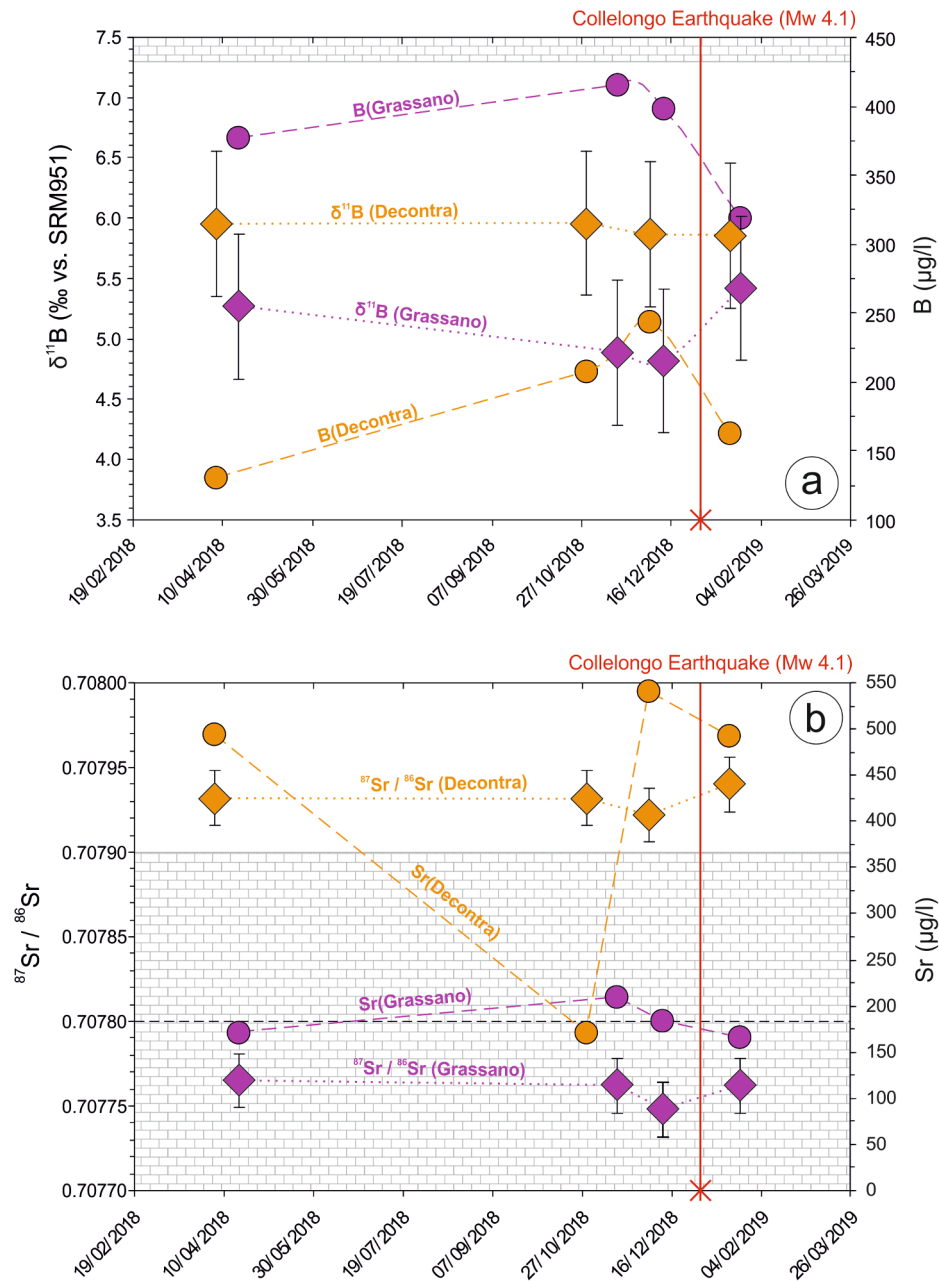


Fig. 10. (a) Short time series (before and after the Collelongo earthquake) of boron concentration and its isotope ratio $\delta^{11}\text{B}$ in Grassano and Deontra springs. (b) Short time series (before and after the Collelongo earthquake) of strontium concentration and isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) in Grassano and Deontra springs. In both diagrams, bricked field depicts the Mesozoic isotope ratio: $^{87}\text{Sr}/^{86}\text{Sr} = 0.7078 \pm 0.0001$ (Boschetti et al., 2005); $\delta^{11}\text{B}$ values of $+8.4 \pm 1.1\text{‰}$ (Pennisi et al., 2006).

however, the 2019 Mw 4.1 Collelongo earthquake. As this earthquake mobilized a large fault (capable of generating Mw 7.0 earthquakes) and occurred at deep crustal levels (~ 17 km), CO_2 -rich deep fluids must have ascended for two months prior to the earthquake (pre-seismic dilatancy), desorbing from host rocks and upward mobilizing B that was detected at the HydroQuakes project springs. In particular, the pre-seismic B variations in both nodes of the HydroQuakes project (Deontra and Grassano springs) and during a previous experience in the Sulmona node (prior to the 2016–2017 seismic crisis of the central Apennines) corroborate the validity and particular hydro-seismo-sensitivity of B and $\delta^{11}\text{B}$ as seismic precursors, at least in the central Apennines.

Most probably, this effect would be plausibly more pronounced and relevant prior to higher magnitude seismic events, during which external (deep) CO_2 migration could trigger the desorption of more B

and other elements, such as As and V. This agrees with previously published models, which have demonstrated the contribution of pre-seismic deep CO_2 -bearing crustal fluids in the study area, and is also indicated in this work by the significant relationship between the deep external carbon source (C_{ext}) and B concentration between all investigated samples (Table S11). These conclusions highlight the relevance of building and operating hydrogeochemical monitoring networks over long periods and large areas to the understanding of seismic precursors. This relevance, in our work, is well shown by the quasi-simultaneous occurrence (or absence) of the same potential precursors (i.e. B anomalies) at two monitoring nodes that are about 75 km distant in a seismic region. We believe, in other words, that operating an hydrogeochemical monitoring network would be fundamental to contribute to the solution of the main problems faced by the science of hydrogeochemical precursors of earthquakes, namely: earthquake size (is there an earthquake

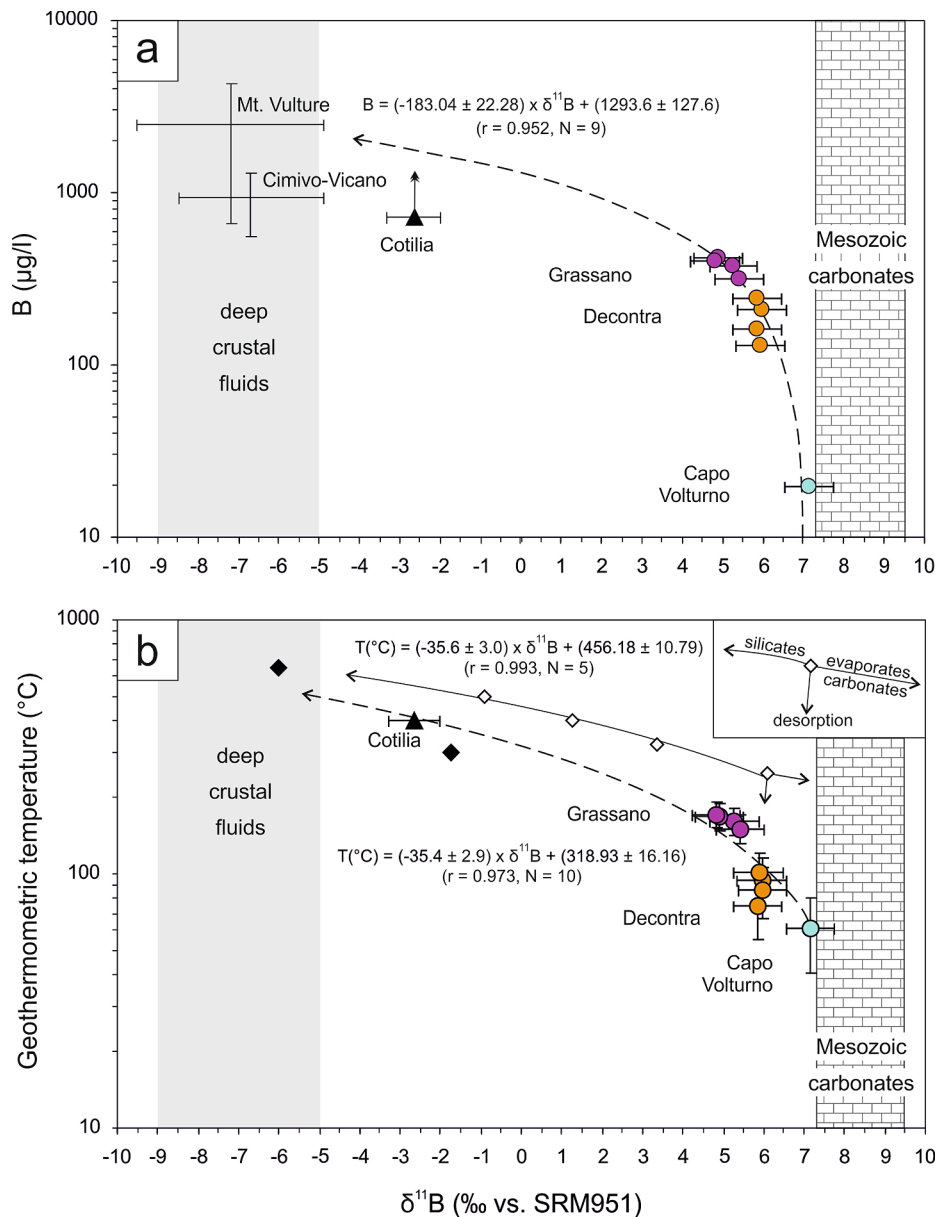


Fig. 11. Boron isotope composition $\delta^{11}\text{B}$ vs. boron concentration (a) and geothermometrically-inferred temperature (b). Coloured symbols are as in previous figures (pink = Grassano Spring; orange = Deontra Spring; and turquoise = Capo Volturmo Spring). The black triangle is Cotilia Thermal Spa sample, $\sim 700\text{--}1400\text{ }\mu\text{g/l}$ of B during 2018–2019, vertical arrow in (a). In (b), closed diamonds are for the composition of tourmaline-equilibrated fluids (Tonarini et al., 1998), whereas open diamonds are for the silicate-fluids equilibria inferred by the global $\Delta^{11}\text{B}$ (silicates-fluids) fractionation factor (Gaillardet and Lemarchand, 2017) and supposing $\delta^{11}\text{B}_{\text{silicates}} = -9\text{‰}$. Mesozoic limestone (bricked field; Pennisi et al., 2006) and crustal fluids derived from the interaction with Apennine silicates (gray field; D’Orazio et al., 2007; Tonarini et al., 2009) are shown in both diagrams as comparison. Statistical significance of regression analyses were verified by ANOVA (slopes are significantly different from zero at the 0.05 level) and Table of Critical Values for Pearson’s r correlation coefficient from N parameter (Two-Tailed Test).

magnitude threshold for the manifestation of potential precursors?); timing (how long before the earthquakes do the precursors manifest themselves?); distance (at what distance from the epicenter do the precursors manifest themselves?); and site-specificity (how specific to the region are these precursors?). These questions will keep directing future monitoring and research in our study areas and elsewhere in seismic domains.

CRediT authorship contribution statement

Stefania Franchini: Formal analysis, Investigation, Validation, Data curation, Visualization, Writing - review & editing. **Samuele Agostini:** Methodology, Data curation, Resources, Writing - review & editing. **Marino Domenico Barberio:** Visualization, Investigation, Formal analysis, Data curation, Writing - review & editing. **Maurizio Barbieri:** Conceptualization, Methodology, Validation, Resources, Supervision, Funding acquisition, Writing - review & editing. **Andrea Billi:** Conceptualization, Validation, Supervision, Project administration, Funding acquisition, Writing - review & editing. **Tiziano Boschetti:** Methodology, Software, Data curation, Validation, Writing - review &

editing. **Maddalena Pennisi:** Methodology, Data curation, Resources, Writing - review & editing. **Marco Petitta:** Conceptualization, Methodology, Validation, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jhydrol.2020.125754>.

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Micro- to nano-scale structural and geochemical evidence of fluid-assisted coseismic slip along the seismogenic carbonate-hosted Mt. Morrone Fault, Italy: implications for earthquake hydrogeochemical precursors

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Abstract

Fluids play an important role in seismic faulting both at hypocentral depths during earthquake nucleation and at shallower crustal levels during rupture propagation. Pre- to co-seismic anomalies of crustal fluid circulation have been identified by hydrogeochemical and seismological monitoring and interpreted as potential precursors of strong earthquakes. To shed light on the role of fluids in seismic and precursory mechanisms, the active carbonate-hosted principal slip zone (7-8 cm thick) of the exhumed (exhumation < 3 km) normal Mt. Morrone Fault (central Apennines) has been investigated with a multi-disciplinary approach from the macro- to the nano-scale. The distal slip zone consists of white cementitious calcite-rich bands and red cataclastic bands composed of dolomite and calcite clasts embedded in a clay-rich matrix. The proximal slip zone consists of subparallel ultracataclastic layers separated by sharp slip surfaces. The ultracataclastic layers mutually inject/overprint, bearing evidence of granular fluidization, dolomite thermal decomposition, and clay amorphization. Fluid inclusions and the distribution of both trace and major elements reveal the inflow of both shallow and deep external fluids into the slip zone. Presumably, the deep fluids originated from a magmatic-like source and ascended along the fault during pre-seismic dilation and seismic ruptures, interacting with shallow phyllosilicate-rich flysch deposits and the fluids hosted within them. In this context, vanadium-rich fluidized microlayers along the exhumed Mt. Morrone Fault are reminiscent of vanadium-rich potential hydrogeochemical precursors arose in the shallow aquifers of the study area since a few months before the 2016 M_w 6.0 Amatrice earthquake.

1. Introduction

Fluids play fundamental roles in many stages of the seismic cycle and can be actively or passively involved in earthquake dynamics (Sibson et al., 1975; Chiodini et al., 2020). Understanding fluid-rock interaction during the seismic cycle is, therefore, of paramount importance to understand the seismic source and related mechanisms. Since active seismic sources are commonly inaccessible

at hypocentral depths, the study of exhumed (paleo)sources can be useful to understand those textural, mineralogical, and geochemical features that were witnesses of fluid circulation at hypocentral or shallower depths along coseismic ruptures ([Smeraglia et al., 2018](#); [Ohl et al., 2020](#)).

Studies of fossil instances of fluid-assisted faulting contribute to address the pivotal issue of whether fluids can be considered as potential earthquake precursors ([Skelton et al., 2014](#)). There is indeed evidence of the variation of the seismic wave velocities (V_p/V_s ratio) due to fluids that drain toward the pre-seismically dilated rocks ([Scholz et al., 1973](#)). For a set of recent $M_w > 5.5$ extensional earthquakes in the Apennines (Italy), large volumes of incoming pressurized fluids at the base of the seismogenic crust and related V_p/V_s anomalies were documented prior to the mainshocks ([Chiarabba et al., 2020](#); see also [De Luca et al., 2018](#)), thereafter inducing a dramatic post-seismic groundwater discharge ([Petitta et al., 2018](#)). Such pre-seismic deep crustal dilatancy and related injecting fluids were also at the origin of pre-seismic (since 4-5 months before the mainshock) geochemical anomalies in spring waters before the 2016 M_w 6.0 Amatrice earthquake in central Italy ([Barberio et al., 2017](#); [Boschetti et al., 2019](#)) and probably at the origin of peaks in the deep CO_2 flux observed in periods of high seismicity and subsequent decays in post-seismic periods during the last ten years in the Apennines ([Barbieri et al., 2020](#); [Chiodini et al., 2020](#)).

We present results from a study of an exhumed carbonate-hosted seismically active normal fault (Mt. Morrone Fault; [Figs. 1 and 2](#)) in the central Apennines, Italy. We adopted a multi-disciplinary approach to characterize the meso- to nano-scale structures observed within the principal slip zone (7-8 cm thick) of the Mt. Morrone Fault, resulting in unique data on the macro- to nano-scale processes of fluid-assisted normal faulting over co- or near-seismic time windows. As the Mt. Morrone Fault is located alongside the springs that recorded the aforementioned pre-seismic hydrogeochemical anomalies ([Barberio et al., 2017](#); [Chiodini et al., 2020](#)), our results contribute to shed light on potential precursors of earthquakes as similarly done in Iceland ([Skelton et al., 2014](#); [Andr n et al., 2016](#)).

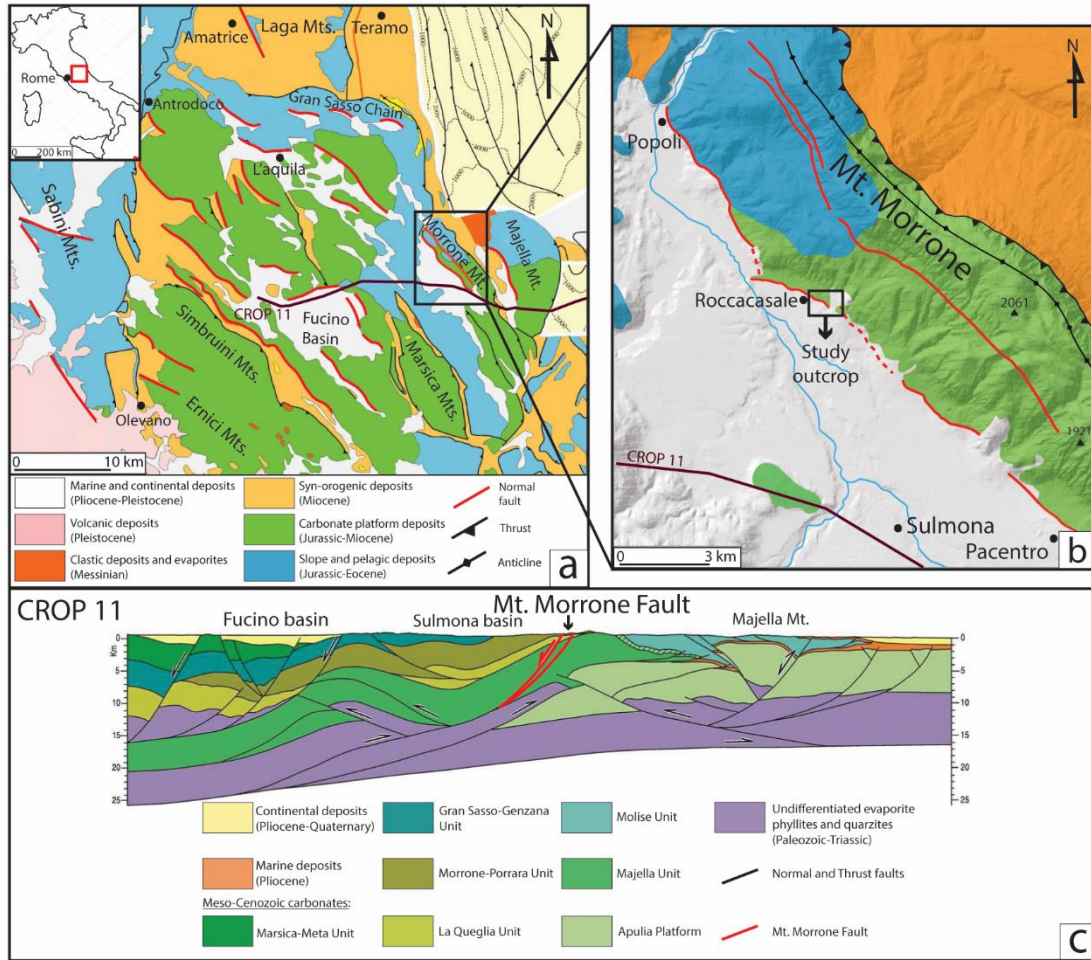


Figure 1. (a) Simplified geological and structural map of the central Apennine fold-thrust belt (modified after Cosentino et al., 2010) and track of the CROP 11 deep seismic reflection profile. The map shows main thrusts that are NW-SE-striking and juxtapose the Triassic-Miocene carbonate platform deposits and slope-to-basin deposits onto the Miocene syn-orogenic flysch deposits. Main post-orogenic normal faults (including the Mt. Morrone Fault) and main intermontane basins filled by Pliocene-Pleistocene continental deposits are also shown. (b) Simplified structural map of the Mt. Morrone area. On the eastern flank of the Mt. Morrone, the carbonate succession is folded to form a thrust-related NE-verging anticline. On the western flank, a ~23-km long system of NW-SE-striking normal faults borders the Sulmona basin. The fault system is named Mt. Morrone Fault in this work and consists of a set of sub-parallel segments. Dashes along red normal faults indicate fault hangingwall. The study outcrop (Mt. Morrone Fault) occurs at Lat. 42° 07'14.63''N, Long. 13°53'35.49''E, and elevation of 480 m a.s.l. (c) Interpretation of the CROP 11 deep seismic reflection profile (modified from Patacca et al., 2008). Two main segments of the Mt Morrone normal fault system are in red. These segments are exposed along the Mt. Morrone flank and cut across the crust down to about 12 km.

2. Geological setting

The central Apennines (Fig. 1a) are a NW-SE-trending fold-thrust belt, which has developed since the late Oligocene as a result of the westward subduction of the Adria microplate underneath the Eurasian plate. The belt mostly consists of northeastward-verging imbricate thrust sheets dominated by Meso-Cenozoic carbonate successions overriding onto Miocene–Pliocene syntectonic (flysch) clastic clay-rich sediments deposited in foreland or piggy-back basins (Patacca et al., 2008; Cosentino et al., 2010). The Apennine belt has experienced post-orogenic eastward-migrating extension that started in the inner sector (west) of the Apennines from about the Messinian, associated with the opening of the Tyrrhenian back-arc basin (Cosentino et al., 2010). The recent extensional regime is testified by a NW-SE-oriented normal fault system that have dissected the Apennine belt, forming large intermontane basins where Pliocene-Quaternary marine and continental clastic sediments have been deposited (Fig 1a).

The Mt. Morrone Fault is a post-orogenic seismically active normal fault in the central Apennines. The fault is a NW-SE-striking segmented en-échelon structure that is collectively ~23 km long. This fault borders, to the east, the Sulmona basin, which is one of the most recent and external (eastern) intermontane extensional structures of the central Apennines (Figs. 1a, 1b). The Mt. Morrone Fault extends downward to about 12 km into the crust (Patacca et al., 2008) and includes two main parallel branches (Fig. 1c), characterized by a total stratigraphic vertical offset ≥ 400 m, probably up to 1000 m or even more (Ghisetti and Vezzani, 2000; Patacca et al., 2008; Ferraro et al., 2018).

This study focuses on a ~25 m long segment of the principal slip surface (Mt. Morrone Fault), which is hosted in the Jurassic Palaeodasycladus Limestone Fm. (including limestone and dolostone) and is exposed near the village of Roccacasale (Figs. 1b and 2a). This fault segment, which was previously studied (Ferraro et al., 2018, 2019), was exhumed from a depth < 3 km (Ghisetti and Vezzani, 2000).

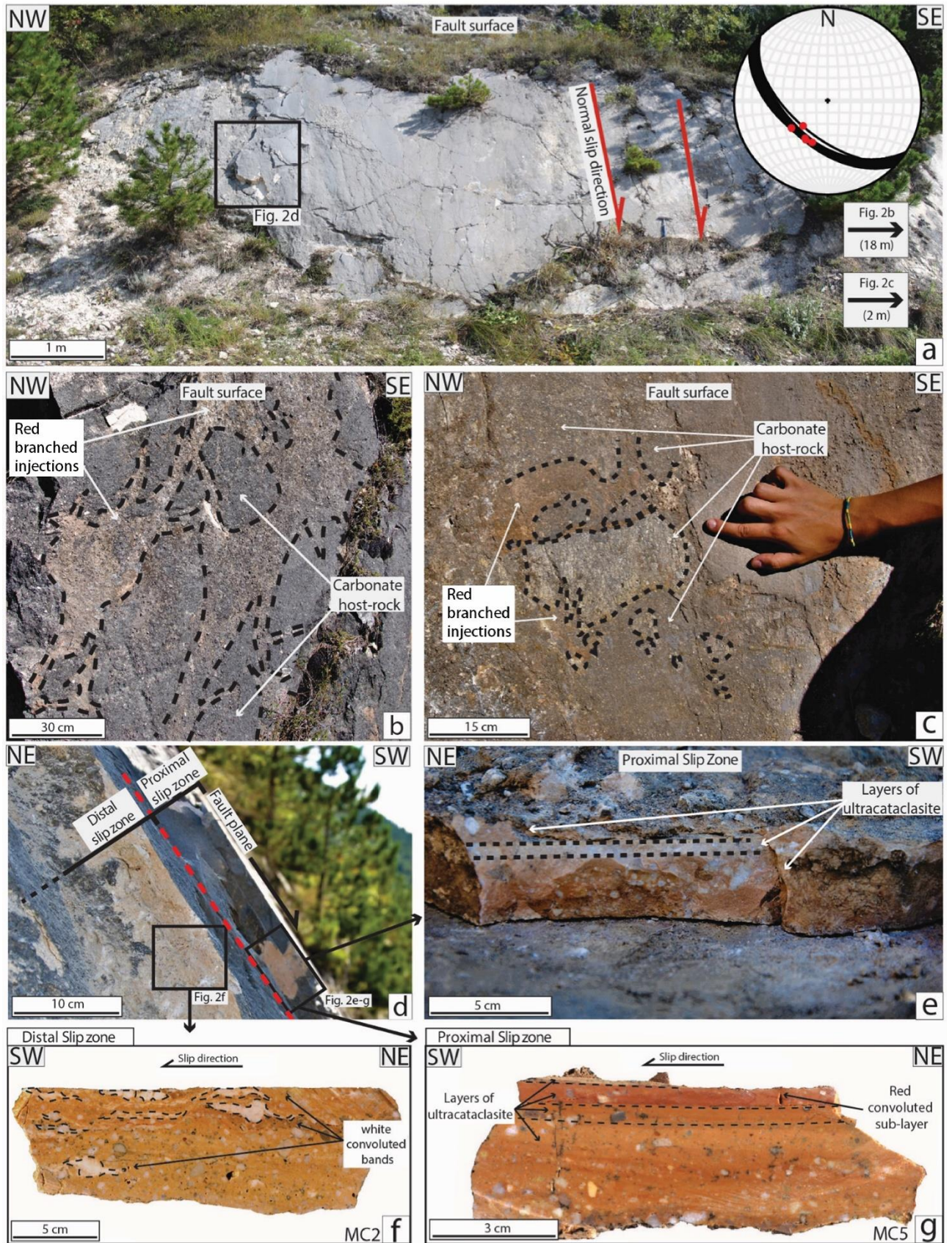


Figure 2. (a) Study outcrop along the Mt. Morrone Fault. Schmidt net shows attitude of the principal slip surface and related slickenlines (Mt. Morrone normal fault). (b) Red injections broadly permeate the principal slip surface as seen from the top. (c) View of the principal slip surface showing red

injections bearing host-rock clasts that are fully surrounded by the red matrix. (d) Cross-sectional view of the fault core lying beneath the principal slip surface of the Mt. Morrone Fault. The fault core includes a proximal and a distal slip zone. Proximal and distal refer to the distance from the principal slip surface. (e) Proximal slip zone consisting of thin ultracataclasite layers separated by sharp slip surfaces. (f) Hand sample of the distal slip zone consisting of a cataclasite partly overprinted by white bands stretched and deformed coherently with the slip sense. (g) Hand sample of the proximal slip zone showing some ultracataclasite layers. Note a layer with red fluidal fossil structures within the ultracataclasite.

3. Methods

We studied the principal slip zone of the Mt. Morrone Fault, moving from the principal slip surface (Figs. 2a-2c) downward into the footwall by 7-8 cm (Figs. 2d, 2e). To reach our aims, we performed *in-situ* structural investigation and rock sampling followed by micro- to nano-scale textural and geochemical analyses (Table S1): transmitted-light optical microscopy (OM) and optical cathodoluminescence (CL); field emission-scanning electron microscopy (FE-SEM) with energy dispersive spectroscopy (EDS); transmission electron microscopy (TEM) with EDS and selected area electron diffraction analysis (SAED); inductively coupled plasma mass-spectrometry (ICPMS); electron probe micro-analyzer (EPMA); laser ablation ICPMS (LA-ICPMS); and Raman spectroscopy. The laboratory analyses are fully described in the [Supplementary Material](#) together with supplemental evidence and data in supplementary figures (Figs. S1-S9) and tables (Tables S1-S7).

4. Results and Discussion

4.1. Rationale

To keep the results and related discussion and conclusions close to each other, we present them here in the same section. Below, the first seven subsections (4.2-4.8) mainly include results from different methods of investigation, while the subsection 4.9 mainly includes discussions on the

origin of the observed microstructures and paleofluids, in relation with the seismic cycle. Finally, subsection 4.10 includes some conclusive statements.

4.2. The Mt. Morrone principal slip zone

The studied segment of the Mt. Morrone principal slip surface (Fig. 2a) strikes NW–SE, dips by 50°–55° toward SW, and separates Lower Jurassic limestones, dolomitic limestones, and dolostones (Palaeodasycladus Limestone Fm.) in the footwall block (NE) from Pleistocene alluvial and lacustrine gravel-to-clay deposits of the Sulmona basin (Catignano unit) in the hangingwall block (SW) (Fig. 1b). In the fault hangingwall, beneath the Pleistocene deposits, thick deposits of Miocene clay-rich flysch occur. Kinematic indicators on the principal slip surface show an extensional dip-slip kinematics (Fig. 2a). In addition to kinematic indicators, the exposed principal slip surface is characterized by diffuse red branched injections of ultracataclastic material (Figs. 2b and 2c), which is characterized in detail in this study.

Immediately beneath the principal slip surface and roughly parallel to it, we identified two texturally distinct slip zones:

The distal slip zone is up to 3–4 cm thick and lies beneath the proximal slip zone (Fig. 2d). It consists of cataclasites with rounded and angular carbonate clasts, either dispersed in a red fine-grained matrix or arranged in white fluidal-like bands deformed coherently with the slip direction and producing an incipient dynamic foliation (Figs. 2f and 3a–3d) comparable with those described by Smith et al. (2017).

The proximal slip zone is up to 3–4 cm thick and is bounded by the principal slip surface above (Figs. 2d, 2e, 2g, and 3e). The proximal slip zone includes pink-to-white ultracataclasite layers (Layers A–C in Fig. 3e), locally embedding a thin dull-red convolute sub-layer of ultracataclasite

(sub-Layer B' in Figs. 3g and 3h). Due to erosion or displacement, the proximal slip zone is absent in some places.

4.3. The distal slip zone

The distal slip zone consists of rounded to angular calcite and dolomite clasts up to a few centimeters in size, dispersed within a red matrix (Figs. 2d-2f and 3a-3d). Under optical CL light (Fig. S1), the distal slip zone shows dull to bright red luminescence of the fine-grained reddish matrix that embeds the carbonate clasts. Carbonate clasts show either non luminescence (black) or dull red luminescence (Figs. S1c and S1d), where the luminescent clasts are reworked fragments of cemented granular matrix.

Locally, the red matrix is partly overprinted by less porous white cementitious bands to form alternated red and white bands (Fig. 3a). Scanning electron microscopy (SEM) coupled with EDS and EPMA point chemical analyses show that the white bands are dominated by cementitious calcite and minor dolomites, (EPMA measured $\text{Ca}/(\text{Ca}+\text{Mg})$ mole ratio of 0.53 ± 0.03), whereas the more porous red band matrix is dominated by clays (EPMA Si/Al mole ratio in the range 2.13–3.51 and minor quantities of K, Na, Sr, Fe, Ni), although some cementitious calcite is also present in micropores (Tables S3-S4). The red and white bands show convolute to wavy boundaries with asymmetric shapes verging consistently with the slip direction and sense, and mutual cusate-lobate folds to intrusive geometries (Figs. 3a-3d, and 4a).

Unlike the white bands, the red bands are characterized by a porous microgranular matrix (Figs. 4a, 4b, S2e, and S2f). Both FE-SEM and TEM (see next sections) images of the red intrusions revealed the occurrence of $< 1 \mu\text{m}$ in size, rounded calcite particles and dolomite plastically strained nano clasts (200–500 nm in size) wrapped by nanocylindrical phyllosilicates with typical tabular elongated shape (Figs. 4b-4c and S3e). Electron microprobe analyses show significant contents of Si

and Al in bulk area data (Figs. 6 and S6; Table S3) that suggest the pervasive occurrence of layer silicates within the fine-grained porous matrix. The acquisition of high-resolution images by FE-SEM does support the occurrence of Al- and Si-rich minerals within the matrix of the red bands. These minerals are characterized by elongated cylindrical morphology (Figs. 4c, 4d, and S3) and chemical composition typical of phyllosilicates. Importantly, we noted the presence of subspherical voids (or micropores) with diameters of 1–3 μm frequently distributed in between spherical calcite clasts (Figs. 4b, S2e, and S2f; see next section).

Dolomitic clasts fragmented down to microscale, either surrounded by a calcite matrix or sealed and pervaded by a calcite cement, are locally observed in the distal slip zone (Figs. S2a-S2d). These fragmentated clasts are characterized by pulverized or crackle breccia textures, finely comminuted with the pristine shape substantially preserved (Figs. S2a, S2b, S2d).

4.4. The proximal slip zone

The proximal slip zone consists of ultracataclasites with angular and sub-rounded calcite and dolomite clasts up to 3 mm in size, dispersed within a fine-grained red matrix (Figs. 3e-3h). Under optical CL light, the proximal slip zone shows a dull red luminescence color of the fine-grained matrix between carbonate clasts. Carbonate clasts show either non luminescence (black) or red luminescence brighter than that of the matrix (Figs. S1e-S1h).

The slip zone is arranged in multiple ultracataclastic layers macroscopically distinguishable, based on color, grain size, and matrix abundance (Figs. 3e, S4a, and S4b). We recognized at least three main different layers (Layers A–C) closely beneath the principal slip surface, separated by sharp secondary slip surfaces (Fig. 3e). Due to erosion and/or fault displacement, not all three layers always occur in the proximal slip zone. Moving downward from the principal slip surface, the three main layers are:

- Layer A is a grey ultracataclasite up to a few millimeters in thickness with an ultrafine grained matrix. Locally, the layer includes lenses containing large (up to 1 mm in size) packed clasts and some matrix, likely derived by the disruption of former lithified slip zones. These lenses overlap one another and are intruded by the ultrafine grained matrix of Layer A (Figs. 3e and 3f).
- Layer B is a red ultracataclasite ~5 mm thick consisting of an ultrafine grained carbonate matrix, in which carbonate clasts with a diameter of ~1 mm are dispersed (Figs. 3e, S4c, and S4d). Layer B is characterized at its base by the occurrence of a peculiar dull red convolute sub-layer (sub-Layer B' in Figs. 3e, 3g, 3h, S4a, and S4b). Sub-Layer B' is probably the most significant microstructure of this study, reminiscent of the potential precursors of earthquakes recently identified through hydrogeochemical monitoring in central Italy (Barberio et al., 2017), as it will be further discussed below. The sub-layer is variable in thickness (up to about 1 mm) and shows a wavy and highly irregular, fluidal flame-like textured upper boundary, with flame tongues being usually deflected coherently with the sense of slip (Figs. 3g, 3h, S4a, and S4b). The bottom of Layer B is represented by a sharp minor slip surface truncating the underlying ultracataclasites (Fig. 3h).
 - Layer C is a cataclastic ~1.5 cm thick layer presenting a number of coarse clasts larger than the number of coarse clasts in layers A and B. Layer C is composed by angular to sub-rounded carbonate clasts ranging from 0.5 to 3 mm in diameter (Fig. 3e). The bottom of Layer C is represented by a sharp slip surface delimiting the top of the distal slip zone.

At the microscale, the three layers A–C display similar textures with poorly-rounded calcite and dolomite clasts with Ca# (calculated as $\text{Ca}/(\text{Ca}+\text{Mg})$ mole ratio) ranging from 0.43 to 0.59 surrounded by either dolomite (Fig. 4f) or calcite (Fig. 4g and 4h) matrices. Intergranular calcite cement and calcite micro-veins are also present (Fig. S4c). The layer boundaries are usually marked by slip surfaces and truncated clasts, often accompanied by thin calcite veins (Figs. 4e, 4f, and S4b).

On the contrary, the convolute sub-Layer B' appears texturally distinct at the microscale, with large ($>1\ \mu\text{m}$ in size) subangular calcite clasts entrapped within a very fine-grained ultracataclasite (average grain size $50\ \mu\text{m}$) (Fig.4f and S4d). Peculiar dolomite clasts ($20\text{--}50\ \mu\text{m}$ in size) are characterized by rounded and embayed borders and are surrounded by a thin calcite rim (Figs. 4g and 4h).

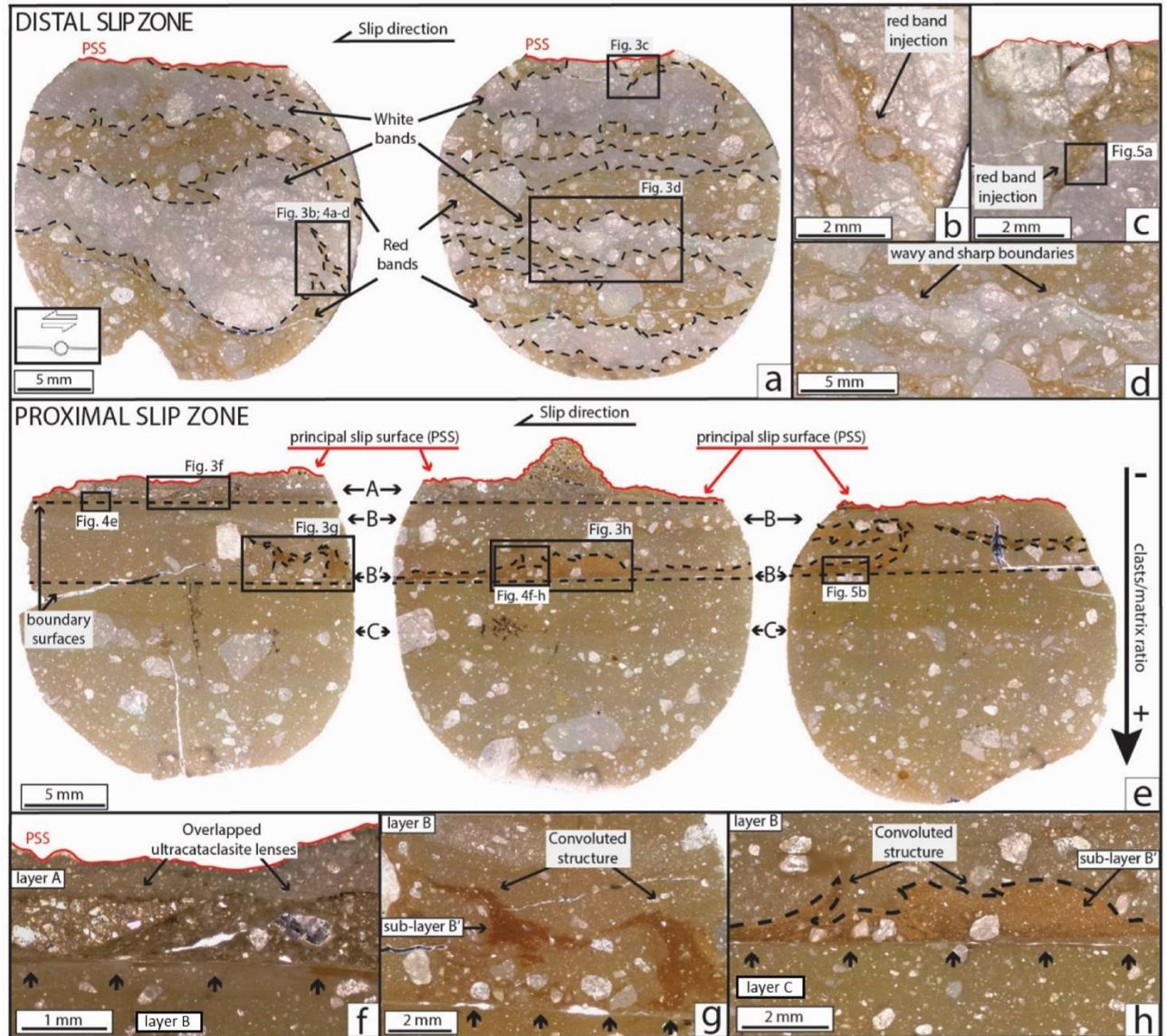
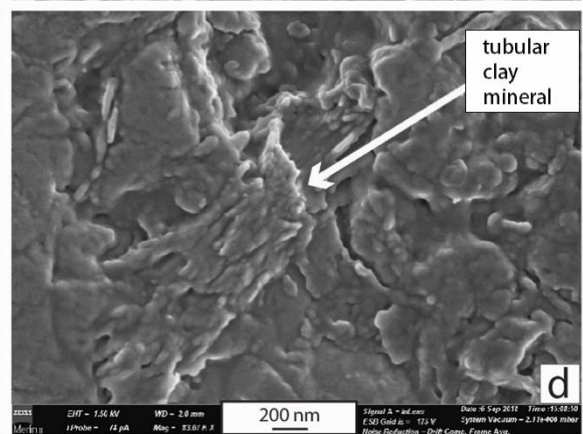
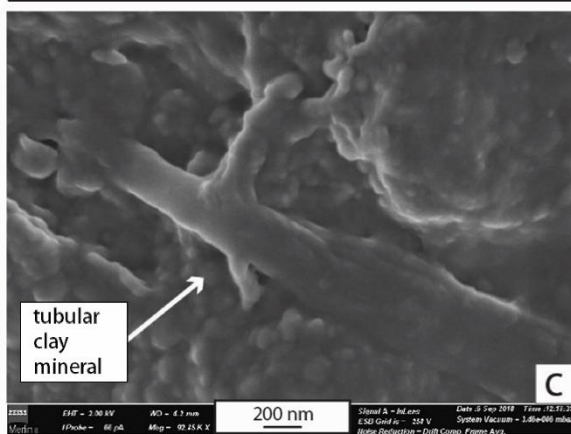
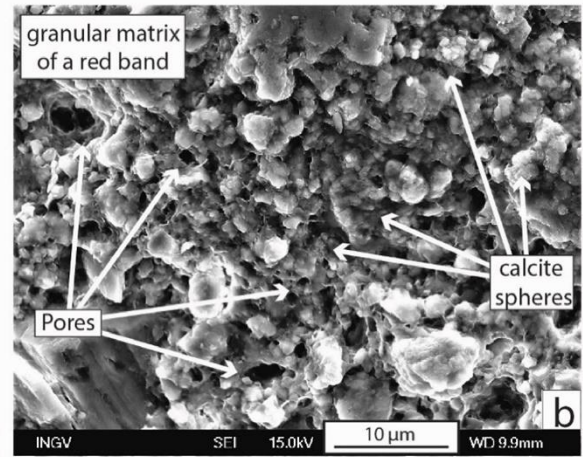
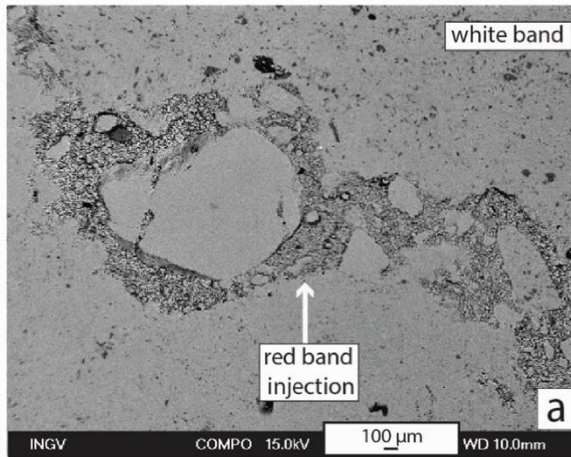


Figure 3. (a) High-resolution scan views and related line drawing of two thin-sections (2.1, 2.2) from the distal slip zone. Images show the alternation of white and red bands. The white bands overprint the slip zone and appear stretched parallel to the principal fault surface and deformed coherently with the slip direction. (b and c) Injections of the red bands into the white bands. (d) Wavy boundaries between white and red bands. (e) High-resolution scan views and related line drawing of three thin-sections (5.3, 5.2, 5.1) from the proximal slip zone of the Mt. Morrone Fault. Images show the proximal slip zone layering. Layer A: Grey ultracataclasite layer; Layer B: Red ultracataclasite layer; sub-Layer B': fluidal sub-layer; Layer C: cataclasite layer. (f) Stacked and overlapped ultracataclasite lenses of Layer A. (g) Flame-like structure from the fluidal sub-Layer B'. (h) The fluidal sub-Layer

B' penetrates into the Layer B with fluidal-plastic-like structures. Black arrows indicate the boundary surface between the two layers.

DISTAL SLIP ZONE



PROXIMAL SLIP ZONE

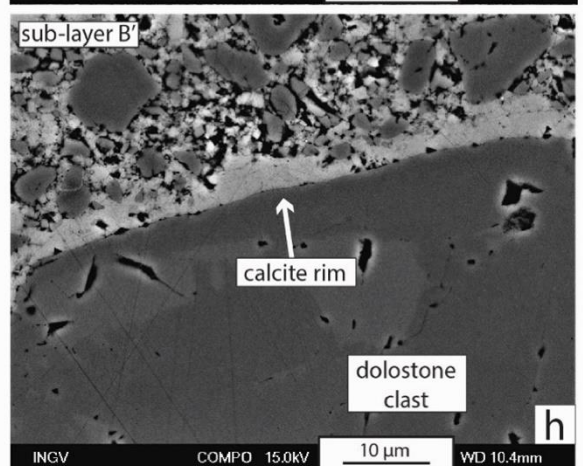
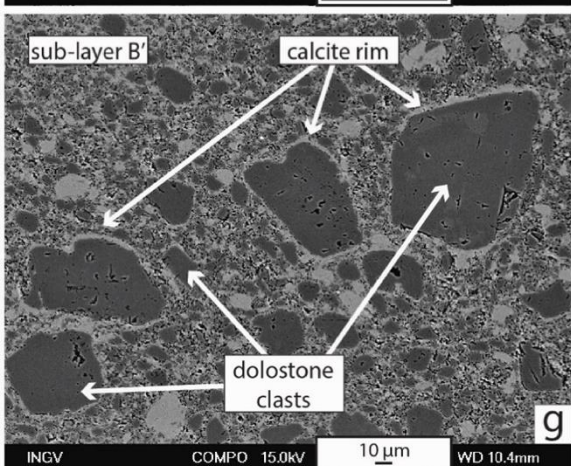
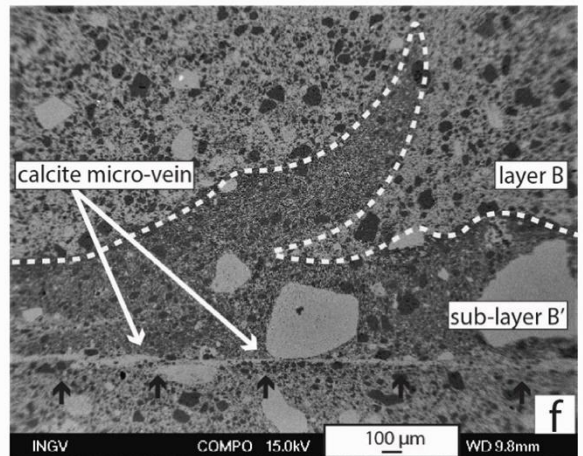
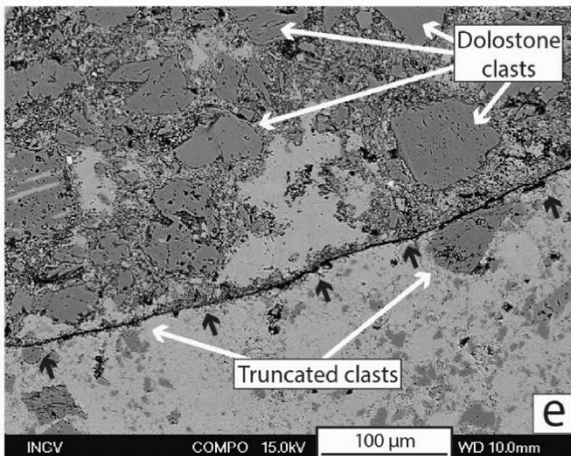


Figure 4. High-resolution SEM images from the distal and the proximal slip zones (squared areas as indicated in Fig. 3). (a) Injection of the red band into the white band of the distal slip zone. (b) Porous granular texture of the red band matrix. This matrix is composed of calcite spheres of $\sim 4\ \mu\text{m}$ in diameter. (c and d) High-resolution SEM images of clay minerals with a fibrous filament-like habit composed of aligned nanospherules and nanocylinders. (e) Dolostone clast truncated by a sharp slip surface dividing the layers of the proximal slip zone. (f) Flame-like structure of the fluidal sub-Layer B' extending into the Layer B. A small micro-calcite vein separates the sub-Layer B' from the underlying Layer C. (g and h) The micro-clasts forming the sub-Layer B' matrix show a small calcite rim around themselves.

4.5. TEM observations

We performed TEM analyses on carbonate grains from the distal slip zone and in the proximal slip zone, on the ultrafine matrix occurring close to the principal slip surface, specifically on sub-Layer B' (Figs. 5 and S5).

In the distal slip zone, crystals (up to $1\ \mu\text{m}$ in size) of dolomite appear often characterized by intense deformation and related grain size reduction (Fig. 5a). This results in the formation of ultrafine grained nano clasts, 200–800 nm or even less in diameter, with sharp and angular grain boundaries. In the distal slip zone, calcite crystals are markedly less abundant than dolomite. The interstitial spaces between dolomite nano clasts are filled by smectite-like layer silicates (Fig. 5b and S5a-c). Layer silicates form a thin envelope around dolomite nano clasts and are a few (001) lattice fringes thick. Moreover, they are deformed, poorly crystalline, and include some amorphous portions.

In the proximal slip zone, in particular in the matrix of sub-Layer B', dolomite grains and nano clasts exhibit more rounded and lobate boundaries, whereas the interstitial smectite clays appear to be partially or fully decomposed, producing a contrast-free amorphous material that typically forms a sort of envelope bridging nearby grains and nano clasts (Figs. 5c and S5d). This feature is consistent with previous SEM observations (Fig. 4g). In some cases, dolomite nano clasts from sub-Layer B' appear to be homogeneous single crystals whereas, in other cases, they exhibit a peculiar heterogeneous contrast, suggesting that they were replaced by nanograins 10–20 nm in diameter with variable orientations (Figs. 5d and S5e). EDS and SAED results indicate that nanograins correspond

to calcite (Figs. 5f) associated with amorphous vesicle-rich material (Figs. 5c, 5d, S5e and S5f). Fig. 5(f) shows a representative ring-shaped SAED pattern of calcite nanograins, characterized by sharp and intense reflections. This evidence is consistent with the occurrence of highly crystalline undeformed calcite in random orientation. Locally, calcite nanograins exhibit sharp polygonal grain boundaries, e.g., inset in Figs. 5e and S5f (compare with Smith et al., 2013).

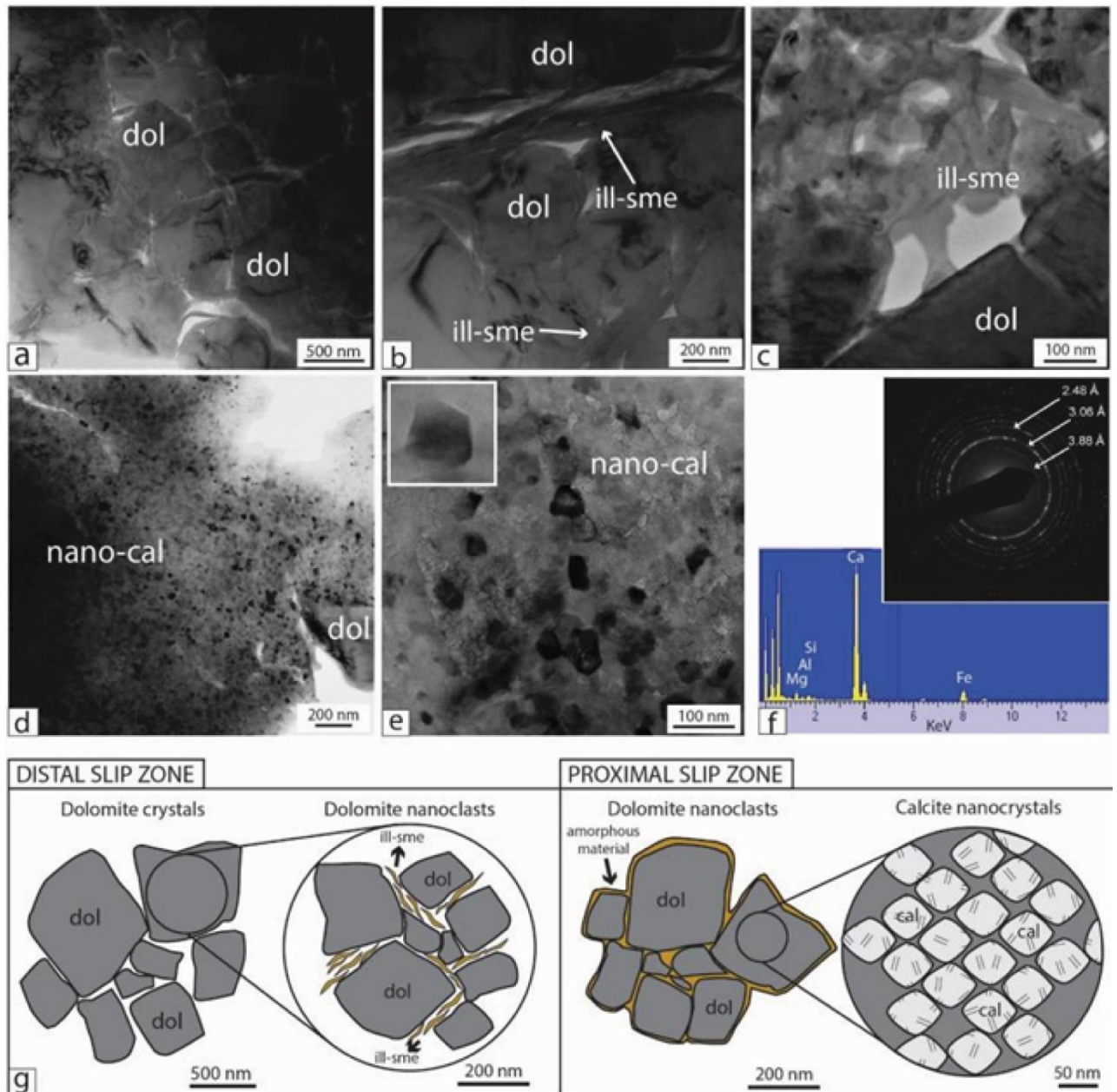


Figure 5. TEM observations on the Mt. Morrone fault slip zones. (a) Dolomite micron-sized crystal from the distal slip zone, showing brittle deformation, grain size reduction, and

nanoclast formation (right side). (b) Detail of dolomite nanoclasts (here around 500 nm in size), wrapped by a thin interstitial film of smectite (layered silicates, Illite-Smectite, in distal slip zone). (c) Dolomite nanoclasts from the sub-Layer B' (proximal slip zone), showing lobate grain boundaries and amorphous interstitial material, often forming a sort of “bridge” between nearby nanoclasts. (d) In the ultrafine matrix of sub-Layer B' (proximal slip zone), dolomite nanoclasts may be replaced by calcite nanograins, 10-50 nm in diameter, with random orientations. (e) Detail of calcite nanograins (proximal slip zone), in places associated with poorly crystalline to amorphous vesicle- and pore-rich material. Inset shows a calcite nanocrystal with sharp polygonal grain boundaries and regularly spaced undeformed lattice fringes. (f) Mg-calcite EDS spectrum and SAED pattern with ring-shaped reflections due to the random orientation of calcite nanograins in the proximal slip zone. (g) Sketches showing distal (left) and proximal (right) slip zones with features observed through TEM and SAED analyses in Figs. 6a-6f.

4.6. Slip zone geochemistry

Through an ICP-MS spectrometer, we measured the bulk chemistry (28 elements) on one sample of the distal slip zone (MC2) and two samples of the proximal slip zone (MC5 and MC7). Results are reported in [Table S2](#) and show the abundance (in ppm) of elements like Al and Fe (> 1500 and 1900 ppm, respectively) and B, Mn, Sr, As, and V (> 60, 70, 50, 20, and 10 ppm, respectively; [Table S2](#)).

We also performed chemical point analyses through EDS and EPMA ([Tables S3 and S4](#)). The EDS map of [Fig. 6a](#) displays an injection of granular red band into a white band of the distal slip zone. The map reveals a granular matrix (diameter < 20 μm) for the red band containing not only Ca and Mg but also large quantities of Si and Al. This granular injection is embedded by a white band (top left of maps in [Fig. 6a](#)) dominated by Ca, accompanied by some Mg, but free of Si and Al.

The EDS map of [Fig. 6b](#) refers to the contact between the fluidal sub-Layer B' and the underlying Layer C from the proximal slip zone. Sub-Layer B' consists of dolomitic clasts with Ca up to ~38wt.% and ~18wt.% of Mg floating within a matrix rich in Ca and Mg but also in Si and Al. In contrast, Layer C (below) consists of Ca-rich compact portions (bottom right of maps in [Fig. 6b](#)) with Ca- and Mg-rich clasts embedded in a granular calcitic matrix. Al- and Si-rich spots occasionally occur (bottom of maps in [Fig. 6b](#)). EDS maps reveal, therefore, a fluidal and granular sub-Layer B'

composed predominantly of dolomite clasts dispersed in an aluminosilicate matrix, which contrasts with the prevalent calcite composition of Layer C that is, at least in part, very compact and only rarely intermixed also with aluminosilicate matrix.

Chemical and textural features very similar to those observed in [Fig. 6](#) for the distal and the proximal slip zones are also observed in [Figs. S6, S7, and S8](#). In this latter cases, a fluidal Al- and Si-bearing (in addition to Ca and Mg) granular matrix embedding dispersed Mg- and Ca-rich clasts is injected into or cut by one or multiple Ca-rich veins and/or mineralizations.

4.7. Spot geochemistry through LA-ICPMS measurements

We performed spot-analyses of trace elements on clasts, veins, and matrices of three thin sections from the proximal (Sections 5.1 and 5.2, [Table S1](#)) and distal (Section 2.1, [Table S1](#)) slip zones of the Mt. Morrone Fault using LA-ICPMS. In detail, we investigated the trace element distribution and abundance in Layer B and sub-Layer B', where this latter intrudes the Layer B with a typical fluidal texture ([Fig. 3e, 3g and 3h](#)). All results are reported in [Table S4](#).

In general, the abundance of most trace elements, including rare-earth elements (REE) from sub-Layer B', is on average higher than that of trace elements from Layer B, which in contrast exhibits absolute elemental concentrations comparable to those of carbonate clasts and veins from the investigated slip zones ([Fig. 7](#)). For instance, an enrichment in Ba and Sr in sub-Layer B' with respect of Layer B is shown in LA-ICPMS transects of [Fig. 7b](#). Moreover, the measured REE concentrations of the carbonates from the Mt. Morrone Fault are very low, ranging between 0.002 to 15 ppm ([Fig. 7a](#)). Post-Archean Australian Shale (PAAS)-normalized patterns of Layer B, sub-Layer B', carbonate clasts, and veins are all comparable, exhibiting, on average, flat profiles (i.e., $(La/Yb)_N$ ranges between 0.2 and 2; [Fig. 7a](#)). Cerium negative anomalies characterize most samples (Ce/Ce^* ranges between 0.3-1.4; [Fig. 7a](#)) and reflect the oxic conditions of the seawater setting, where these carbonate

rocks were deposited ([Elderfield and Greaves, 1982](#)). Normalized-PAAS spider diagrams of the entire analyzed samples are all comparable, showing marked positive anomalies of K and Ti ([Table S5](#)).

We compared the data from our samples with those of some limestone fragments from the Polino carbonates in the central Apennines, Italy ([Rosatelli et al., 2010](#)), as representing a local example of undisturbed carbonate rocks, i.e. the Polino carbonates pertain to the Jurassic Massiccio Fm. that is equivalent to the Jurassic Palaeodasycladus Limestone Fm. hosting the study fault outcrop. The Polino carbonates present REE concentrations intermediate between those of Layer B and sub-Layer B', and a similar REE pattern ([Fig. 7a](#)). Also, to investigate possible relationships between the studied fault system and a deep magmatic source, we compared the trace element composition from the Mt. Morrone Fault slip zones with a few volcanic rocks outcropping in the central Apennines, i.e., Roman and Intra-Apennine magmatic provinces in [Fig. 7a](#). Results show that REE content is one or more orders of magnitude higher in the volcanic rocks than in the carbonates, with similar flat patterns and no Ce anomaly ([Fig. 7a](#)).

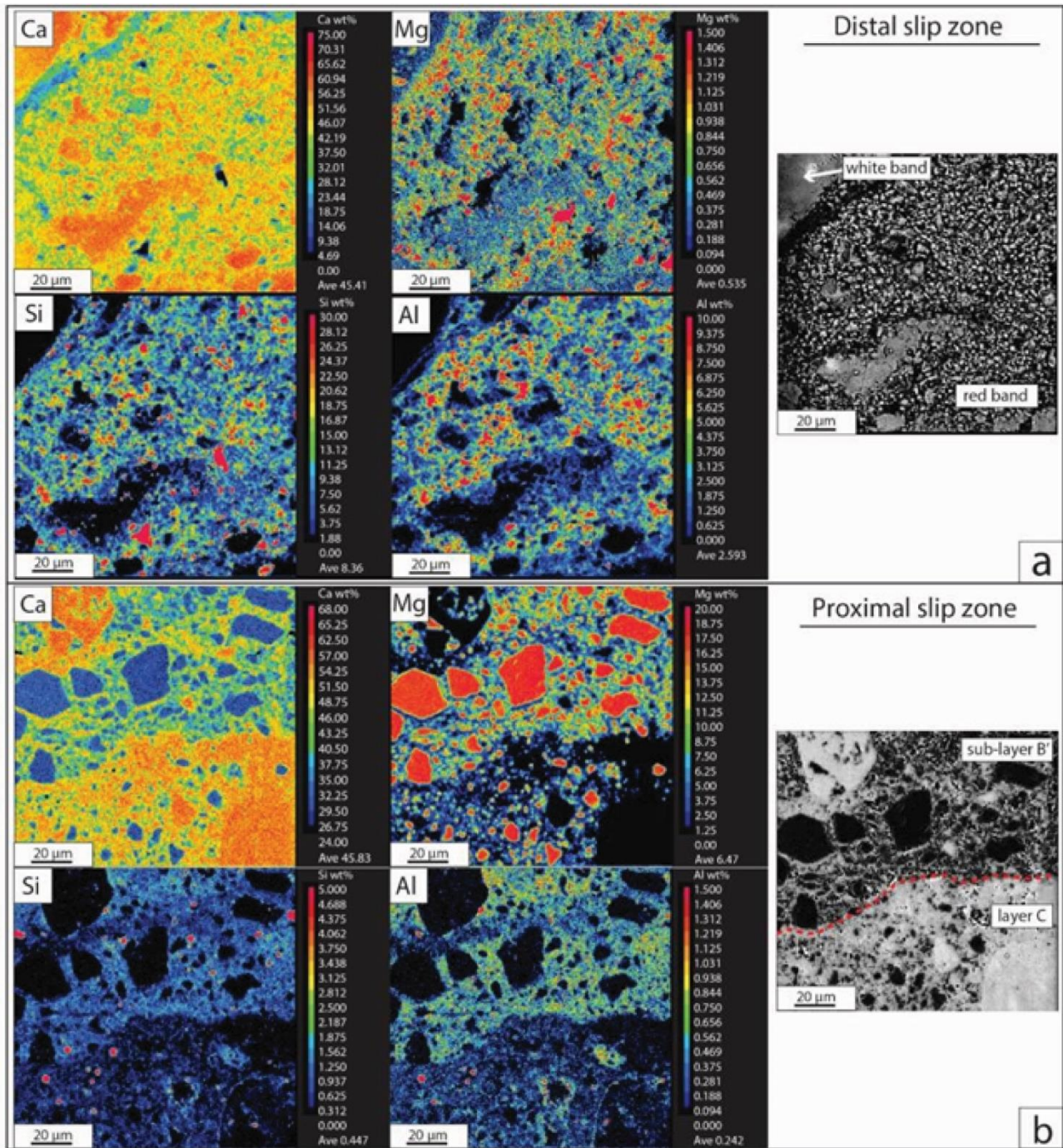


Figure 6. EDS maps (maps on the left) from the distal and proximal slip zones (location of the maps is indicated in Fig. 3). On the right, SEM images corresponding to the maps on the left. (a) Distal slip zone. Injection of a red band into a white band. The red band has a granular texture and contains not only Ca and Mg but also Si and Al. (b) Proximal slip zone. Portion of the contact between the sub-Layer B' and the underlying Layer C. Sub-Layer B' is composed by a high content of Mg in the clasts that are embedded into a Ca-rich rim. The matrix has a high content of Ca and a considerable content of Mg, Si, and Al. Layer C has a higher content in Ca and Mg and poorer content in Si and Al than sub-Layer B'.



Figure 7. REE-diagram of Layer B and sub-Layer B'. For comparison, REE composition from the Polino carbonates (Calcare Massiccio Fm. from central Apennines) and some volcanic rocks from the central Apennines (the intra-Apennine and Roman magmatic provinces) are reported. Volcanoclastic product data are from Peccerillo (2005 and references therein) and are for the intra-Apennine and Roman magmatic provinces (i.e., Vico, Colli Albani, and Mt. Sabatini in central intra-Apennines). Carbonate rock data are from Rosatelli et al. (2010) and are for the Polino carbonates in central Apennines. (b) Trace element (Ba and Sr) tracks of Layer B and sub-Layer B' where this latter

intrudes, with its typical fluid-type texture, into the Layer B. Grey portion is for sub-Layer B' whereas white portions are for Layer B.

4.8. Raman spectroscopy of fluid inclusions

We performed confocal micro-Raman spectra measurements on tiny inclusions (diameter $\leq \sim 30 \mu\text{m}$) observed in calcite veins and mineralizations under polarized transmitted light (Fig. 8) from the proximal slip zone (Layer A and Layer B) and from related slip surfaces. The collected spectra (Fig. 8) are characterized by sharp peaks relative to the crystalline calcite matrix at 280, 710, and 1085 cm^{-1} associated to the symmetric stretching vibration (ν_1) in-plane bending mode (ν_4) of the carbonate group. In addition, broad overlapping bands ranging from 1200 to 1700 cm^{-1} are visible and can be referred to as vibrations of structurally disordered carbon; however, these features are difficult to deconvolve with the typical D and G bands (Frezzotti et al. 2012), likely due to the presence of intermediate C-H bending vibrations (Orange et al. 1996), which have often been referred to as carbon (either amorphous or with disordered crystalline structure) from solid bitumen, precipitated by hydrocarbon-rich fluids (Schito et al. 2017).

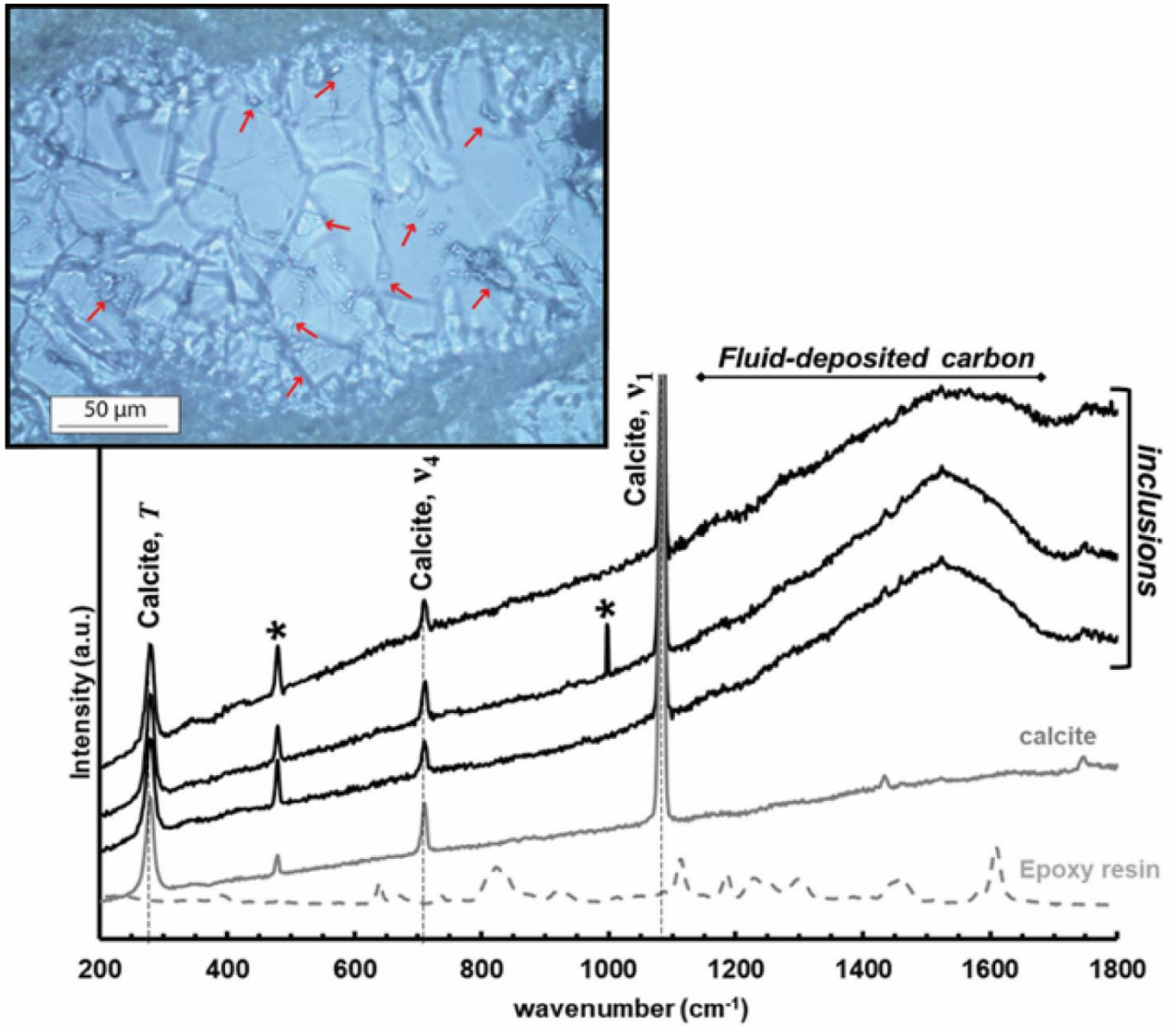


Figure 8. Raman spectra of three inclusions observed within calcite mineralizations from the proximal slip zone. Each spectrum shows the frequency interval of disordered carbon (see text). Sharp peaks are relative to crystalline calcite from the matrix, the spectrum of which is also shown in grey. The spectrum of epoxy resin is also shown for comparison. Inset (top left) shows the location of the fluid inclusion within the sparry calcite observed under transmitted light. Asterisks are relative to unidentified peaks.

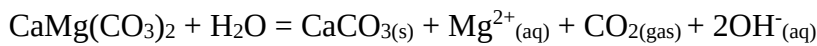
4.9. Fluid-assisted deformation and implications for seismic and precursory mechanisms

Micro- to nano-structural observations within the Mt. Morrone Fault distal and proximal slip zones suggest that the individual ultracataclastic layers and sub-layers behaved as fluidized granular materials during fluid-assisted deformation. The overprinting relationships between these layers as well as the mutual crosscutting and injection patterns (Figs. 3 and 4) indicate, in places, the

contemporaneity of formation of the layers (i.e. mutual injection) and, in other places, the multiplicity of slip events (i.e. crosscutting or overprinting relationships). In particular, the injecting layers (red bands within the distal slip zone and sub-Layer B' within the proximal slip zone) are characterized by higher porosity compared to the surrounding materials (Figs. 3e, 3g, 3h, 4f, and S4a and S4b). Similar structures have been previously described in natural fault cores and in rock deformation experiments performed at seismic slip rates and were frequently associated to co-seismic pressurization of fluids trapped or injected within the slip zones (Brodsky et al., 2009; Smith et al., 2011; Fondriest et al., 2012; Smeraglia et al., 2017a; Ferraro et al., 2019). In the case of a seismic origin, the fluid pressure increase may be generated by a focused and rapid flow of deep external fluids (seismic pumping; Sibson et al., 1975), and/or thermo-chemical pressurization of pore fluids (e.g. water and CO₂) associated to frictional heating (De Paola et al., 2011; Collettini et al., 2013). Mechanical pressurization can also occur within actively compacting gouge layers, particularly within low permeability ones, deformed both at sub-seismic and co-seismic slip rates (Faulkner et al., 2018). Recently, Demurtas et al. (2020) reported the development of fluidal features within wet mixed calcite-dolomite experimental gouges also at sub-seismic slip rates, likely due to local pressure increase within isolated fluid saturated gouge patches. Nevertheless, such a process is expected to be more relevant for underconsolidated gouges and less within gouges which have been fully compacted by slip on mature faults (e.g. Faulkner et al., 2018).

In addition, the proximal slip zone is characterized by multi-compositional ultracataclasite micro-layers with sharp boundary truncating each other and suggestive of cyclic shear strain localization possibly during individual seismic slip events (Figs. 4e and 4f; Smith et al., 2011, 2017). Moreover, exploded (pulverized) dolostone clasts (Figs. S2a-S2d), which are highly comminuted but with a recognizable original grain shape, are immersed within calcite matrix and might result from impulsive dynamic load associated to earthquake ruptures (Dor et al., 2006). Further micro- to nano-scale evidence is compatible with the activation of mineral decomposition possibly associated to co-

seismic frictional heating (i.e., at slip ~ 1 m/s). In particular, the occurrence of dolomite nanoclusters (Figs. 5d and 5e) and especially Mg-calcite nanograins (Figs. 5d-f) could be interpreted as the result of extreme comminution and dolomite decarbonation in the presence of an aqueous solution (Han et al., 2010; De Paola et al., 2011;). Mg-calcite nanograins exhibiting sharp polygonal grain boundaries, e.g., insets in Figs. 5e and S5f, could be interpreted as the result of co-seismic thermally driven dynamic recrystallization similarly to calcite foam textures reported in Smith et al. (2013). This interpretation would imply thermal decomposition of dolomite by frictional heating ($T > 550$ °C, De Paola et al., 2011); alternatively, a mechanism of low-temperature mechanical decarbonation and amorphization similar to the one proposed by Ohl et al. (2020) might be invoked to explain these microstructures. The co-seismic interpretation might also explain the presence of micropores and the absence of MgO after decomposition of dolomite by the reaction:



assuming the involvement of an aqueous fluid during decarbonation, induced by a seismic event. In the same way, the ultrathin films of amorphous silicate material found in the proximal slip zone may be related to clay dehydroxylation due to co-seismic frictional heating ($T > 400$ °C) (Figs. 5c and S5d; Collettini et al., 2013; see also Kuo et al., 2009), although similar structures were also produced in laboratory experiments at subseismic slip rates (Aretusini et al., 2019; Wu et al., 2020). In general, the occurrence of subspherical micropores associated to amorphous material within the studied slip zone (Figs. 4b, S2e, and S2f) might be consistent with carbonate decomposition or clay dehydroxylation (Collettini et al., 2013) triggered by coseismic frictional heating (e.g. Kuo et al., 2011).

The occurrence of nanocylindrical structures—carbonate or phyllosilicate—(Figs. 4c and 4d) is debated and dubitatively interpreted as coseismic (Hirono et al., 2014; Verberne et al., 2014; Smeraglia et al., 2017b) (Figs 4c, 4d and S2). For instance, Smeraglia et al. (2017a), with carbonates and clays very similar to those found in the Mt. Morrone slip zone and in very similar boundary

conditions (< 3 km depth), produced nanocylindrical structures similar to those shown in [Figs. 4c, 4d, S3e, and S3f](#) in laboratory only at seismic velocities (1 m/s).

In synthesis, micro- to nano-evidence from the Mt. Morrone slip zone strongly suggest the occurrence of multiple episodes of fluid-assisted faulting and gouge fluidization, likely associated to earthquake ruptures.

To understand the origin of fluids that contributed to form the studied slip zone, we compare trace element ratios from Mt. Morrone and Polino (central Apennines) carbonates, and from volcanic rocks of the Roman and Intra-Apennine (central Apennines) Provinces ([Figs. 9 and 10a](#)). We also consider two flysch deposits: a proximal one (Popoli flysch from the hangingwall of the Mt. Morrone Fault) and a distal one (Flysch Rosso from the southern Apennines, circa 200 km from the Mt. Morrone Fault). We show some trace element couples featured by similar geochemical incompatibility to minimize the effect of the differentiation processes on the magmatic endmembers and to retain source information. We focus on sub-Layer B' that is the most fluidal-like layer among those closest to the principal slip surface, i.e., within the proximal slip zone ([Figs. 3e, 3g and 3h](#)).

[Fig. 9](#) shows Rb/Ba vs. Rb/Sr and Rb/Sr vs. La/Yb diagrams and evidences a marked difference between sub-Layer B' and Layer B. The fluidal sub-Layer B', where trace elements were exclusively measured on matrix (i.e., no clasts or veins), is, on average, featured by Rb/Ba, Rb/Sr, and La/Yb ratios higher than those of Layer B, where, conversely, the analyses were carried out on both matrices, carbonate veins, and clasts. The lowest values of Rb/Ba, Rb/Sr, and La/Yb in Layer B are exhibited by the clasts. The results highlight an intermediate zone where the two matrices overlap ([Fig. 9](#)). Also, the Rb/Ba, Rb/Sr, and La/Yb values of sub-Layer B' are compatible with volcanic rocks from the Intra-Apennine and Roman magmatic provinces, whereas the composition of Layer B is similar to the undisturbed carbonates from Polino. Interestingly, the fact that the most trace element-enriched samples of sub-Layer B' fall in the field of the volcanic deposits suggests that sub-Layer B' is somehow linked to the interaction with fluids having a magmatic signature and whose

nature and genesis will be discussed later. In this context, the most trace element-enriched values of the dark matrix (sub-Layer B') would track the most advanced degree of interaction with magmatic fluids, whereas the carbonate clasts of Layer B would be representative of the practically unmodified carbonates. The compositional overlap of the two layers would indicate an intimate degree of mixing between the two matrices.

The confirmation that the fluid that flowed into the slip zone originated by interaction between magmatic and carbonate sources is provided by the chemical variability recorded over some micro-profiles crossing the B-B' interface, where sub-Layer B' injects the carbonate rock of Layer B (Fig. 7b). An increase in concentration of some trace elements, i.e., Sr and Ba, is observed moving from the middle portion of the injection toward the two lateral boundaries, showing 'V'-like or 'U'-like compositional profiles. Conversely, when moving from the interface into the Layer B, the trace element contents drop sharply. This peculiar pattern has been suggested to be produced by dissolution-recrystallization processes at the interface of the interaction zone between a circulating fluid and the country rock (Renard et al., 2019). Therefore, a key question concerns the origin of the trace-element-rich fluid. Two different main processes can be hypothesized:

(1) In a first scenario, the studied slip zone may have been affected by percolation of surface waters that interacted with the trace-element-rich tephritic products that are present in the Sulmona basin as intercalations at depths less than about 100 m (Giaccio et al., 2013). Such hypothesis seems highly unlikely for several reasons. First, it is geochemically unlikely that trace elements including REE were simply dissolved and carried by low-temperature and poorly acidic surface fluids, e.g., meteoric waters. Indeed, Fig. 7 shows REE contents in sub-Layer B' much higher than in Layer B and undisturbed carbonates. Also, percolating meteoric waters should exhibit a REE pattern with a general monotonic increase from light REE (LREE) to heavy REE (HREE) (Tostevin et al., 2016), as the HREE solubility is higher than that of LREE (particularly La). Conversely to the expected behavior, the REE pattern of sub-Layer B' is mainly flat, with an almost comparable enrichment of

LREE, middle REE (MREE), and HREE in [Fig. 7a](#). Moreover, the tephra deposits from the Sulmona basin are very thin—only a few cm or less—and their distribution is spatially discontinuous due to erosion ([Giaccio et al., 2013](#)), making it unlikely for an advanced degree of chemical interaction with meteoric waters percolating downward along fault zones.

(2) A second hypothesis ([Fig. 10b](#)) suggests that the geochemical signature of sub-Layer B' is partly the consequence of the interaction between the Mt. Morrone carbonate and/or flysch deposits and magmatic-derived fluids rising from deep crustal levels along deeply-rooted faults, particularly during pre-seismic dilation phases (since 4-5 months before mainshock according to [Barberio et al., 2017](#)). It is known, indeed, that magmatic-derived fluids, featured by high temperature and acidic conditions, can carry large amounts of REE, both LREE and HREE, for kilometers through the crust ([Michard and Albarede, 1986](#)). Therefore, the interaction of these deep fluids with authigenic carbonate and flysch deposits along a fault zone would produce a REE enrichment and a flat REE pattern, as observed for sub-Layer B'. The recent discovery of CO₂ peaks from deep crustal sources during seismic phases of central Apennines in the last ten years supports this hypothesis ([Chiodini et al., 2020](#)). The inflow of external fluids is also consistent with some different CL colors of sub-Layer B', suggesting multiple injections of external fluids, characterized by slightly different chemical compositions, i.e., different CL colors ([Fig. S1](#)). The same applies to some dolomite clasts characterized by rim embayments ([Figs. 4e, S2c, and S4a](#)), which suggest interaction with external (deep) aggressive fluids.

Further constraints on the nature of the trace-element-rich signature of sub-Layer B' issue from the vanadium content. [Fig. 10a](#) compares the Sr/V ratios of the studied carbonates with those of some oxic groundwater from the Latium volcanic province in central Italy, which have crossed and partially dissolved the local volcanoclastic units ([Sappa et al., 2014](#)). The Sr/V ratios of these cold waters are almost coincident with those of the volcanic products from the Intra-Appenine and Roman provinces. In contrast, the Sr/V ratios of sub-Layer B' fall outside the field of the aforementioned

groundwaters or volcanic deposits, reaching much lower values. This evidence allows us to exclude that a typical oxic meteoric water that interacted with volcanoclastic deposits may have geochemically imprinted the signature of sub-Layer B'. Conversely, the lower Sr/V ratios highlighted in the sub-Layer B' with respect to those of a volcanic endmember may be consistent with the aforementioned second hypothesis, supporting the ascent of a deep crustal fluid along the Mt. Morrone Fault. Indeed, V in its oxidized states (V^{+4} and V^{+5}) is highly insoluble, with solubility increasing with the reducing conditions typical of magmatic-derived fluids, eventually resulting in a decrease of Sr/V ratios, as observed in sub-Layer B'. It is also true, however, that the high V content of the sub-Layer B' is consistent with V-rich clay flysch deposits lying on the Mt. Morrone Fault hangingwall (Fig. 10a) and it is reminiscent of the V-rich hydrogeochemical precursors arose in central Italy near the Mt. Morrone Fault 4-5 months before the 2016 Mw 6.0 Amatrice earthquake (Barberio et al., 2017); i.e., note that no motions were recorded along the Mt. Morrone Fault during the 2016 earthquakes and, hence, the sub-Layer B' must have formed in previous (seismic) events.

The potential hydrogeochemical precursors of the 2016 earthquakes (Barberio et al., 2017) were interpreted as being connected with the upwelling of pre-seismic (4-5 months before the mainshock) deep aggressive fluids (CO_2 -rich) and ensuing interaction with shallow host rocks such as the clay flysch (i.e. desorption of metal and metalloid ions from clay mineral surfaces; Boschetti et al., 2019; Barbieri et al., 2020). Similar co-seismic V-rich fluidal structures occur also in other active faults of the central-southern Apennines, such as some micro-layers from the slip zone of the Tre Monti Fault (Fig.10a), located in one of the most seismic areas of the Apennines (Fucino basin; Smith et al., 2011; Smeraglia et al., 2016). Accordingly, we speculate on the formation of the fluidal sub-Layer B', proposing that pre-seismic ascent of magmatic-derived fluids along faults in authigenic carbonates and their aggressive interaction (i.e. desorption) with shallower host rocks (e.g. clay-rich flysch) changed the chemistry of shallower fluids (< 3 km deep) surrounding or infiltrating along the fault zone, which was prone and close to the seismic rupture. In the case of the 2016 Amatrice

earthquake, for instance, geological and geophysical evidence showed an increase of fluid pressure right before the mainshock (De Luca et al., 2018; Petitta et al., 2018; Chiarabba et al., 2020). Hence, we speculate that, also in past seismic events, pre-seismic chemically-rich pressurized fluids may have infiltrated into the fault slip zone (Fig. 10b) at the time of earthquake rupture and contributed to form coseismic fluidal structures rich in exotic chemical elements (e.g. vanadium) such as the sub-Layer B' (Figs. 3e-3h), similarly to previously observed coseismic fluidal fault structures elsewhere (Rowe and Griffith, 2015). In the case of the Mt. Morrone Fault, the occurrence of fluid inclusions bearing traces of hydrocarbons (Fig. 6), which are common at intermediate crustal levels beneath the Mt. Morrone-Majella area (Iadanza et al., 2016), further corroborates the above-described process of pre-/co-seismic upwelling of mid-crustal fluids.

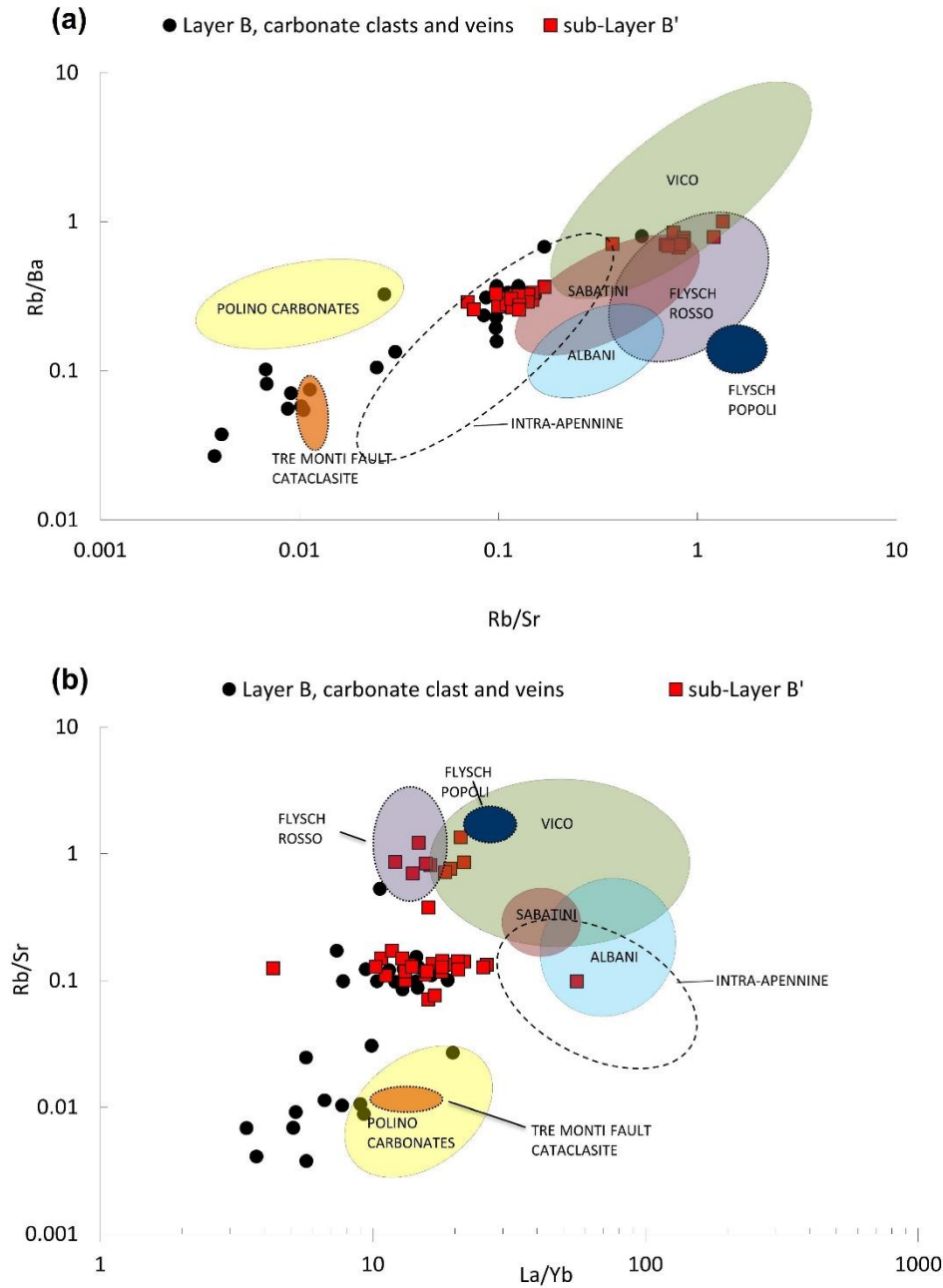


Figure 9. (a) La/Yb vs. Rb/Sr and (b) Rb/Sr vs. Rb/Ba ratios for the analyzed slip zones along the Mt Morrone Fault. Volcanoclastic product data are from Peccerillo (2005 and references therein; see also Supplemental Material) and are for the intra-Apennine and Roman magmatic provinces in central Apennines (i.e., Vico, Colli Albani, and Mt. Sabatini). Carbonate rock data are from Rosatelli et al. (2010) and are for the Polino carbonates in central Apennines (Calcare Massiccio Fm.). Flysch data are from Fiore et al. (2000) and from this work (Table S7). Tre Monti Fault data are from Smeraglia et al. (2016; Table S6).

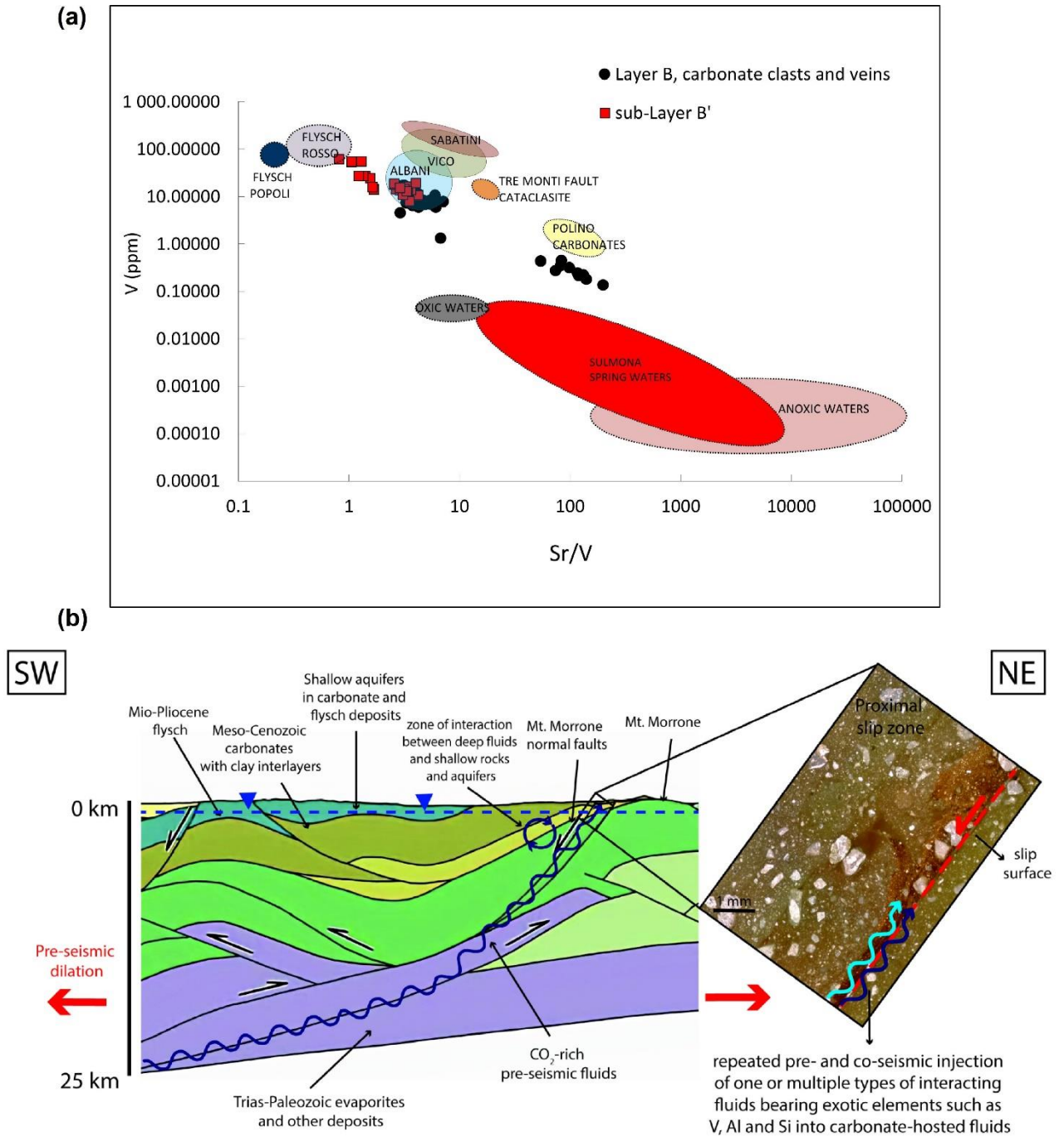


Figure 10. (a) Sr/V ratio vs. Sr contents of carbonates from the Mt Morrone Fault. Volcanoclastic product data are from Peccerillo (2005 and references therein; see also Supplemental Material) and are for the intra-Apennine and Roman magmatic provinces in central Apennines (i.e., Vico, Colli Albani, and Mt. Sabatini). Carbonate rock data are from Rosatelli et al. (2010) and are for the Polino carbonates in central Apennines (Calcare Massiccio Fm.). Flysch data are from Fiore et al. (2000) and from this work (Table S7). Tre Monti Fault data are from Smeraglia et al. (2016; Table S6). Oxic and anoxic fluid data are from Sappa et al. (2014) and Boschetti et al. (2005), respectively. (b) Schematic model of pre-seismic deep CO₂-rich fluid ascent along the Mt. Morrone Fault and consequent formation of V-rich fluidal micro-layers in the slip zone (i.e. sub-Layer B'). Geological cross-section is from Fig. 1 (Patacca et al., 2008).

4.10. Conclusions

As the knowledge of potential hydrogeochemical precursors of earthquakes advances (e.g. [Skelton et al., 2014](#); [Franchini et al., 2021](#)), a corroboration from exhumed paleofluid-related structures becomes necessary to understand the frequency and reliability of such potential precursors. This study and a previous one in Iceland ([Andr  n et al., 2016](#)) have this merit, indicating the future research necessary to validate, through fossil structures, potential hydrogeochemical precursors of earthquakes. At the same time, such a corroboration or validation is feasible only if paleofluid data come from clearly identified pre-/co-seismic structures (e.g. veins, micromineralizations, and related fluid inclusions). This study and several previous ones cited above contribute to the identification of paleofluid-related pre-/co-seismic microstructures along faults, where such microstructures are therefore fundamental not only in the understanding of fault friction or healing processes but also in the advancing the knowledge of earthquake precursory signals.

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Supplemental Material for:

“Micro- to nano-scale structural and geochemical evidence of fluid-assisted coseismic slip along the seismogenic carbonate-hosted Mt. Morrone Fault, Italy: implications for earthquake hydrogeochemical precursors”

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Introduction

This supplement contains three main sections:

Section 1 is devoted to the methods used in this work to achieve the related aims.

Section 2 is devoted to nine supplemental figures (Figs. S1-S9) that support the results obtained in this work.

Section 3 is devoted to seven supplemental tables (Tables S1-S7) that bear all numerical data produced and/or used in this work. All these tables are also provided as external Excel files.

Section 1: Methods

Introduction

We collected hand samples from different portions of the Mt. Morrone principal slip zone (Fig. 2d) and prepared them for accurate microstructural and microanalytical examinations. The investigated slip zone is within a few (~8) centimeters from the principal slip surface, downward into the fault footwall (Figs. 2d-2g). In addition to visual, (micro)photographic, and high-resolution scanner inspections of the polished slabs, we further analyzed the thin sections and/or the slabs using the following techniques: transmitted-light optical microscopy (OM) and optical cathodoluminescence (CL); two types of field emission-scanning electron microscopy (FE-SEM) with energy dispersive spectroscopy (EDS); transmission electron microscopy (TEM) with selected area electron diffraction analysis (SAED). In addition to the EDS, we performed chemical analyses on the same thin sections and/or slabs using mass spectrometry (ICP-MS), electron probe micro-analyzer (EPMA), and laser ablation mass-spectrometry (LA-ICPMS). Additionally, we analyzed fluid inclusions on polished calcite mineralization using Raman spectroscopy. Table S1 shows a list of the polished thin sections and the techniques used for each.

Samples

Six oriented hand samples (MC1, MC2, MC4, MC5, MC6, and MC7; Table S1) were collected from the slip zones (distal and proximal) below the Mt. Morrone principal fault surface. The collected samples were cut normally to the fault surface along the slip direction. The resulting slabs (~10) were inspected visually as well as with magnifying glasses. They were also scanned using an Epson Perfection V370 high-resolution scanner available at the Department of Earth Sciences, Sapienza University of Rome (Italy). Some slab areas in proximity of the fault plane were chosen to prepare eight circular thin-sections of 2.5 cm of diameter and of ~80 μm of thickness each, as well as a rectangular thin-section of 5 x 2 cm and ~30 μm in thickness for analytical purposes. All slabs and thin-sections were polished using an abrasive paper and diamond-based powders. Some thin-sections were re-thinned down to 30 μm or less after the first round of analyses to be re-analyzed with transmitted-light optical microscopy. In addition, three circular thin sections of 2.5 cm of diameter and ~30 μm of thickness each were glued with a heat-sensitive glue and prepared for transmission electron microscope analyses (Table S1).

Optical microscopy and cathodoluminescence (CL)

Optical microscope analyses of thin-sections were performed using a Zeiss Axiophot transmitted-light optical microscope at the Department of Earth Sciences, Sapienza University of Rome (Italy). The analyses

were conducted to investigate the petrography and deformations of the fault rocks (fabric, foliations, grain size variations, and preferred orientation of the clasts) at the micro-scale. A set of microphotographs were taken using an Olympus C4040 camera in order to create a map of each thin section by assembling all the microphotographs.

Cathodoluminescence analyses were performed on two thin-sections (2.1 and 5.2) about 30- μm thick with a CITL Cold Cathode Luminescence 8200 mk3 optical cathodoluminescence microscope at the Optical Laboratory of the Geosciences Department of the University of Padua (Italy). This technique is widely used in the study of intergranular cements of sedimentary rocks, either diagenetic or hydrothermal, and of fault rocks. In our case, the aim of the analysis was to detect different luminescence levels within the ultracataclasites of the Mt. Morrone slip zones due to the presence of trace elements derived by the interaction of the rocks with deep fluids (Pierson, 1981; Reed, 2005). As written also in the main text, the analyzed samples showed very low luminescence levels. This could be due to the very fine-grained nature of the analyzed fault rocks and/or the absence of significant quantities of cement.

Field emission-scanning electron microscopy (FE-SEM) with energy dispersive spectroscopy (EDS) and electron probe micro-analyzer (EPMA)

Micro- structural and semiquantitative chemical analyses were performed using both the JEOL JSM-6500F field emission scanning electron microscope (FE-SEM) at the Istituto Nazionale di Geofisica e Vulcanologia (INGV) in Rome (Italy) and the thermal Zeiss Merlin Gemini 2 field-emission scanning electron microscope (FE-SEM) at the CERTEMA Multidisciplinary Laboratory in Grosseto (Italy). The analyzed thin-sections were coated with 10 nm of graphite to avoid drifting and image artifacts caused by charging of the sample surface. The former instrument (JEOL) was used for imaging both through secondary electrons (SE) and through back-scattered electrons (BSE). Higher-resolution images and semiquantitative analyses were collected using the instrument at the CERTEMA Laboratory calibrated using the co-energy peak position.

Chemical quantitative analyses and elemental mapping were performed using energy dispersive spectroscopy (EDS) within the two aforementioned FE-SEM instruments and also using the JEOL JXA 8200 SuperProbe Electron Probe MicroAnalyzer (EPMA) at the Istituto Nazionale di Geofisica e Vulcanologia (INGV) in Rome (Italy) to determine the chemistry of clasts, matrix, and vein/mineralization of the polished samples in terms of major (Si, Ca, Fe, Mg, Al, Na and K) and trace elements (Sr, Ni), benchmarked against a set of natural and synthetic standards such as orthoclase for K_2O , albite for Na_2O , SiO_2 , and Al_2O_3 , apatite for CaO, forsterite for MgO , pyrite for FeO , celestine for SrO , and metallic nickel for NiO . An accelerated voltage of 15 kV and beam current of 7.5 nA were used along with a spot beam of 2-3 μm of diameter. Measurements were performed on individual clasts, on the surrounding matrix, and along transects to investigate potential chemical heterogeneities.

Transmission electron microscopy (TEM) with selected area electron diffraction analysis (SAED)

TEM observations were performed at the Dipartimento di Scienze Fisiche, della Terra e dell'Ambiente, Siena University (Italy), through the JEOL 2010 microscope working at 200 kV, with ultra-high resolution (UHR) pole piece and point-to-point resolution of 0.19 nm. The microscope is equipped with semi-STEM control and ultra-thin window energy dispersive spectrometer (EDS–ISIS Oxford). Data were recorded by an Olympus Tengra CCD camera (2k x 2k x 14 bit). Films were extracted from polished rock thin sections and deposited on TEM copper (Cu) grids, selecting all the most significant sites, i.e. the carbonate clasts far from the principal slip zone, the ultrafine material in the proximal slip zone, and the amorphous films around some carbonate clasts. Selected grids were thinned by Ar⁺ ion milling using both Gatan Dual Ion Mill and PIPS.

Raman spectroscopy

Raman spectra were acquired using the Horiba LabRam HR 800 spectrometer at the Department of Science, Roma Tre University (Italy). Data were collected by using a 600 grooves/mm spectrometer grating and a CCD detector. A Nd-YAG laser at 532 nm (green laser) was used as the light source with 60 mW laser power, with a confocal hole of 300 μm , slit of 200 μm , and an exposure time of 60 s. The Raman scattering was collected by a 100 $\times$ objective and $\sim 5 \mu\text{m}^2$ spot size on the polished sample surface over a range from 200 to 4000 cm^{-1} . Two to three measurements were performed on each inclusion to verify the reproducibility of the acquired spectrum.

Laser ablation mass-spectrometry (LA-ICPMS)

Trace elements concentrations of selected areas in the polished thin-sections were measured at the Istituto Nazionale di Geofisica e Vulcanologia (INGV) in Palermo (Italy) with a GeoLasPro 193nm ArF Excimer laser ablation (LA) system, connected to an Agilent 7500ce quadrupole ICP–MS. The analyses were performed with a constant laser repetition rate of 10 Hz, a fluency of 15 J/cm² and a He flux of 0.8 L/min in the ablation cell.

Each analysis was carried out with a 44- μm spot, for a total analysis time of 2 min per spot, including 1 min of background acquisition. MACS3 carbonate standard was used as external standard and was measured at the beginning, in the middle, and at the end of each analytical sequence. ⁴³Ca, estimated by SEM measurements, was used as the internal standard. The data were processed using the Glitter program (Van Achterbergh et al. 2001). The accuracy of the analyses (RSD%) was calculated by repeated analyses of the USGS basaltic reference glass BCR-2G and resulted to be $\leq 15\%$ for all the elements except Ti and Tm, for

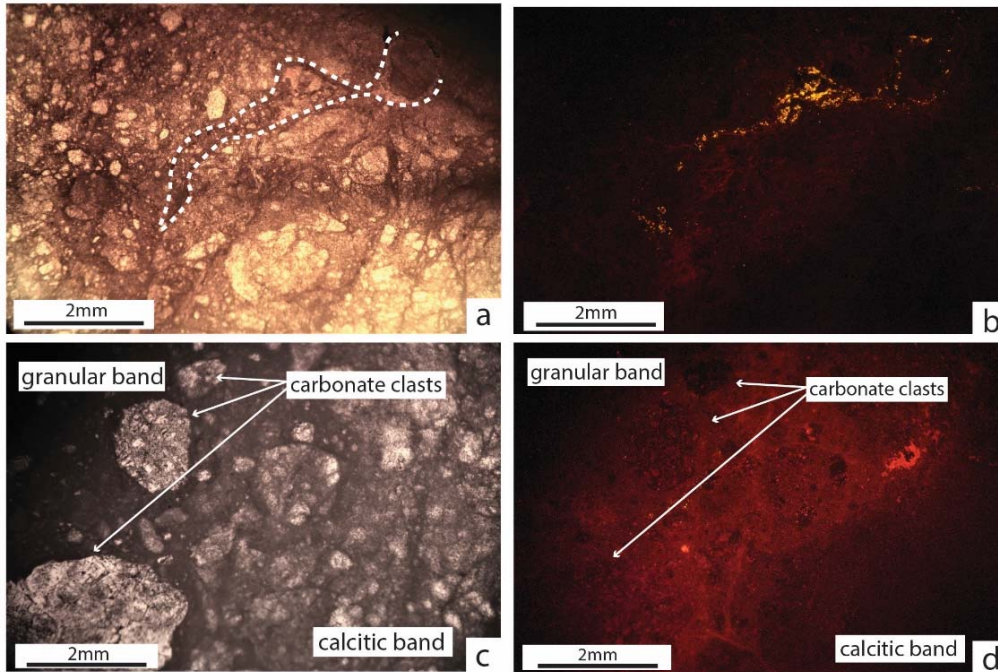
which accuracy was $\leq 20\%$. The precision was calculated by repeated analyses of the MACS3 carbonate standard and resulted to be $\leq 20\%$ for all the elements except B and Cs. Data of volcanoclastic products from intra-Apennine and Roman magmatic provinces (Vico, Colli Albani and Mt Sabatini; Figs. 9 and 10a) are from Fornaseri et al. (1963), Cundari, (1979), Peccerillo et al. (1984), Barbieri et al. (1988), Trigila et al. (1995), Conticelli et al. (1997, 2002), Freda et al. (1997), Perini et al. (1997, 2004), and Peccerillo (2005). Data of Polino carbonates are from Rosatelli et al. (2010).

Inductively coupled plasma-mass spectrometry (ICP-MS)

Chemical analysis of minor elements was performed on the bulk rock using a mass spectrometer ICP-MS (X Series 2 Thermo Fisher Scientific) at the Geochemical Laboratory, Department of Earth Sciences, Sapienza University of Rome (Italy). For this analysis, we considered the upper part (2 cm from the fault surface) of the hand samples MC2, MC5, and MC7. The samples (< 2 g each) were crushed and quartered. A portion of each sample (0.250 g) was treated with hydrochloric acid and, once all the acid evaporated, the solid residue was diluted in 50 ml of acidified water with HNO_3 . The solution was, then, analyzed with the inductively coupled plasma-mass spectrometer (ICP-MS). We used an internal standard, Rh, to correct the ICP-MS instrumental drift. We used ultrapure water (Millipore, Milli-Q, 16 $\text{M}\Omega$ cm) to prepare blanks, standard solutions, and sample dilutions. The analytical accuracy of this method ranges between 2% and 5% (Nigro et al., 2017).

Section 2: Supplementary Figures

Distal slip zone



Proximal slip zone

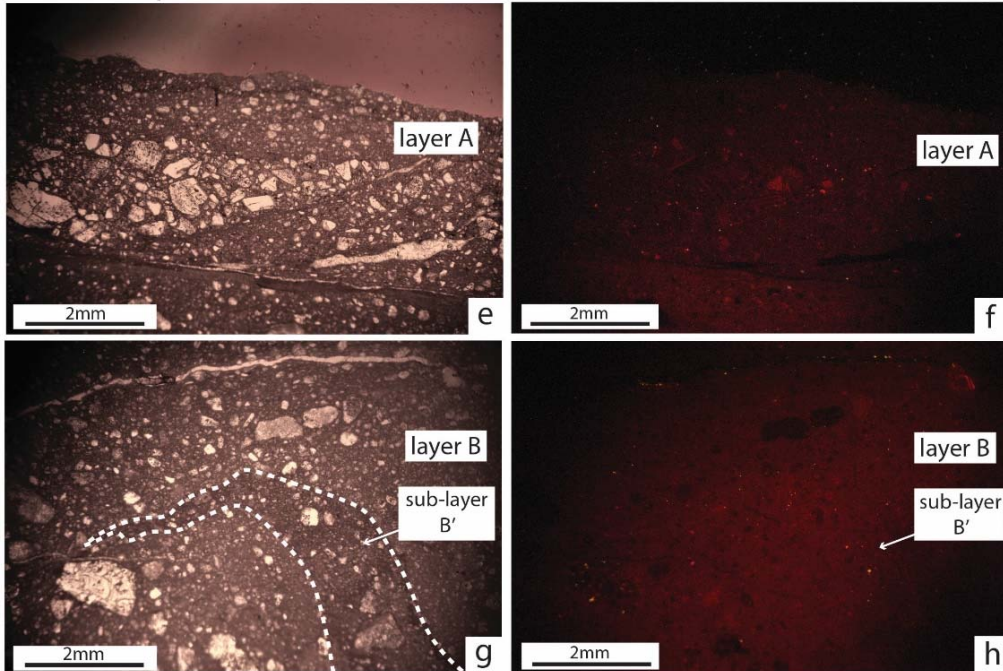


Figure S1. Optical microscope and cathodoluminescence (CL) images of distal (a-d; thin section 2.1) and proximal (e-h; thin section 5.3) slip zones. (a) Optical microscope image of an injection of the granular band in the calcite band in the distal slip zone (thin section 2.1). (b) Image corresponding to (a) under CL showing the calcite bands with a dark red matrix and completely black carbonate clasts floating inside. The calcite bands contrast with the granular bands, which show a matrix with a very dark red luminescence and some bright yellow particles scattered inside. (c) Detail of a boundary between the calcite band and the granular band. (d) Image corresponding to (c) under CL. (e) Optical microscope image of Layer A. (f) Image corresponding to (d) under CL. The layer shows a uniform dark red color. (g) Optical microscope image of the Layer b and the fluidized sub-Layer B'. (h) Image corresponding to (g) under CL with a uniform dark red color.

DISTAL SLIP ZONE

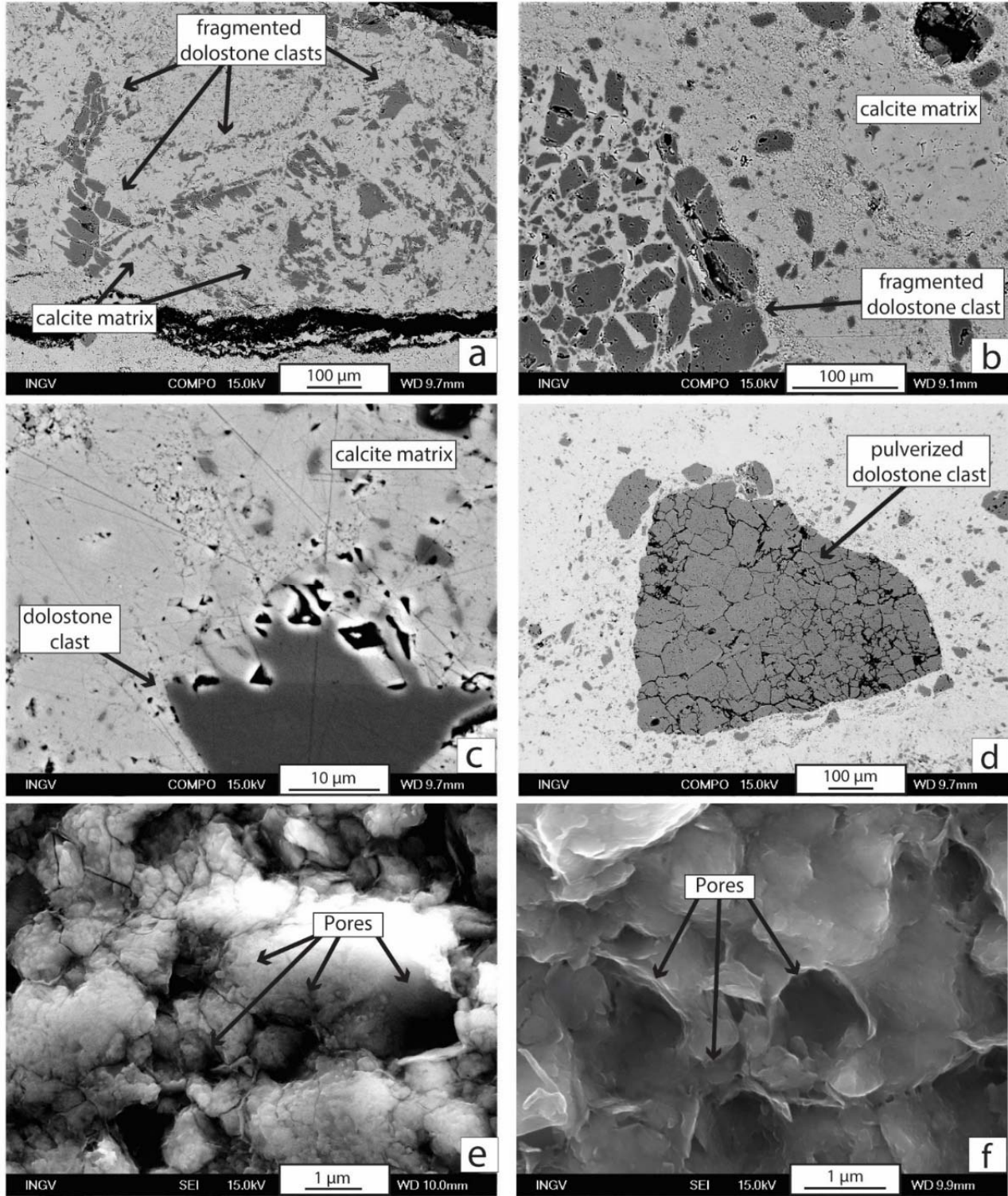


Figure S2. FE-SEM images. (a) Fragmented dolostone clasts embedded by the calcite matrix forming the white bands in the distal slip zone (thin section 2.1). (b) Exploded-like (i.e., pulverized) dolostone clast permeated by calcite matrix (thin section 2.1) (c) Boundary of a dolostone clast blending into the calcite matrix (thin section 6). (d) Exploded-like (i.e., pulverized) dolostone clast non permeated by the calcite matrix (thin section 6). (e and f) Secondary electron images of micro-pores occurring in the matrix of red bands within the distal slip zone (thin section 6 and 2.2).

DISTAL SLIP ZONE - Al- Si-rich minerals/matrix

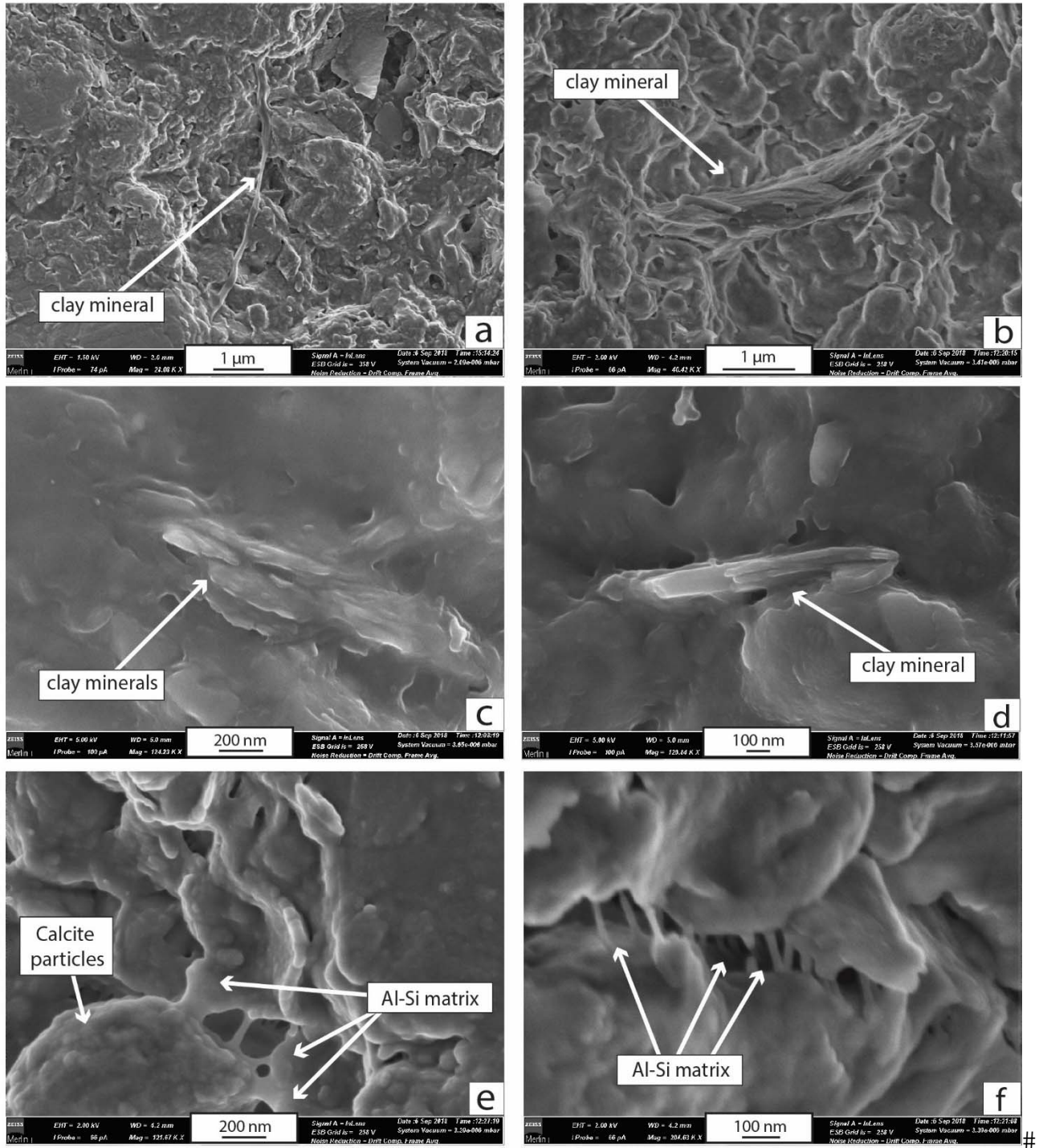


Figure S3. FE-SEM images (thin section 2.2). Habits of the nanometric clay minerals in the red bands of the distal fault core. These minerals usually encompass dolomite or calcite clasts. (a-d) Nanotubular elongated phyllosilicates. (e and f) Fibrous and stringy texture of strained phyllosilicates.

PROXIMAL SLIP ZONE

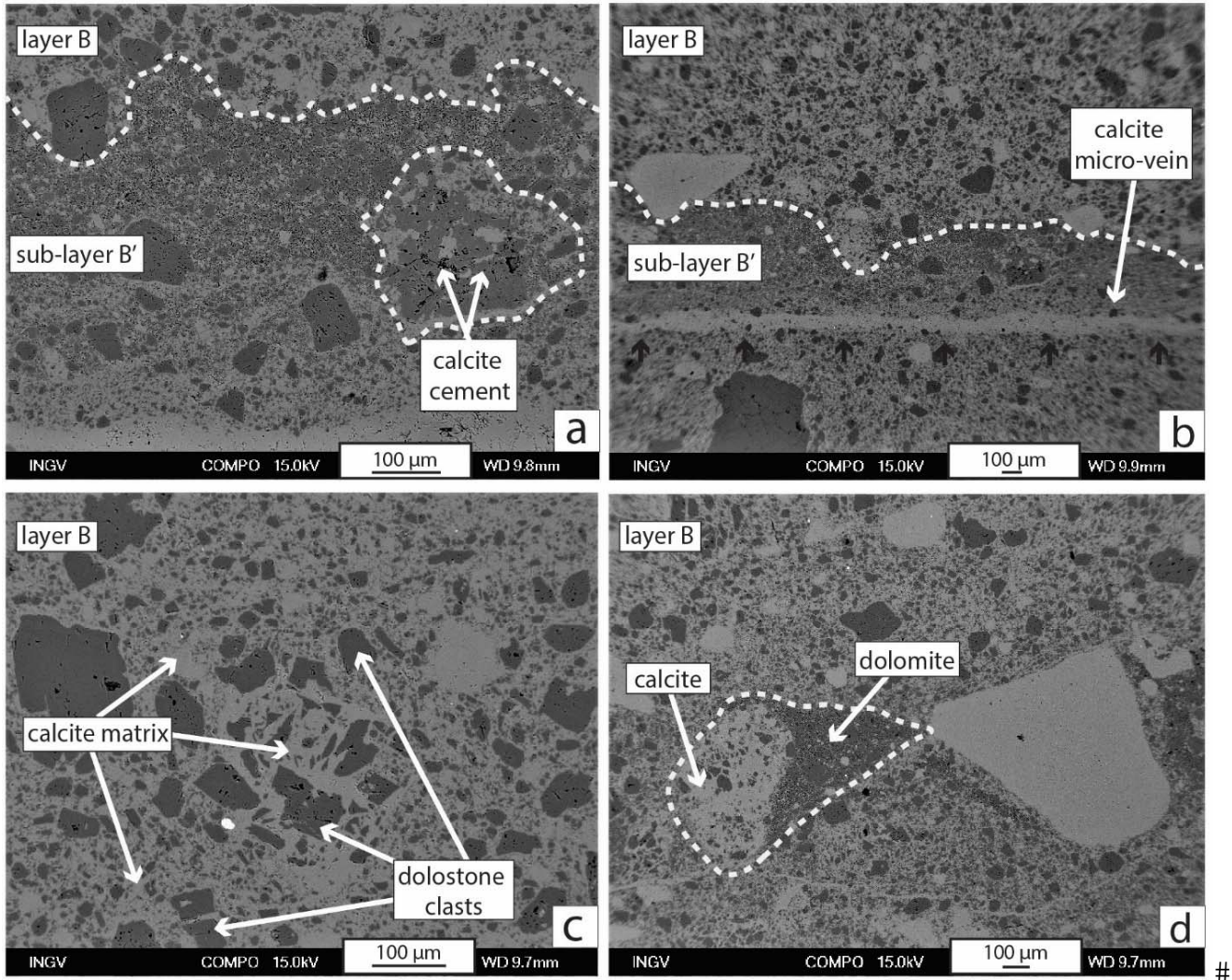


Figure S4. FE-SEM images of the proximal slip zone (thin section 5.2). (a) The sub-Layer B' embeds, in its matrix, carbonate clasts of different sizes (10-100 μm). The largest one on the right shows evidence of dissolution. (b) The sub-Layer B' extends into the Layer B with a wavy structure above a calcite micro-vein, which marks the boundary between Layer B and the underlying Layer C. (c) Dolostone clasts (< 100 μm) embedded in a calcite matrix in Layer B. (d) Calcite and dolomite clasts (up to 600 μm) of Layer B, in places embedded in an ultra-thin dolomite matrix.

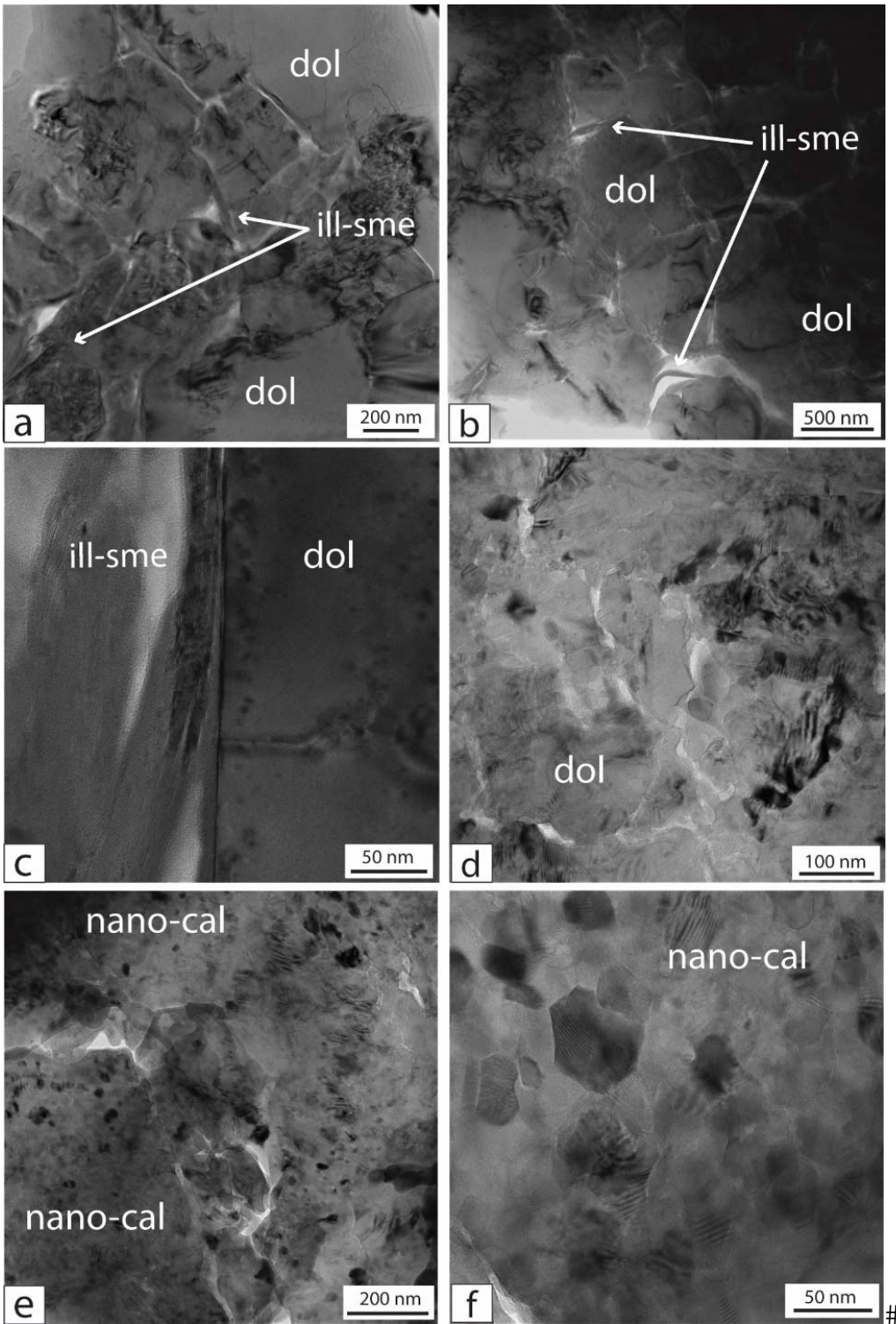


Figure S5. TEM images of the distal slip zone (a, b, c) (thin section 2.1a and 2.2 a) and the proximal slip zone (d, e, f) (thin section 5.2). (a, b) Dolomite nanoclusters (~ 500 nm in size) of the distal slip zone produced by grain size reduction processes and enveloped by ultrathin films of layered phyllosilicates (illite-smectite). (c) Detail of a dolomite nanoclast boundary characterized by the occurrence of ultrathin flakes of phyllosilicates such as illite-smectite. (d) Dolomite nanoclusters in the proximal slip zone are characterized by highly anhedral and lobate habit and are typically associated with ultrathin films of amorphous material. (e) Differently from what observed in the distal slip zone, dolomite nanoclusters (~500 nm) display a heterogeneous TEM contrast, suggesting the occurrence of calcite nanocrystals, a few tens of nm in size, in variable crystal orientation. (f) Detail of calcite nanocrystalline portions characterized by compact polygonal boundaries.

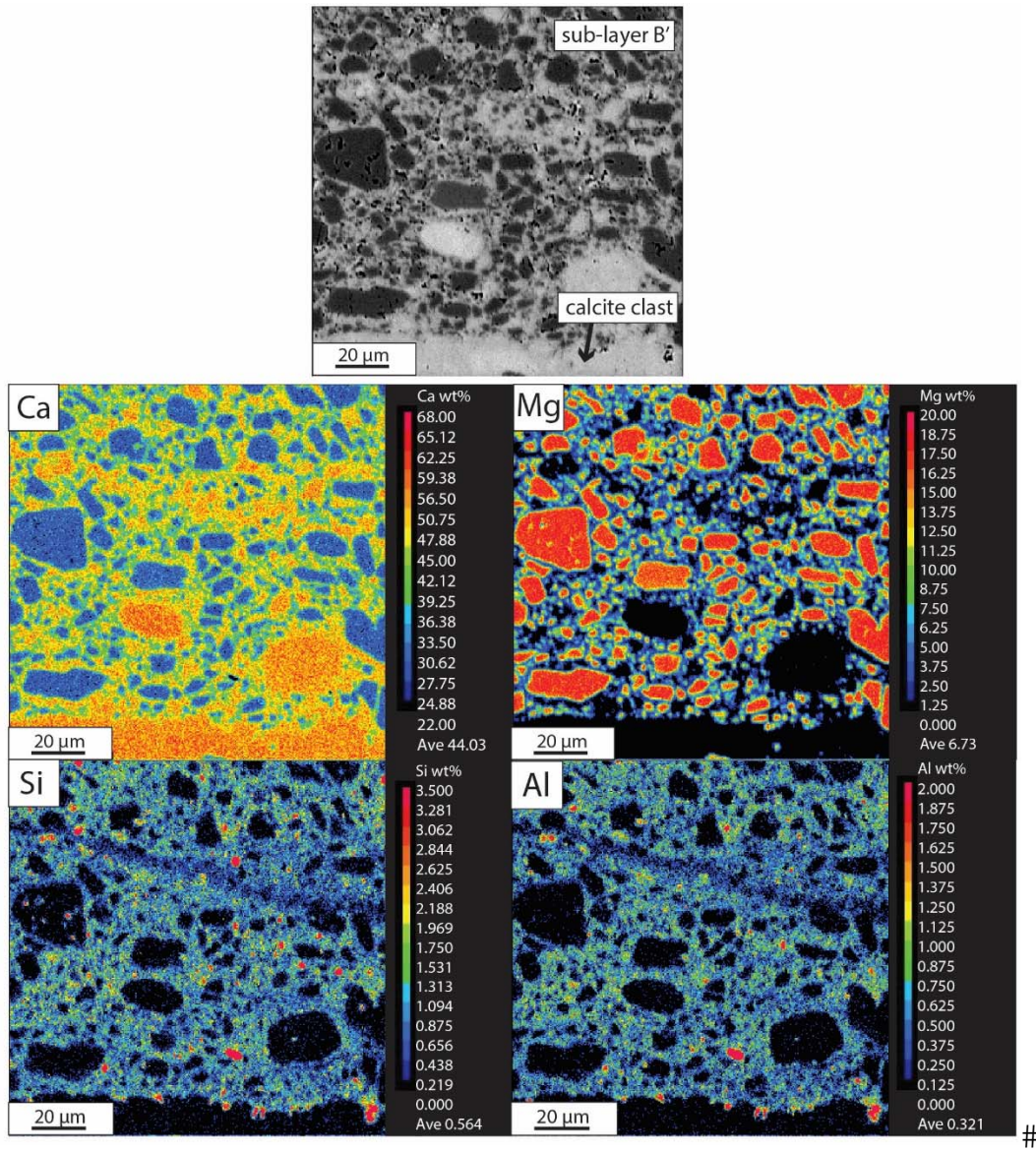


Figure S6. SEM image (top) and four EDS maps (bottom) showing the chemical composition of the sub-Layer B' (proximal slip zone, thin section 5.1). The clasts have Mg- and a Ca-rich borders/rims and are embedded in a Si- and Al-rich matrix, which contains also large amounts of Ca and Mg. Toward the bottom of all the five images, the boundary contact between sub-Layer B' and Layer C is marked by a compact calcite mineralization.

#

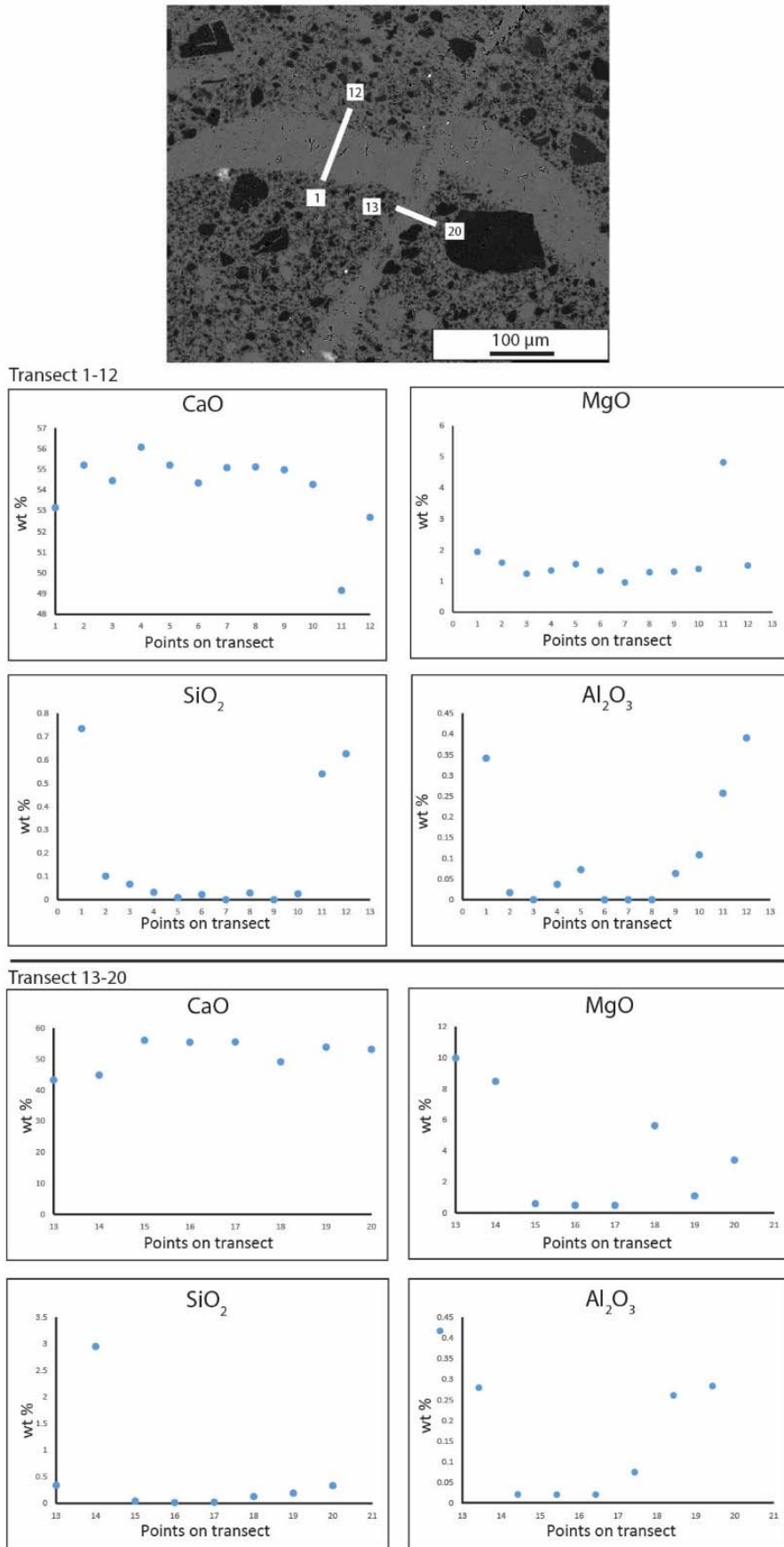


Figure S7. SEM image (top) and eight diagrams (bottom) from two chemical transects (see 1-12 and 13-20 tracks in the SEM image) performed through laser ablation (LA-ICPMS) in the distal slip zone (thin-section 4). In the SEM image, note a thin calcite vein displacing a previous thick calcite vein.#

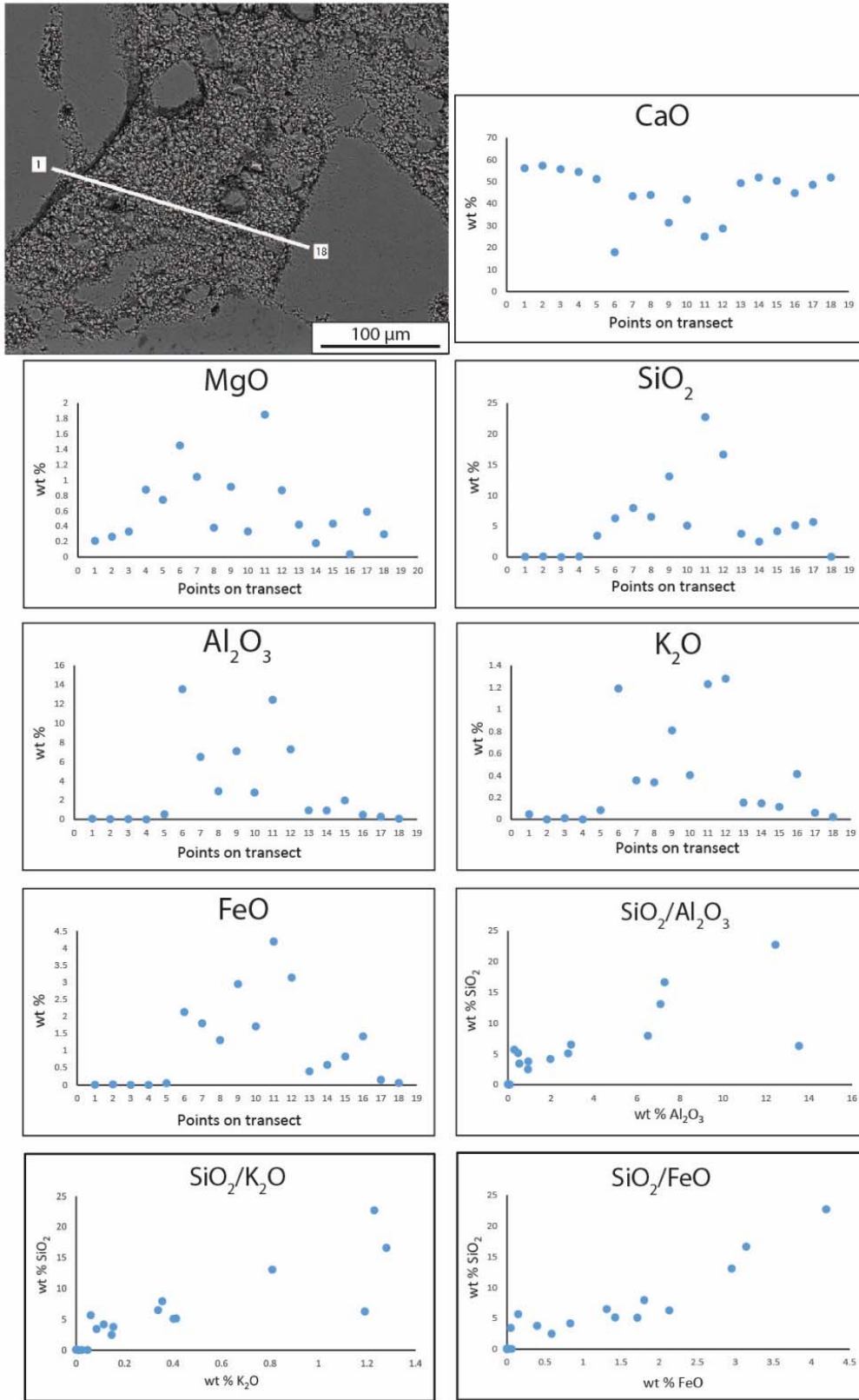


Figure S8. SEM image (top left) and nine diagrams (bottom) from one chemical transect (see 1-18 track in the SEM image) performed through laser ablation (LA-ICPMS) in the distal slip zone (thin-section 2.2). In the SEM image, note a granular injection of Al- Si-rich material (sub-Layer B') in between calcite blocks.

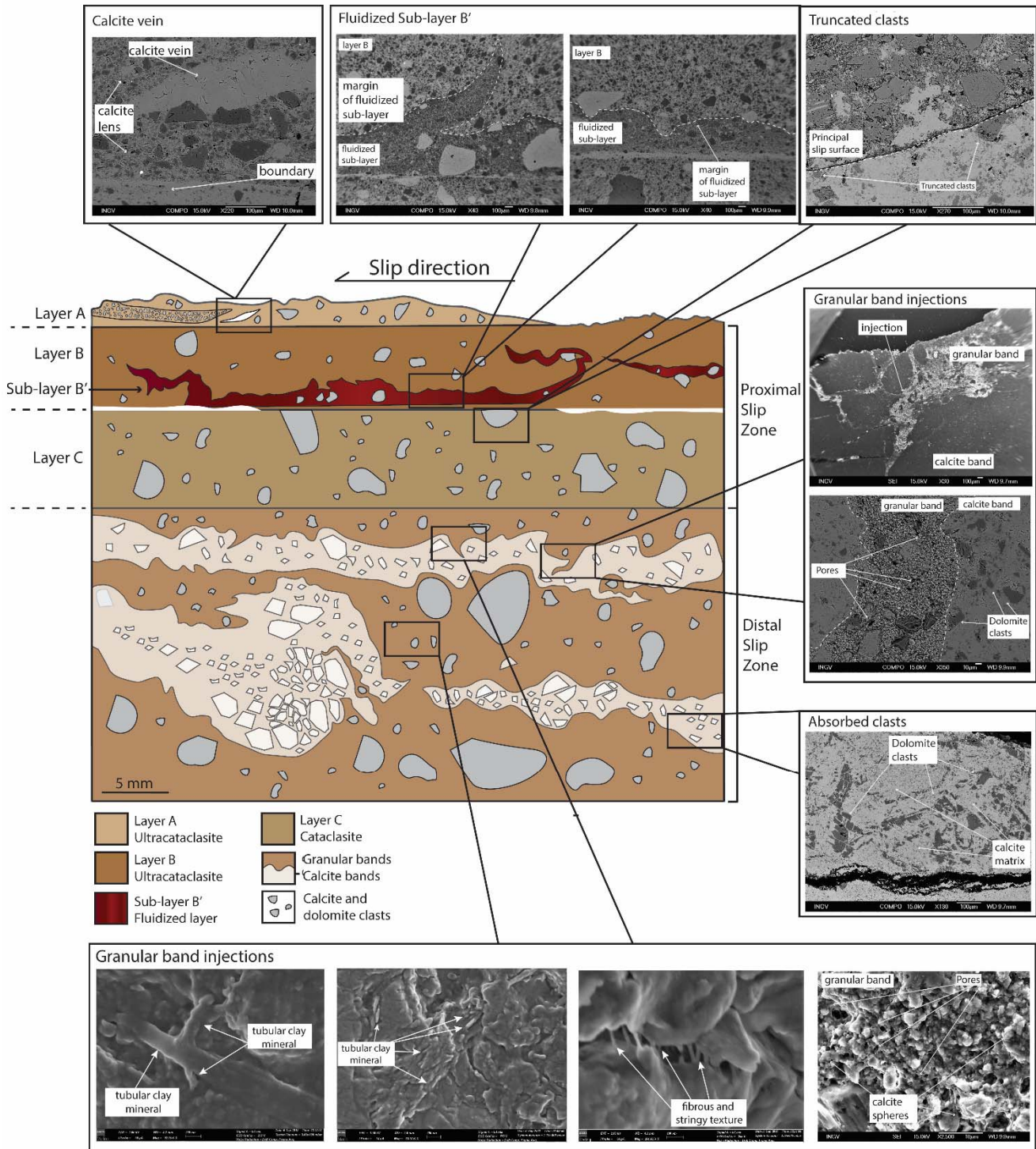


Figure S9. Synthetic reconstruction of the Mt. Morrone Fault-related slip zone highlighting the main micro- and nano-structures that were identified through FE-SEM analyses.

Section 3: Supplementary Tables

Table S1. Summary of the analyses performed on each sample and thin-section. ICP-MS stays for inductively coupled plasma-mass spectrometry; OM for optical microscopy; SEM stays for field emission-scanning electron microscopy (FE-SEM) with energy dispersive spectroscopy (EDS); EPMA is electron probe microanalyzer; CL is optical cathodoluminescence; LA-ICPMS is laser ablation-inductively coupled plasma-mass spectrometry; and TEM is transmission electron microscopy with selected area electron diffraction analysis (SAED); Raman is Raman spectroscopy. This table is also provided as external Excel file.

Sample	ICP-MS	thin-section	slip zone	OM	SEM	EPMA	CL	RAMAN	TEM	LA-ICPMS
MC1		2	Distal	X	X	X				
MC2	X		Distal							
		2.1	Distal	X	X	X	X			
		2.1a	Distal	X					X	
		2.2	Distal	X	X	X				X
		2.2a	Distal	X					X	
MC4		4	Distal	X	X	X				
MC5	X		Proximal							
		5.1	Proximal	X	X	X		X		X
		5.2	Proximal	X	X	X		X		X
		5.2a	Proximal	X					X	
		5.3	Proximal	X	X	X	X	X		
MC6		6	Distal	X	X	X				
MC7	X	7	Proximal	X						

Table S2. Trace element analyses (reported in ppm) obtained by using the ICP-MS (X Series 2 Termo Fisher Scientific). The table shows the number of measurements (1,2,3), the average of measurements (x), and the standard deviation (σ and %RSD) for each hand sample analyzed (MC2, MC5, MC7). This table is also provided as external Excel file.

MC2	Li	Be	B	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1	1.702	0.097	66.41	2270	10.96	8.079	82.9	2209	1.902	17.73	3.977	14.19	0.825	22.18
2	1.718	0.088	68.85	2299	10.73	7.955	87.46	2202	1.928	17.98	3.946	14.33	0.823	21.06
3	1.715	0.1	69.17	2307	10.53	7.865	90.6	2184	1.888	17.38	3.88	14.11	0.805	21.42
X	1.712	0.095	68.14	2292	10.74	7.966	86.99	2198	1.906	17.7	3.934	14.21	0.818	21.55
Σ	0.008	0.006	1.509	19.84	0.218	0.107	3.87	12.77	0.02	0.305	0.049	0.11	0.011	0.571
%RSD	0.482	6.388	2.214	0.866	2.032	1.349	4.449	0.581	1.072	1.721	1.248	0.776	1.315	2.65

MC2	Rb	Sr	Mo	Ag	Cd	In	Sn	Sb	Cs	Ba	W	Hg	Pb	U
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1	3.926	51.15	0.245	1.56	0.233	0.006	0.614	0.171	0.8	16.69	0.168	-0.003	27.82	0.583
2	3.894	52.84	0.237	1.6	0.238	0.006	0.615	0.174	0.818	17.05	0.172	0.003	29.94	0.621
3	3.88	54.23	0.24	1.636	0.244	0.006	0.639	0.176	0.804	17.1	0.18	0.001	31.68	0.648
X	3.9	52.74	0.241	1.599	0.238	0.006	0.623	0.174	0.807	16.95	0.173	0	29.81	0.618
Σ	0.024	1.546	0.004	0.038	0.005	0	0.014	0.002	0.009	0.226	0.006	0.003	1.935	0.033
%RSD	0.603	2.932	1.823	2.386	2.294	4.038	2.273	1.397	1.156	1.331	3.549	1224	6.489	5.327

MC5	Li	Be	B	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1	1.186	0.291	87.28	1876	14.49	13.44	94.69	2124	1.877	40.33	8.641	92.8	1.166	25.56
2	1.177	0.279	86.29	1870	14.55	13.37	93.98	2097	1.88	40.02	8.505	91.26	1.171	25.38
3	1.214	0.291	88.6	1899	14.54	13.38	93.72	2117	1.876	40.2	8.643	91.51	1.19	26.09
x	1.192	0.287	87.39	1882	14.53	13.4	94.13	2113	1.878	40.18	8.596	91.86	1.176	25.67
σ	0.019	0.007	1.158	15.06	0.034	0.041	0.504	13.6	0.002	0.153	0.079	0.824	0.013	0.37
%RSD	1.606	2.395	1.326	0.8	0.234	0.308	0.535	0.644	0.131	0.38	0.922	0.896	1.071	1.439

MC5	Rb	Sr	Mo	Ag	Cd	In	Sn	Sb	Cs	Ba	W	Hg	Pb	U
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1	2.686	57.9	0.421	0.519	0.451	0.007	0.62	0.212	0.516	24.16	0.248	0.02	31.17	1.132
2	2.632	57.99	0.416	0.538	0.45	0.006	0.603	0.207	0.52	23.98	0.248	0.023	31.14	1.131
3	2.658	59.49	0.413	0.512	0.459	0.007	0.623	0.209	0.519	24.18	0.257	0.009	31.88	1.159
x	2.659	58.46	0.417	0.523	0.453	0.007	0.615	0.209	0.518	24.11	0.251	0.017	31.4	1.141
σ	0.027	0.889	0.004	0.014	0.005	0	0.011	0.003	0.002	0.108	0.005	0.007	0.418	0.016
%RSD	1.001	1.52	0.914	2.599	1.151	6.994	1.798	1.274	0.442	0.449	2.141	42.35	1.331	1.368

MC7	Li	Be	B	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1	1.19	0.379	62.67	1735	13.06	7.758	73.88	1908	1.576	12.04	3.014	7.859	1.134	23.19
2	1.202	0.374	64.31	1744	13.17	7.758	73.52	1902	1.616	12.19	3.024	7.82	1.151	24.03
3	1.208	0.371	64.9	1762	13.31	7.831	73.62	1907	1.61	12.33	3.03	7.774	1.147	24.48
x	1.2	0.375	63.96	1747	13.18	7.782	73.68	1906	1.6	12.19	3.022	7.817	1.144	23.9
σ	0.009	0.004	1.155	14.04	0.121	0.042	0.185	3.083	0.022	0.148	0.008	0.042	0.009	0.659
%RSD	0.79	1.082	1.805	0.804	0.921	0.544	0.251	0.162	1.358	1.213	0.27	0.543	0.778	2.757

MC7	Rb	Sr	Mo	Ag	Cd	In	Sn	Sb	Cs	Ba	W	Hg	Pb	U
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1	2.554	57.55	0.347	0.358	0.382	0.013	0.52	0.315	0.49	30.1	0.22	0.014	28.14	1.141
2	2.532	57.64	0.363	0.367	0.377	0.012	0.533	0.316	0.503	30.1	0.227	0.001	28.26	1.152
3	2.549	58.22	0.355	0.351	0.401	0.012	0.527	0.309	0.5	30.4	0.219	0.011	28.37	1.161
x	2.545	57.8	0.355	0.358	0.387	0.012	0.527	0.313	0.498	30.2	0.222	0.008	28.26	1.151
σ	0.012	0.363	0.008	0.008	0.012	0	0.007	0.004	0.007	0.173	0.005	0.007	0.115	0.01
%RSD	0.46	0.628	2.349	2.201	3.197	3.928	1.267	1.255	1.362	0.573	2.118	80.43	0.408	0.839

Table S3. Quantitative chemical analyses (reported in wt %) on specific spots from the analyzed thin-sections obtained by using a JEOL JXA 8200 SuperProbe Electron Probe MicroAnalyzer (EPMA). The table shows: the measurement area (a, b, c ...) for each thin section, the number of point measurements on each area, the mineral phase and the average of the measurements of the oxides for the major elements (K₂O, SiO₂, CaO, MgO, Al₂O₃) and for some minor elements (Na₂O, SrO, FeO, NiO). This table is also provided as external Excel file.

Proximal slip zone

Thin-section	Meas.#	Phase#	K ₂ O#	Na ₂ O#	SiO ₂ #	CaO#	MgO#	SrO#	FeO#	Al ₂ O ₃ #	NiO#	Total#
Thin-section 5.1#	A#	3#	0.02±0.02#	0.00±0.00#	0.00±0.00#	56.06±2.38#	0.73±0.15#	0.00±0.00#	0.11±0.11#	0.11±0.00#	0.00±0.00#	57.26±2.13#
	#	Calcite#	0.00±0.00#	0.05±0.00#	0.00±0.00#	31.06±0.00#	21.95±0.00#	0.09±0.00#	0.00±0.00#	0.07±0.00#	0.03±0.00#	53.23±0.00#
	B#	3#	0.01±0.01#	0.01±0.01#	0.00±0.00#	55.42±0.37#	0.59±0.24#	0.02±0.02#	0.03±0.03#	0.12±0.12#	0.00±0.00#	56.29±0.23#
	#	Dolomite#	0.00±0.00#	0.00±0.00#	0.08±0.02#	22.50±0.17#	21.02±0.47#	0.04±0.03#	0.00±0.00#	0.05±0.03#	0.03±0.03#	43.72±0.23#
Thin-section 5.2#	Meas.#	Phase#	K ₂ O#	Na ₂ O#	SiO ₂ #	CaO#	MgO#	SrO#	FeO#	Al ₂ O ₃ #	NiO#	Total#
	4#	Calcite#	0.02±0.02#	0.04±0.03#	0.00±0.00#	54.98±0.44#	0.50±0.06#	0.00±0.00#	0.15±0.15#	0.18±0.16#	0.02±0.02#	56.05±0.42#
	#	Calcite#	0.00±0.00#	0.01±0.01#	0.01±0.01#	31.35±0.56#	21.50±0.91#	0.02±0.02#	0.01±0.01#	0.01±0.01#	0.00±0.00#	52.90±1.48#
	2#	Dolomite#	0.00±0.00#	0.01±0.01#	0.01±0.01#	31.35±0.56#	21.50±0.91#	0.02±0.02#	0.01±0.01#	0.01±0.01#	0.00±0.00#	52.90±1.48#
Thin-section 5.3#	Meas.#	Phase#	K ₂ O#	Na ₂ O#	SiO ₂ #	CaO#	MgO#	SrO#	FeO#	Al ₂ O ₃ #	NiO#	Total#
	2#	Calcite vein#	0.00±0.00#	0.01±0.00#	0.03±0.01#	53.51±1.07#	0.76±0.17#	0.02±0.02#	0.09±0.02#	0.06±0.04#	0.00±0.00#	54.47±1.17#
	#	Calcite clast#	0.00±0.00#	0.01±0.01#	0.00±0.00#	55.72±0.09#	1.08±0.18#	0.00±0.00#	0.00±0.00#	0.00±0.00#	0.01±0.01#	56.85±0.32#
	2#	Calcite clast#	0.00±0.00#	0.01±0.01#	0.00±0.00#	55.72±0.09#	1.08±0.18#	0.00±0.00#	0.00±0.00#	0.00±0.00#	0.01±0.01#	56.85±0.32#
Thin-section 6#	Meas.#	Phase#	K ₂ O#	Na ₂ O#	SiO ₂ #	CaO#	MgO#	SrO#	FeO#	Al ₂ O ₃ #	NiO#	Total#
	1#	Calcite#	0.02±0.00#	0.03±0.00#	0.01±0.00#	57.80±0.00#	0.54±0.00#	0.01±0.00#	0.00±0.00#	0.00±0.00#	0.00±0.00#	58.40±0.00#
	#	Calcite#	0.00±0.00#	0.00±0.00#	0.01±0.01#	31.23±0.53#	21.97±0.69#	0.05±0.05#	0.00±0.00#	0.13±0.06#	0.00±0.00#	53.43±0.26#
	3#	Dolomite#	0.00±0.00#	0.00±0.00#	0.01±0.01#	31.23±0.53#	21.97±0.69#	0.05±0.05#	0.00±0.00#	0.13±0.06#	0.00±0.00#	53.43±0.26#

Distal slip zone

Thin-section	Meas.	Phase	K ₂ O	Na ₂ O	SiO ₂	CaO	MgO	SrO	FeO	Al ₂ O ₃	NiO	Total
Thin-section 2	A	4	0.01±0.01	0.02±0.02	0.03±0.02	55.49±1.33	1.34±0.50	0.02±0.04	0.00±0.00	0.00±0.00	0.00±0.00	56.94±0.96
	2	Dolomite	0.02±0.01	0.02±0.02	0.00±0.00	32.51±0.88	20.66±0.05	0.01±0.01	0.01±0.01	0.01±0.01	0.03±0.03	53.29±1.02
	B	2	0.01±0.01	0.02±0.02	0.01±0.01	57.94±0.77	1.20±0.97	0.03±0.04	0.00±0.00	0.09±0.03	0.00±0.00	59.30±0.21
	4	Dolomite	0.02±0.02	0.01±0.01	0.29±0.27	34.10±2.01	19.38±1.48	0.01±0.01	0.08±0.11	0.25±0.35	0.00±0.00	54.15±1.68
	5	Calcite	0.01±0.03	0.03±0.03	0.01±0.01	57.26±0.96	0.52±0.16	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	57.94±1.19
	6	Dolomite	0.01±0.01	0.00±0.00	0.00±0.00	32.32±1.20	21.86±0.75	0.00±0.00	0.00±0.00	0.08±0.07	0.01±0.01	54.39±1.63
Thin-section 2.1	Meas.	Phase	K ₂ O	Na ₂ O	SiO ₂	CaO	MgO	SrO	FeO	Al ₂ O ₃	NiO	Total
	2	Calcite	0.00±0.00	0.00±0.00	0.32±0.16	55.86±0.16	0.56±0.09	0.01±0.01	0.08±0.00	0.19±0.08	0.05±0.03	57.04±0.14
Thin-section 2.2	Meas.	Phase	K ₂ O	Na ₂ O	SiO ₂	CaO	MgO	SrO	FeO	Al ₂ O ₃	NiO	Total
	2	Dolomite	0.00±0.00	0.00±0.00	0.00±0.00	31.75±0.94	20.88±0.88	0.00±0.00	0.02±0.02	0.06±0.06	0.00±0.00	52.76±0.09
Thin-section 4	Meas.	Phase	K ₂ O	Na ₂ O	SiO ₂	CaO	MgO	SrO	FeO	Al ₂ O ₃	NiO	Total
	2	Dolomite	0.01±0.01	0.01±0.01	0.02±0.02	34.46±2.98	19.07±2.03	0.02±0.01	0.01±0.02	0.05±0.04	0.00±0.00	53.65±0.98
Thin-section 6	Meas.	Phase	K ₂ O	Na ₂ O	SiO ₂	CaO	MgO	SrO	FeO	Al ₂ O ₃	NiO	Total
	7	Calcite	0.02±0.01	0.02±0.02	0.00±0.00	54.59±1.09	1.31±0.53	0.02±0.01	0.05±0.04	0.05±0.05	0.01±0.01	56.11±0.72
Thin-section 6	Meas.	Phase	K ₂ O	Na ₂ O	SiO ₂	CaO	MgO	SrO	FeO	Al ₂ O ₃	NiO	Total
	6	Dolomite	0.01±0.01	0.02±0.01	0.04±0.03	31.06±0.55	21.06±0.36	0.00±0.00	0.01±0.01	0.13±0.06	0.00±0.00	52.36±0.56
Thin-section 6	Meas.	Phase	K ₂ O	Na ₂ O	SiO ₂	CaO	MgO	SrO	FeO	Al ₂ O ₃	NiO	Total
	1	Calcite	0.02±0.00	0.03±0.00	0.01±0.00	57.80±0.00	0.54±0.00	0.01±0.00	0.00±0.00	0.00±0.00	0.00±0.00	58.40±0.00
Thin-section 6	Meas.	Phase	K ₂ O	Na ₂ O	SiO ₂	CaO	MgO	SrO	FeO	Al ₂ O ₃	NiO	Total
	3	Dolomite	0.00±0.00	0.00±0.00	0.01±0.01	31.23±0.53	21.97±0.69	0.05±0.05	0.00±0.00	0.13±0.06	0.00±0.00	53.43±0.26

Table S4. Quantitative chemical analyses (reported in wt %) on specific spots on transects from the analyzed thin-sections obtained by using a JEOL JXA 8200 SuperProbe Electron Probe MicroAnalyzer (EPMA). The table shows: the number of point measurements on each transect, the mineral phase and the measurements of the oxides of the major elements (K₂O, SiO₂, CaO, MgO, Al₂O₃) and some minor ones (Na₂O, SrO, FeO, NiO). This table is also provided as external Excel file.

Thin-section 2.1#	Phase#	K ₂ O#	Na ₂ O#	SiO ₂ #	CaO#	MgO#	SrO#	FeO#	Al ₂ O ₃ #	NiO#	Total#
1#	Calcite#	0.05#	0.04#	0.04#	56.14#	0.21#	0.00#	0.00#	0.08#	0.00#	56.57#
2#	Calcite#	0.00#	0.04#	0.09#	57.27#	0.27#	0.05#	0.02#	0.03#	0.00#	57.75#
3#	Calcite#	0.01#	0.00#	0.00#	55.76#	0.33#	0.00#	0.00#	0.03#	0.05#	56.18#
4#	Calcite#	0.00#	0.04#	0.08#	54.46#	0.88#	0.01#	0.00#	0.00#	0.05#	55.51#
5#	Calcite#	0.08#	0.47#	3.45#	51.24#	0.74#	0.00#	0.05#	0.53#	0.10#	56.67#
6#	Calcite#	1.19#	0.10#	6.30#	17.92#	1.45#	0.01#	2.13#	13.53#	0.04#	42.68#
7#	Calcite#	0.36#	0.06#	7.96#	43.43#	1.04#	0.00#	1.80#	6.50#	0.01#	61.16#
8#	Calcite#	0.34#	0.03#	6.52#	43.97#	0.38#	0.00#	1.31#	2.93#	0.01#	55.49#
9#	Calcite#	0.81#	0.02#	13.10#	31.35#	0.91#	0.08#	2.95#	7.09#	0.00#	56.31#
10#	Calcite#	0.40#	0.03#	5.10#	41.96#	0.33#	0.01#	1.71#	2.80#	0.00#	52.34#
11#	Dolomite#	1.23#	0.11#	22.73#	25.07#	1.85#	0.05#	4.19#	12.43#	0.05#	67.71#
12#	Dolomite#	1.28#	0.16#	16.64#	28.76#	0.87#	0.00#	3.14#	7.28#	0.04#	58.17#
13#	Calcite#	0.15#	0.00#	3.79#	49.39#	0.42#	0.00#	0.40#	0.94#	0.00#	55.10#
14#	Calcite#	0.15#	0.01#	2.50#	51.95#	0.18#	0.04#	0.59#	0.93#	0.00#	56.34#
15#	Calcite#	0.11#	0.19#	4.19#	50.42#	0.43#	0.00#	0.83#	1.97#	0.00#	58.15#
16#	Calcite#	0.41#	0.05#	5.15#	44.87#	0.04#	0.00#	1.42#	0.47#	0.05#	52.46#
17#	Calcite#	0.06#	1.44#	5.69#	48.59#	0.59#	0.06#	0.15#	0.29#	0.04#	56.91#
18#	Calcite#	0.02#	0.00#	0.04#	51.94#	0.30#	0.05#	0.06#	0.08#	0.07#	52.56#

Thin-section 2.2	Phase	K ₂ O	Na ₂ O	SiO ₂	CaO	MgO	SrO	FeO	Al ₂ O ₃	NiO	Total
1	Calcite	0.01	0.00	0.14	55.48	0.46	0.00	0.01	0.12	0.00	56.22
2	Calcite	0.07	0.02	0.87	29.43	0.20	0.00	0.18	0.48	0.00	31.25
3	Calcite	0.13	0.00	2.70	50.72	0.50	0.01	0.48	1.46	0.00	56.01
4	Calcite	0.10	0.06	1.45	52.92	0.65	0.00	1.33	0.95	0.00	56.46
5	Calcite	0.09	0.00	2.53	52.37	0.48	0.01	0.58	1.43	0.01	57.50
6	Calcite	0.12	0.00	2.26	52.14	0.42	0.02	0.35	1.20	0.03	56.53
7	Calcite	0.19	0.41	4.33	48.07	0.73	0.00	1.05	2.68	0.00	57.46
8	Calcite	0.08	0.09	1.99	52.30	0.57	0.03	0.13	0.93	0.00	56.12

Thin-section 4 Tran. 1-9	Phase	K ₂ O	Na ₂ O	SiO ₂	CaO	MgO	SrO	FeO	Al ₂ O ₃	NiO	Total
1	Calcite	0.00	0.00	0.10	55.20	1.59	0.00	0.05	0.02	0.03	57.00
2	Calcite	0.00	0.00	0.07	54.45	1.23	0.00	0.00	0.00	0.01	55.76
3	Calcite	0.00	0.02	0.03	56.07	1.34	0.03	0.02	0.04	0.00	57.55
4	Calcite	0.00	0.03	0.01	55.20	1.54	0.00	0.01	0.07	0.02	56.89
5	Calcite	0.02	0.03	0.02	54.34	1.33	0.04	0.00	0.00	0.08	55.86
6	Calcite	0.01	0.02	0.00	55.08	0.95	0.05	0.04	0.00	0.00	56.14
7	Calcite	0.01	0.06	0.03	55.12	1.28	0.00	0.00	0.00	0.01	56.51
8	Calcite	0.00	0.06	0.00	54.98	1.30	0.04	0.05	0.06	0.00	56.49
9	Calcite	0.00	0.03	0.03	54.27	1.39	0.01	0.00	0.11	0.00	55.83

Thin-section 4 Tran. 10-16	Phase	K ₂ O	Na ₂ O	SiO ₂	CaO	MgO	SrO	FeO	Al ₂ O ₃	NiO	Total
10	Calcite	0.03	0.05	0.34	43.25	9.98	0.02	0.52	0.40	0.00	54.59
11	Calcite	0.00	0.00	0.04	56.01	0.60	0.00	0.04	0.00	0.00	56.71
12	Calcite	0.00	0.02	0.02	55.41	0.50	0.01	0.05	0.00	0.00	56.01
13	Calcite	0.00	0.05	0.02	55.52	0.49	0.11	0.05	0.00	0.02	56.27
14	Calcite	0.02	0.00	0.13	49.13	5.63	0.03	0.01	0.05	0.00	55.00
15	Calcite	0.00	0.02	0.19	53.85	1.10	0.00	0.20	0.24	0.05	55.66
16	Calcite	0.01	0.04	0.33	53.15	3.41	0.02	0.52	0.26	0.00	57.74

Thin-section 5.1 Tran. 1-13	Phase	K ₂ O	Na ₂ O	SiO ₂	CaO	MgO	SrO	FeO	Al ₂ O ₃	NiO	Total
1	Calcite	0.01	0.00	0.04	55.19	0.40	0.01	0.04	0.06	0.00	55.74
2	Calcite	0.04	0.03	1.05	38.05	10.49	0.00	0.88	0.84	0.01	51.40
3	Calcite	0.09	0.02	1.08	35.62	2.93	0.04	0.06	0.00	0.00	39.84
4	Calcite	0.00	0.02	0.22	27.91	2.99	0.00	0.12	0.02	0.07	31.37
5	Calcite	0.02	0.02	0.23	27.62	3.01	0.00	0.15	0.05	0.00	31.11
6	Calcite	0.01	0.00	0.29	28.98	2.84	0.05	0.14	0.19	0.04	32.55
7	Calcite	0.00	0.00	0.19	27.76	2.96	0.01	0.08	0.07	0.03	31.10
8	Calcite	0.01	0.01	0.27	27.96	2.96	0.00	0.06	0.12	0.00	31.38
9	Calcite	0.00	0.00	0.22	28.62	2.89	0.02	0.10	0.03	0.00	31.87
10	Calcite	0.03	0.00	0.10	53.69	1.60	0.05	0.10	0.07	0.07	55.71
11	Calcite	0.06	0.05	1.13	46.89	6.68	0.00	0.68	0.92	0.00	56.42

12	Calcite	0.01	0.04	0.08	35.08	17.83	0.00	0.00	0.00	0.00	53.04
13	Calcite	0.06	0.02	1.08	51.26	2.89	0.03	0.37	0.66	0.04	56.43
Thin-section 5.1 Tran.14-21	Phase	K ₂ O	Na ₂ O	SiO ₂	CaO	MgO	SrO	FeO	Al ₂ O ₃	NiO	Total
14	Calcite	0.01	0.03	0.29	37.11	14.67	0.00	0.17	0.18	0.02	52.48
15	Calcite	0.02	0.00	0.40	50.94	3.60	0.00	0.23	0.33	0.00	55.52
16	Calcite	0.00	0.03	0.00	31.49	21.40	0.03	0.00	0.09	0.01	53.04
17	Calcite	0.02	0.04	0.03	32.72	21.86	0.00	0.08	0.10	0.07	54.90
18	Calcite	0.02	0.09	0.43	38.81	14.73	0.00	0.15	0.24	0.00	54.47
19	Calcite	0.05	0.00	0.90	50.32	1.17	0.00	0.55	0.68	0.07	53.74
20	Calcite	0.06	0.05	1.02	50.46	2.88	0.00	0.63	0.76	0.02	55.88
21	Calcite	0.00	0.00	0.00	31.64	21.97	0.06	0.00	0.01	0.00	53.69

Thin-section 5.2#	Phase#	K ₂ O#	Na ₂ O#	SiO ₂ #	CaO#	MgO#	SrO#	FeO#	Al ₂ O ₃ #	NiO#	Total#
1#	Calcite#	0.03#	0.00#	0.05#	55.90#	0.48#	0.00#	0.06#	0.01#	0.00#	56.53#
2#	Calcite#	0.00#	0.00#	0.00#	55.76#	0.53#	0.02#	0.02#	0.04#	0.00#	56.37#
3#	Calcite#	0.02#	0.03#	0.19#	58.62#	0.42#	0.00#	0.00#	0.11#	0.00#	59.38#
4#	Calcite#	0.02#	0.02#	0.74#	54.78#	0.57#	0.03#	0.27#	0.55#	0.00#	56.99#
5#	Calcite#	0.04#	0.00#	0.98#	52.33#	3.28#	0.09#	0.53#	0.64#	0.05#	57.94#
6#	Calcite#	0.05#	0.08#	0.38#	55.05#	1.56#	0.01#	0.14#	0.26#	0.03#	57.54#

Thin-section 6	Phase	K ₂ O	Na ₂ O	SiO ₂	CaO	MgO	SrO	FeO	Al ₂ O ₃	NiO	Total
1	Calcite	0.00	0.00	0.09	53.23	1.93	0.01	0.07	0.13	0.01	55.48
2	Calcite	0.00	0.00	0.09	55.60	0.64	0.02	0.03	0.16	0.01	56.56
3	Calcite	0.00	0.00	0.03	55.92	0.69	0.00	0.00	0.07	0.00	56.71
4	Calcite	0.00	0.02	0.02	54.99	0.68	0.08	0.05	0.02	0.01	55.88
5	Calcite	0.02	0.04	0.37	54.23	0.66	0.00	0.10	0.29	0.00	55.70
6	Calcite	0.00	0.02	0.21	51.73	2.76	0.01	0.03	0.10	0.06	51.92

	carbonate vein				carbonate vein				carbonate vein				Layer B				Layer B				Layer B				Layer B													
	Li	Be	B	Sc	Ti	V	Cr	Mn	Co	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Pb	Th	U
	0.78	1.07	2.47	0.23	95.56	5.94	4.56	55.30	1.54	5.45	2.17	9.05	2.50	25.42	2.74	27.96	0.55	0.53	15.92	1.33	1.98	0.16	0.58	0.10	0.02	0.11	0.02	0.12	0.03	0.09	0.02	0.13	0.10	0.02	0.16	0.28	0.23	0.60
	1.38	0.61	1.71	0.17	81.21	7.81	4.52	36.42	1.34	3.73	1.60	7.26	1.70	55.92	1.93	19.22	0.41	0.35	12.73	1.02	1.64	0.14	0.53	0.08	0.02	0.10	0.01	0.13	0.03	0.08	0.02	0.10	0.10	0.02	0.11	0.04	0.23	0.81
	0.96	0.70	2.24	0.55	111.84	5.95	7.05	14.36	0.41	2.91	1.34	8.44	3.09	36.46	4.40	23.82	0.48	0.65	13.17	2.76	3.52	0.34	1.27	0.24	0.05	0.31	0.04	0.26	0.06	0.19	0.03	0.21	0.21	0.03	1.63	0.41	0.66	
	1.02	1.03	2.86	0.38	174.01	9.28	11.82	53.43	1.33	5.92	2.58	11.50	3.87	39.77	3.07	28.63	0.96	0.87	20.01	1.73	2.68	0.23	0.83	0.15	0.03	0.21	0.02	0.15	0.04	0.12	0.02	0.14	0.03	0.18	0.40	0.86		
	2.04	0.45	4.05	0.56	133.03	7.39	10.52	20.19	0.68	3.74	1.74	6.73	4.14	33.79	2.26	6.62	0.66	0.77	12.86	2.31	4.73	0.44	1.67	0.33	0.06	0.31	0.05	0.23	0.07	0.12	0.02	0.18	0.03	0.11	1.30	1.01	0.70	
	2.58	0.48	3.97	0.82	119.09	9.19	10.87	20.28	0.76	4.68	2.04	10.27	5.29	53.83	4.57	13.07	0.68	1.00	14.32	2.84	2.67	0.54	2.22	0.40	0.08	0.40	0.07	0.42	0.09	0.28	0.05	0.36	0.06	0.28	1.38	0.43	1.18	
	2.30	0.49	3.03	0.91	123.28	6.93	10.59	24.79	0.75	4.71	1.93	9.23	4.58	37.65	5.90	9.45	0.79	0.96	15.47	3.52	3.53	0.64	2.60	0.44	0.10	0.53	0.08	0.54	0.12	0.37	0.05	0.37	0.07	1.56	0.40	0.80		
	2.86	0.49	4.02	1.20	173.97	8.40	11.53	21.27	0.73	5.02	2.20	9.28	5.51	46.05	6.19	13.41	1.11	1.06	18.37	4.17	3.33	0.76	3.16	0.57	0.10	0.47	0.09	0.51	0.12	0.41	0.06	0.36	0.21	1.90	0.38	0.87		
	2.42	0.61	5.83	0.74	405.38	11.54	16.02	17.92	0.56	5.24	2.56	11.07	6.09	48.19	2.34	13.29	1.44	1.37	16.51	1.93	2.83	0.34	1.33	0.22	0.05	0.24	0.03	0.22	0.04	0.10	0.03	0.13	0.03	0.17	1.57	0.46	1.04	
	1.08	0.64	3.06	0.65	144.58	6.86	9.71	17.05	0.53	3.83	1.49	8.08	3.78	33.73	2.43	14.73	0.66	0.77	11.31	2.16	3.12	0.42	1.64	0.32	0.06	0.31	0.04	0.28	0.05	0.16	0.03	0.14	0.02	0.29	1.28	0.41	0.70	
	1.86	0.56	2.79	0.63	192.36	7.18	9.80	16.62	0.49	3.42	1.51	8.41	3.55	40.79	2.08	8.19	0.71	0.68	11.49	1.96	3.35	0.39	1.62	0.25	0.06	0.31	0.04	0.28	0.05	0.15	0.02	0.13	0.03	0	0	0		

Cu	2.44	1.48	2.23	2.95	1.99	3.08	2.98	2.66	2.29	2.57	3.28	2.47
Zn	5.88	4.75	6.61	9.40	9.67	12.22	8.35	7.64	6.79	8.23	11.83	10.24
Rb	4.54	3.03	4.68	5.74	3.43	5.05	5.22	5.06	4.62	5.32	6.43	4.11
Sr	41.86	42.98	37.82	38.57	45.37	50.52	38.77	45.89	36.10	43.71	48.42	34.96
Y	1.35	0.79	1.66	2.83	1.40	2.33	2.85	1.71	1.78	2.53	2.59	1.86
Zr	11.21	7.94	15.81	18.48	14.82	20.76	17.91	16.25	36.24	16.84	21.95	16.97
Nb	1.16	0.74	1.42	1.62	0.77	1.49	1.48	1.53	1.51	1.66	1.70	1.16
Cs	1.10	0.73	1.08	1.32	0.79	1.19	1.24	1.17	1.06	1.27	1.45	0.89
Ba	14.82	10.52	14.93	19.33	13.34	18.76	16.94	18.21	15.90	17.81	21.41	15.50
La	1.31	0.75	1.28	2.25	1.13	1.67	2.54	1.84	1.43	2.33	2.31	1.50
Ce	1.99	1.32	2.04	2.21	1.84	3.10	3.12	2.80	2.20	3.88	3.83	2.31
Pr	0.21	0.13	0.21	0.34	0.16	0.24	0.43	0.28	0.22	0.43	0.39	0.24
Nd	0.77	0.46	0.81	1.72	0.68	0.85	1.46	1.00	0.88	1.57	1.41	0.83
Sm	0.11	0.09	0.16	0.22	0.10	0.14	0.24	0.17	0.12	0.21	0.26	0.18
Eu	0.03	0.02	0.03	0.04	0.02	0.03	0.04	0.03	0.03	0.05	0.07	0.04
Gd	0.17	0.09	0.18	0.25	0.10	0.18	0.20	0.17	0.13	0.22	0.30	0.13
Tb	0.02	0.01	0.04	0.04	0.01	0.02	0.03	0.02	0.02	0.03	0.03	0.02
Dy	0.19	0.06	0.40	0.20	0.08	0.16	0.18	0.15	0.13	0.23	0.21	0.10
Ho	0.03	0.02	0.09	0.04	0.02	0.04	0.05	0.03	0.04	0.04	0.04	0.03
Er	0.12	0.05	0.30	0.16	0.06	0.11	0.14	0.11	0.11	0.12	0.13	0.11
Tm	0.01	0.01	0.05	0.03	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Yb	0.12	0.05	0.30	0.21	0.07	0.13	0.15	0.12	0.14	0.13	0.12	0.10
Lu	0.02	0.01	0.04	0.03	0.01	0.03	0.03	0.02	0.02	0.02	0.02	0.02
Hf	0.16	0.11	0.52	0.27	0.13	0.24	0.23	0.23	0.97	0.24	0.25	0.22
Ta	0.06	0.05	0.08	0.08	0.05	0.07	0.07	0.09	0.08	0.08	0.08	0.05
Pb	1.59	0.93	1.43	2.07	1.47	2.25	1.95	2.04	1.81	2.06	2.61	1.83
Th	0.47	0.29	0.45	0.60	0.33	0.55	0.52	0.58	0.58	0.69	0.72	0.46
U	0.76	0.86	0.99	0.83	1.37	1.06	0.70	1.21	0.80	0.90	1.01	0.70
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	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'
Li	2.41	1.71	1.65	1.56	1.04	1.79	1.28	1.66	1.34	1.15	1.39	0.65
Be	0.56	0.60	0.75	0.55	0.52	0.54	0.47	0.22	0.69	0.53	0.66	0.32
B	4.98	6.24	7.85	17.01	3.46	6.13	4.45	5.06	5.49	3.83	3.70	2.02
Sc	0.62	0.53	0.60	0.39	0.42	0.59	0.49	0.54	0.73	0.57	0.49	0.27
Ti	386.48	252.87	302.48	233.03	334.23	463.55	582.99	482.61	528.78	243.19	199.34	135.44
V	15.59	13.81	16.18	11.83	13.79	18.84	19.45	17.80	18.88	14.52	12.50	8.02
Cr	27.26	13.64	11.22	9.22	11.05	23.62	20.84	21.34	17.84	11.50	9.35	6.01
Mn	34.13	31.09	45.21	27.67	32.86	43.04	43.19	39.09	41.19	29.46	24.55	17.15
Co	0.65	0.75	1.32	0.50	0.46	0.68	0.63	0.60	0.57	0.83	0.75	0.45
Ni	5.75	5.18	6.79	4.69	4.80	6.27	6.31	5.88	6.06	5.24	4.39	3.19
Cu	3.04	2.57	3.57	2.40	3.12	4.08	4.40	3.39	3.45	2.64	2.51	1.69
Zn	10.15	11.79	14.13	10.13	12.47	17.11	18.64	13.38	13.58	10.55	9.64	8.07
Rb	6.36	7.09	7.25	4.70	5.60	7.17	7.64	6.45	6.84	5.59	5.09	3.30
Sr	48.16	41.43	54.79	40.13	39.85	48.31	78.30	45.47	48.56	46.00	40.28	28.29
Y	3.82	1.50	1.95	0.98	1.07	1.34	1.22	1.00	1.16	1.31	1.19	0.75
Zr	18.32	13.23	24.72	11.41	16.89	20.74	18.18	15.01	15.50	15.55	13.92	10.45
Nb	2.05	1.33	1.51	1.01	1.66	2.02	2.37	1.98	1.96	1.59	1.14	0.74

Cs	1.46	1.46	1.63	1.09	1.41	1.84	1.89	1.59	1.66	1.32	1.15	0.79
Ba	20.81	19.54	23.22	15.10	18.18	21.45	23.31	19.96	23.73	17.36	16.02	10.90
La	3.12	1.39	3.36	1.24	1.37	2.11	5.39	1.53	1.46	1.46	2.29	0.85
Ce	3.43	2.74	7.06	3.10	2.85	2.79	6.35	2.53	2.71	2.89	4.15	1.86
Pr	0.53	0.24	0.63	0.24	0.32	0.28	0.58	0.25	0.25	0.25	0.37	0.14
Nd	1.88	1.01	2.43	0.91	0.80	1.05	2.14	0.96	1.42	1.10	1.35	0.64
Sm	0.35	0.19	0.46	0.16	0.13	0.19	0.39	0.15	0.16	0.14	0.22	0.09
Eu	0.05	0.05	0.08	0.03	0.03	0.04	0.08	0.03	0.03	0.04	0.05	0.02
Gd	0.33	0.19	0.38	0.17	0.13	0.21	0.21	0.14	0.09	0.14	0.17	0.07
Tb	0.04	0.03	0.04	0.02	0.02	0.03	0.03	0.02	0.02	0.02	0.02	0.01
Dy	0.28	0.18	0.27	0.11	0.11	0.20	0.15	0.12	0.12	0.15	0.11	0.08
Ho	0.07	0.04	0.04	0.02	0.03	0.04	0.03	0.02	0.03	0.03	0.03	0.02
Er	0.22	0.12	0.12	0.06	0.06	0.17	0.09	0.08	0.10	0.09	0.09	0.05
Tm	0.03	0.02	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.01
Yb	0.23	0.12	0.13	0.09	0.06	0.16	0.10	0.09	0.07	0.07	0.09	0.05
Lu	0.04	0.02	0.02	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01
Hf	0.32	0.22	0.36	0.17	0.29	0.40	0.28	0.30	0.23	0.22	0.23	0.14
Ta	0.10	0.08	0.08	0.06	0.09	0.12	0.16	0.12	0.11	0.10	0.06	0.04
Pb	2.28	2.06	2.47	1.47	2.18	2.71	2.76	2.34	2.39	1.93	1.60	1.12
Th	0.64	0.51	0.93	0.51	0.53	0.69	0.99	0.66	0.82	0.47	0.47	0.27
U	1.01	0.89	1.06	0.77	0.80	0.96	0.98	0.90	1.02	0.98	0.80	0.57

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	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'	sub-Layer B'
Li	1.34	1.39	25.96	26.61	26.15	13.47	11.71	13.53	6.47	7.50	8.66	13.44
Be	0.60	0.85	1.16	0.64	1.31	1.04	1.13	0.98	0.51	0.52	0.81	0.50
B	3.05	4.39	38.73	42.12	40.19	17.19	19.35	16.28	11.32	11.21	18.43	15.23
Sc	0.37	0.48	4.38	3.77	3.93	2.10	1.62	1.78	1.02	1.12	1.21	2.13
Ti	209.97	274.12	893.49	751.72	648.91	336.12	429.41	420.73	199.46	251.93	288.20	631.70
V	10.89	13.05	62.39	55.13	54.32	27.57	24.38	27.15	14.18	15.40	16.05	27.28
Cr	7.02	8.91	71.74	71.44	93.13	47.05	49.59	47.18	29.62	27.90	28.20	46.88
Mn	27.92	31.62	69.81	65.60	81.89	53.28	58.95	52.09	27.24	33.54	28.00	47.94
Co	0.81	0.74	4.48	3.95	4.28	2.73	2.19	2.05	1.17	1.26	1.22	1.87
Ni	4.44	5.24	41.87	37.17	42.18	21.57	17.00	19.28	10.01	10.40	12.00	19.58
Cu	2.17	3.01	27.83	14.76	27.13	8.37	7.35	7.77	4.60	4.21	6.10	9.69
Zn	9.06	13.46	101.76	53.96	112.52	30.60	30.82	27.96	16.61	15.12	19.70	33.28
Rb	4.28	5.52	68.47	54.47	69.65	33.29	30.66	31.22	16.52	16.66	18.76	27.81
Sr	33.49	43.42	50.97	71.55	57.43	38.75	37.96	36.54	23.80	44.52	26.31	33.46
Y	1.35	2.10	6.42	6.41	13.09	6.69	8.87	7.24	4.94	5.70	6.03	6.89
Zr	16.32	23.42	39.30	33.14	46.38	26.05	28.12	25.08	14.08	14.82	16.43	18.96
Nb	1.08	1.33	4.60	5.50	5.55	2.74	3.29	2.73	1.03	1.22	1.27	2.83
Cs	0.97	1.24	12.78	10.67	15.07	6.82	6.32	6.59	3.14	3.38	3.69	5.62
Ba	15.53	21.58	68.37	64.87	88.48	43.00	45.87	42.33	23.61	23.56	27.40	39.46
La	1.10	2.14	11.38	13.34	14.74	8.38	9.02	10.46	4.65	6.57	6.23	7.57
Ce	2.68	5.30	12.24	16.64	14.88	7.77	7.81	9.18	2.54	4.53	4.48	4.69
Pr	0.18	0.40	1.83	2.55	2.65	1.19	1.34	1.74	0.74	1.12	0.96	1.21
Nd	0.74	1.50	6.45	10.57	10.25	5.10	4.84	6.28	2.90	4.42	3.87	6.07
Sm	0.13	0.24	0.97	1.64	1.61	0.76	0.79	0.93	0.42	0.72	0.62	0.77

Eu	0.02	0.04	0.22	0.36	0.35	0.15	0.17	0.25	0.13	0.15	0.14	0.16
Gd	0.17	0.23	1.04	1.99	2.04	0.75	0.79	0.79	0.46	0.68	0.58	0.83
Tb	0.02	0.03	0.15	0.16	0.28	0.13	0.12	0.12	0.06	0.08	0.09	0.12
Dy	0.12	0.18	0.79	0.99	1.78	0.79	0.80	0.80	0.47	0.55	0.63	0.79
Ho	0.03	0.04	0.17	0.20	0.34	0.19	0.18	0.17	0.11	0.14	0.12	0.20
Er	0.08	0.11	0.65	0.61	1.09	0.52	0.50	0.51	0.28	0.33	0.36	0.45
Tm	0.01	0.01	0.08	0.08	0.14	0.08	0.07	0.07	0.04	0.05	0.05	0.06
Yb	0.08	0.12	0.54	0.69	1.00	0.69	0.55	0.48	0.33	0.41	0.34	0.48
Lu	0.02	0.02	0.09	0.10	0.15	0.10	0.09	0.09	0.06	0.06	0.06	0.07
Hf	0.16	0.20	0.72	0.84	1.63	0.58	0.49	0.52	0.24	0.46	0.27	0.37
Ta	0.05	0.09	0.24	0.32	0.28	0.15	0.14	0.13	0.06	0.08	0.07	0.14
Pb	1.63	2.35	5.26	5.63	6.37	2.74	2.77	2.51	1.37	1.49	1.85	2.49
Th	0.40	0.57	2.62	4.04	2.61	1.18	1.28	1.30	0.57	0.67	0.76	0.96
U	0.81	0.93	0.92	1.13	1.07	0.52	0.61	0.53	0.31	0.75	0.36	0.47

Table S6. Results from chemical whole-rock analysis in two samples (Cataclasite 1 and Cataclasite 2) from the Tre Monti Fault slip zone (central Apennines). Data are from Smeraglia et al. (2016) and are shown in Figs. 9 and 10a. This table is also provided as external Excel file.

Analyte	Unit	Detection Limit	Analysis Method	Cataclasite1	Cataclasite2
Sc	ppm	1	FUS-ICP	1	1
Be	ppm	1	FUS-ICP	< 1	< 1
V	ppm	5	FUS-ICP	17	12
Sr	ppm	2	FUS-ICP	256	238
Y	ppm	2	FUS-ICP	< 2	5
Zr	ppm	4	FUS-ICP	15	9
Ba	ppm	3	FUS-ICP	36	88
Lu	ppm	0.04	FUS-MS	< 0.04	< 0.04
W	ppm	1	FUS-MS	2	1
Cr	ppm	20	FUS-MS	30	< 20
Co	ppm	1	FUS-MS	< 1	< 1
Ni	ppm	20	FUS-MS	< 20	< 20
Cu	ppm	10	FUS-MS	< 10	< 10
Zn	ppm	30	FUS-MS	< 30	< 30
Ga	ppm	1	FUS-MS	< 1	< 1
Ge	ppm	1	FUS-MS	< 1	< 1
As	ppm	5	FUS-MS	< 5	< 5
Rb	ppm	2	FUS-MS	3	3
Nb	ppm	1	FUS-MS	< 1	6
Mo	ppm	2	FUS-MS	< 2	< 2
Ag	ppm	0.5	FUS-MS	< 0.5	< 0.5
In	ppm	0.2	FUS-MS	< 0.2	< 0.2
Sn	ppm	1	FUS-MS	< 1	< 1
Sb	ppm	0.5	FUS-MS	0.8	< 0.5
Cs	ppm	0.5	FUS-MS	< 0.5	< 0.5
La	ppm	0.1	FUS-MS	2.1	3.4
Ce	ppm	0.1	FUS-MS	4.3	4.5
Pr	ppm	0.05	FUS-MS	0.47	0.69
Nd	ppm	0.1	FUS-MS	1.7	2.3
Sm	ppm	0.1	FUS-MS	0.4	0.5
Eu	ppm	0.05	FUS-MS	0.08	0.15
Gd	ppm	0.1	FUS-MS	0.4	0.6
Tb	ppm	0.1	FUS-MS	< 0.1	< 0.1
Dy	ppm	0.1	FUS-MS	0.3	0.5
Ho	ppm	0.1	FUS-MS	< 0.1	< 0.1
Er	ppm	0.1	FUS-MS	0.2	0.2
Tm	ppm	0.05	FUS-MS	< 0.05	< 0.05
Yb	ppm	0.1	FUS-MS	0.2	0.2
Hf	ppm	0.2	FUS-MS	0.3	< 0.2
Ta	ppm	0.1	FUS-MS	< 0.1	< 0.1
Tl	ppm	0.1	FUS-MS	< 0.1	< 0.1
Pb	ppm	5	FUS-MS	< 5	< 5
Bi	ppm	0.4	FUS-MS	< 0.4	< 0.4
Th	ppm	0.1	FUS-MS	0.6	1.1
U	ppm	0.1	FUS-MS	0.8	4.3
SiO ₂	%	0.01	FUS-ICP	1.94	1.67
Al ₂ O ₃	%	0.01	FUS-ICP	0.95	0.68
Fe ₂ O ₃ (T)	%	0.01	FUS-ICP	0.34	0.31
MnO	%	0.001	FUS-ICP	0.007	0.014
MgO	%	0.01	FUS-ICP	0.62	0.56
CaO	%	0.01	FUS-ICP	52.09	53.59
Na ₂ O	%	0.01	FUS-ICP	0.05	0.08
K ₂ O	%	0.01	FUS-ICP	0.06	0.08
TiO ₂	%	0.001	FUS-ICP	0.041	0.025
P ₂ O ₅	%	0.01	FUS-ICP	0.05	0.05
LOI	%		FUS-ICP	42.31	42.7
Total	%	0.01	FUS-ICP	98.47	99.74

Table S7. Trace element and REE analyses (reported in ppm) carried out by ICP-MS (X Series 2 Termo Fisher Scientific) on four samples from the Popoli Flysch that lies on the Mt. Morrone Fault hangingwall. Sample location: Lat. 42°11'17.7''N, Long. 13°49'25.8''E. This table is also provided as external Excel file.

Analyte	FP1	FP2	FP3	FP4
Li	27.06	27	26.34	23.98
Be	0.763	0.747	0.766	0.7
B	1000	524.9	1176	1091
Al	15310	12130	11940	10710
V	68.68	66.88	71.7	64.99
Cr	39.55	37.43	39.16	34.8
Mn	263.8	266.8	277	261.2
Fe	734.4	718	735	678.2
Co	30.13	29.99	30.26	30.02
Cu	12.29	10.67	12.02	9.283
Zn	24.52	23.23	24.57	22.19
Ga	7.456	7.267	7.53	7.057
As	2.825	2.249	2.757	2.48
Rb	30.98	25.13	24.32	22.82
Sr	16.26	15.6	15.1	15.51
Mo	2.652	2.544	2.584	2.475
Cs	1.34	1.392	1.137	1.099
Ba	205.9	191.6	185	189.7
La	9.004	8.318	7.932	8.079
Ce	14.16	12.85	11.98	12.26
Pr	1.951	1.725	1.518	1.533
Nd	7.687	6.967	6.094	6.13
Sm	1.693	1.588	1.359	1.349
Sm	4.262	3.9	3.398	3.398
Eu	0.367	0.347	0.298	0.29
Eu	0.399	0.375	0.324	0.318
Gd	1.693	1.579	1.355	1.329
Tb	0.298	0.287	0.245	0.236
Dy	1.053	1.04	0.882	0.844
Ho	0.273	0.271	0.228	0.219
Er	0.53	0.526	0.444	0.425
Tm	0.094	0.093	0.078	0.075
Yb	0.357	0.352	0.294	0.28
Lu	0.087	0.085	0.071	0.068
Pb	15.31	15.12	15.82	15.07
U	0.693	0.643	0.694	0.68

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Changes in groundwater trace element concentrations before seismic and volcanic activities occurred in Iceland during 2010-2018

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Abstract

We analyzed temporal variations of the trace element concentration in groundwater from a 101-m-deep borehole (HA01) in northern Iceland during 2010-2018 and compared them with seismic and volcanic activities in the same period to identify potential hydrogeochemical precursors. An increase of B, Al, V, Li, and Mo concentrations started from eight to one month before the onset of the 2014 Bárðarbunga eruption (~140 km distant from HA01), a major rifting event in central Iceland, while Ga and V concentrations began to increase one day and one month after that event, respectively. We also found that concentrations of some trace elements (Li, B, Ga, Mo, Sr, Rb, and Fe) significantly increased before an M_w 5.2 earthquake, which occurred within 100 km from the borehole in 2018. However, other notable hydrogeochemical changes were detected during the monitoring period without apparent correlation with seismic and volcanic events in the region. This study shows that the systematic long-term hydrogeochemical monitoring of seismic and volcanic areas is a promising method in the science of seismic and eruptive precursors. The use of statistical tools such as principal component analysis (PCA) and change-points (CP) can help identifying the chemical elements most useful for the purpose and validate the trend variability of those elements in the time series.

Keywords: seismic precursors, volcanic precursors, hydrogeochemical anomalies, earthquakes, pre-seismic processes, Bárðarbunga

1. Introduction

Hydrogeochemical changes related to earthquakes have been documented since historical times (Manga and Wang, 2015). Most of these changes were recorded in conjunction with and/or after seismic events (Wakita 1975; Igarashi et al., 1995; Manga et al., 2003; Cucci et al., 2019; Kawabata et al., 2020; Kim et al., 2019; Hosono and Masaki 2020; Sato et al., 2020; Barberio et al., 2020; Chiodini et al., 2020); recently, however, anomalous hydrogeochemical variations prior to $M_w \geq 5$ earthquakes have started to be systematically measured and documented (Claesson et al., 2004; Chen et al., 2013; Skelton et al., 2014, 2019; Chen et al., 2015; Barberio et al., 2017; De Luca et al., 2018; Onda et al., 2018; Boschetti et al., 2019; Sano et al., 2020). Indeed, the lack or paucity, until recent times, of continuous and long-term hydrogeochemical monitoring aimed at investigating the seismic cycle (Ingebritsen and Manga 2014; Skelton et al., 2019; Zhou et al., 2020) have significantly limited the ability of scientists to identify and fully understand any seismic precursors of a hydrogeochemical nature. While seismological and also geodetic (GPS) networks have been active for many years worldwide, providing important information about crustal deformation and seismic cycles (e.g., Chiarabba et al., 2020), hydrogeochemical networks for seismic precursor identification have only recently started to emerge in China, Iceland, Italy, Japan, western USA, and a few other countries (e.g., Chaudhuri et al., 2013; Hosono e Masaki, 2020; Franchini et al., 2021). These new networks or single monitoring stations have produced significant results on pre-seismic hydrogeochemical changes likely connected with the dilatative preparatory phases of intermediate-strong earthquakes. In particular, pre-earthquake changes in groundwater temperature (e.g., Shi and Wang, 2014; He and Singh, 2019) and chemical composition (e.g., Claesson et al., 2004; Barberio et al., 2017; Onda et al., 2018; Boschetti et al., 2019; Nakagawa et al., 2020; Skelton et al., 2019, Shi et al., 2020; Hosono et al., 2020, Franchini et al., 2021), as well as changes in natural gas geochemistry (e.g., Wakita et al., 1980; King et al., 2006; Sano et al., 2016; Buttitta et al., 2020; Martinelli et al., 2020) have been properly documented and interpreted as potential seismic precursors.

As mentioned above, hydrogeochemical monitoring networks are now emerging for seismic precursor identification, whereas volcanic eruption precursors are mainly searched and identified through seismic and geodetic monitoring (Patanè et al., 2003; Sparks, 2003; McNutt, 2015) or through geochemical measurements often (but not only) on proximal emissions such as fumaroles, hot springs, and volcanic lakes (Aiuppa et al., 2007; De Moor et al., 2016). Conversely, the intermediate

or remote hydrogeochemical monitoring of volcanoes for eruption precursor identification, although used, is rarer ([Armienta and De la Cruz Reyna, 1995](#); [Caracausi et al., 2003](#)). Below, we will show that this remote method could be a suitable and reliable one in addition to easier than sampling proximal volcanic fluid emissions.

Since 2002, a hydrogeochemical monitoring system has been running in northern Iceland with the main aim of identifying potential precursors to earthquakes. One monitoring station was set at Húsavík (HU01) and the other at Hafralækur (HA01) ([Claesson et al., 2004, 2007](#); [Skelton et al., 2014, 2019](#); [Andrén et al., 2016](#)). HA01, from which the samples analyzed in this study come, consists of a 101 m deep borehole located at Lat. 65.8722°N and Long. 17.4528°W ([Fig. 1](#)). This borehole has been continuously monitored since 2008. The monitoring system has allowed geoscientists to identify hydrogeochemical changes (interpreted as potential seismic precursors) before three large earthquakes ($M_w > 5.0$) that occurred off northern Iceland on September 16th, 2002, October 21st, 2012, and April 2nd, 2013, respectively. Before the 2012 M_w 5.6 and the 2013 M_w 5.4 earthquakes, significant anomalies in groundwater concentrations of Na, Ca, Si, $\delta^{18}\text{O}$, and $\delta^2\text{H}$ were recorded at the HA01 hydrogeochemical station ([Skelton et al., 2014](#)). These studies were then followed by geochemical modeling and statistical studies to explain and verify previous interpretations ([Andrén et al., 2016](#); [Skelton et al., 2019](#)). Moreover, before the 2002 M_w 5.8 earthquake that occurred off northern Iceland, significant anomalies of Cu, Zn, Mn, and Cr were detected in the analyzed groundwater from the HU01 borehole (20 km distant from the HA01 borehole) at Húsavík (Skjálfandi Bay; [Fig. 1](#)) together with pre- and post-seismic shifts of groundwater concentrations of B, Ca, K, Li, Mo, Na, Rb, S, Si, Sr, Cl, SO_4 , $\delta^{18}\text{O}$, and $\delta^2\text{H}$ ([Claesson et al., 2004](#)).

To expand the hydrogeochemical analyses of the monitored HA01 groundwater and identify further potential precursors of earthquakes in northern Iceland, in 2018, an international collaboration was established between Stockholm University, University of Iceland at Reykjavík, Sapienza University of Rome, and CNR-IGAG of Rome. Within this collaboration, trace element concentrations in the groundwater sampled from the HA01 borehole between 2010 and 2018 were analyzed together with earthquake and volcanic data in the same period. We then used statistical analyses to identify temporal trends and change points in the trace element time series as well as geochemical-thermodynamic computations to constrain the origin of the observed elements. Results show new potential hydrogeochemical precursors of $M_w \geq \sim 5$ earthquakes and potential remote hydrogeochemical precursors of volcanic eruptions. These results are integrated with previous hydrogeochemical findings obtained from the same monitoring system ([Skelton et al., 2019](#)) for a better comprehension of the hydrogeochemical and physical processes occurring during the preparatory phases of intermediate-strong earthquakes and volcanic eruptions in Iceland. Our main

aim is to advance the science of hydrogeochemical precursors of earthquakes and volcanic eruptions. Our results are part of a tentative first step towards forming the background necessary to formulate national protocols aimed at seismic and volcanic precursor identification and related hazard mitigation.

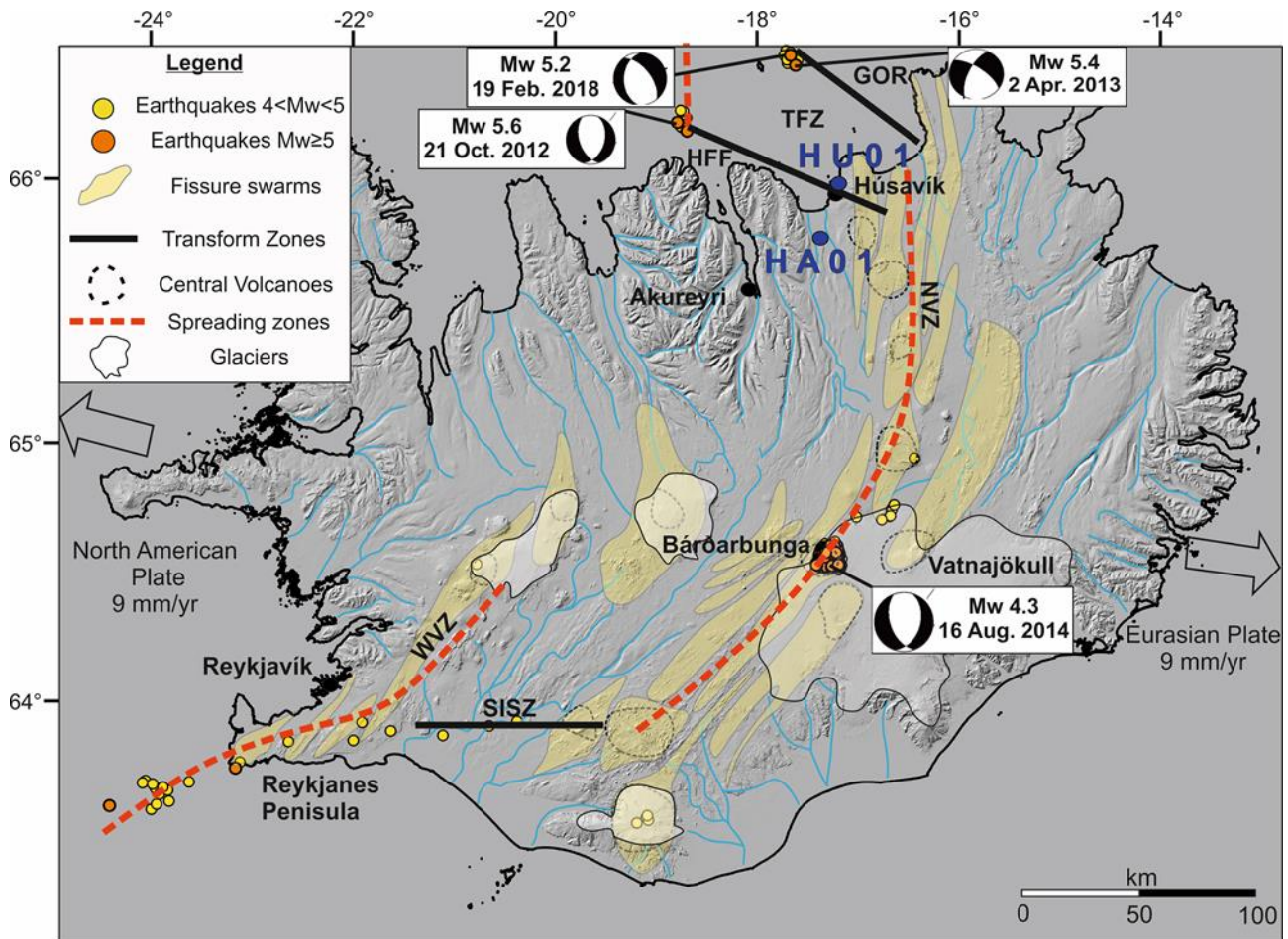


Figure 1 – Map of Iceland. Groundwater sampling sites in Hafralækur (HA01) and Húsavík (HU01), northern Iceland, are displayed with blue symbols. The Bárðarbunga volcano and glaciers (e.g., Vatnajökull) are also shown. Spreading zones and main transform zones are represented with red dotted lines and black solid lines, respectively. Fissure swarms are displayed as yellow shaded areas (from Árnason, 2020). Earthquake epicenters (2010-2018) are represented with orange and yellow dots depending on the magnitude (<http://www.vedur.is>). Focal mechanisms of selected earthquakes (October 21st, 2012, M_w 5.6; April 2nd, 2013, M_w 5.4; August 16th, 2014, M_w 4.0; February 19th, 2018, M_w 5.2) are also shown (<http://www.globalcmt.org/>; Ekström et al., 2012).

2. Geological and Hydrogeological Settings

Iceland is located on the Mid-Atlantic Ridge between the divergent plate margins of Eurasia, to the east, and North America, to the west (e.g., Einarsson 1991, 2008). In detail, it is located between

the Reykjanes ridge, to the south, and the Kolbeinsey ridge, to the north (Einarsson 1991, 2008; Árnadóttir et al., 2008; Fig. 1). The tectonic setting of Iceland is dominated by an eastward shift of the Mid-Atlantic Ridge due to a hot spot currently located approximately under the Vatnajökull glacier, in southeastern Iceland (Thordarson and Larsen, 2007). Two transform zones connect the shifted ridge segment to the Mid-Atlantic Ridge: the South Iceland Seismic Zone (SISZ) to the south and the Tjörnes Fracture Zone (TFZ) to the north (Fig. 1). The TFZ cuts across the area investigated in this work in northern Iceland.

The TFZ is an about 120-km-long and 70-km-wide oceanic oblique transform zone, linking the Northern Volcanic Rift Zone, to the south, and the southern end of the submarine Kolbeinsey Ridge, to the north (Einarsson, 1991, 2008; Stefánsson et al., 2008). This WNW-ESE-trending fracture zone includes two main transform structures, the Grímsey Oblique Rift (GOR) and the Húsavík-Flatey Fault (HFF) (Fig. 1; Gudmundsson et al., 1993, 2007; Rögnvaldsson et al., 1998; Stefánsson et al., 2008; Wästeby et al., 2014; Tibaldi et al., 2020).

Seismic activity in Iceland is mainly linked to the extensional and lateral transfer dynamics associated to the Mid-Atlantic Ridge kinematics. The seismic activity is therefore mainly located along the ridge segments while it is rarer in intraplate areas. Earthquakes in northern Iceland occur mainly in the Tjörnes Fracture Zone (Gudmundsson, 2007), along the Húsavík-Flatey Fault and Grímsey Oblique Rift (IMO, 2016; Fig. 1). Strike-slip and normal fault motions in the Tjörnes Fracture Zone are responsible for the high level of seismic activity of this zone, which has hosted more than ten $M_w > 6$ earthquakes in the past 300 years (Gudmundsson et al., 1993, 2007; Rögnvaldsson et al., 1998; Stefánsson et al., 2008; Wästeby et al., 2014; Skelton et al., 2019). In addition, moderate-strong earthquakes have been recorded associated with the activity of volcanoes such as Katla, Krafla, and Bárðarbunga (Einarsson and Björnsson, 1979; Einarsson, 2008).

During our monitoring period (2010-2018), the main seismic and volcanic events that occurred in central and northern Iceland were four $M_w \geq 5.0$ earthquakes in the TFZ and one volcanic eruption. The earthquakes occurred off northern Iceland along the western HFF in 2012 (M_w 5.4 and 5.6 earthquakes occurred at Lat. 66.333°N and Long. -18.805°W, and at Lat. 66.299°N and Long. -18.714°W, respectively), along the Grímsey Oblique Rift in 2013 (M_w 5.4 earthquake occurred at Lat. 66.547°N and Long. -17.661°W), and in 2018 (M_w 5.2 earthquake occurred at Lat. 66.586°N and Long. -17.708°W) (Fig. 1).

The volcanic eruption occurred in Holuhraun, just north of the Vatnajökull glacier, and was part of a rifting event that originated in the Bárðarbunga volcano (Fig. 1). The rifting event started on August 16th, 2014, with a magmatic dike gradually propagating 48 km toward northeast from the

Bárðarbunga volcano until August 27th, followed by eruptive activity that began on August 29th, 2014, and ended on February 27th, 2015 (Sigmundsson et al., 2015; Andrén et al., 2016).

The HA01 hydrogeochemical monitoring borehole, which is the source of the water samples analyzed in this paper, is located in the Hafralækur area (Fig. 1) and is installed in a low temperature geothermal area, just south of the Tjörnes Fracture Zone (TFZ) and ~20 km to the south of the town of Húsavík (Andrén et al., 2016). In the Hafralækur-Húsavík area, the bedrock mainly consists of mafic and intermediate lavas from Tertiary to Holocene ages with intercalated sediments (Jóhannesson, 2014). The HA01 borehole is 101 m deep and it penetrates a layer of basalt-derived sediments beneath the Younger Laxá Lava and thereafter three lava flows (Andrén et al., 2016). From the borehole, artesian water naturally flows out after circulation into basalts and basalt-derived sediments. The borehole is cased to a depth of 35 m, with filters for water inlet located at 65, 82, and 96 m, yielding a total of 7.7 L/s. The groundwater from the borehole is hot, with temperatures of 71–76°C, and alkaline with a pH of ~10.2 (at 25°C). The groundwater has a low dissolved solid content (240 ppm), which is typical of the fresh low-temperature geothermal groundwater on the flanks of the active rift zone in Iceland (Kristmannsdóttir et al., 2010; Skelton et al., 2014, 2019; Andrén et al., 2016).

3. Data and Methods

We collected water samples from the HA01 borehole, on a weekly basis, from October 2008 to date. In this work, we consider the September 2010 to June 2018 time window. We collected different samples for determination of major (cations and anions) and trace element contents and for isotope analysis. We filtered the groundwater samples in situ through a 0.2 µm filter into acid-washed polyethylene bottles. We added concentrated Suprapur® HNO₃ (Merck KGaA, Darmstadt, Germany) to those samples (1 ml HNO₃ per 100 ml sample) collected for major elements to be analyzed on an ICP-OES (inductively coupled plasma optical emission spectrometer). We refrigerated (~ 5°C) and stored samples in Húsavík (northern Iceland) and then sent to the University of Stockholm and University of Iceland in Reykjavík for analyses of stable isotope ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) and major element concentrations, respectively (see Skelton et al., 2019 for detailed analytical methods). We sent acidified water samples to Rome for trace element concentration analysis (see below and Franchini et al., 2021 for detailed analytical methods). We carried out this latter analysis on the same sample aliquots previously used for the analysis of the major elements (Skelton et al., 2014; 2019; Andrén et al., 2016). We measured the concentration of dissolved trace elements (i.e., lithium, beryllium, boron, aluminum, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, arsenic, rubidium, strontium, molybdenum, cadmium, indium, antimony, caesium, lead, and uranium, Table

S1), at the Geochemistry Laboratory of Sapienza University of Rome with an inductively coupled plasma mass spectrometry ICP-MS (X Series 2 Thermo Fisher Scientific) (Ricolfi et al., 2020). To keep trace element stability in the solutions until analysis, in the ICP-MS laboratory, we re-checked the pH of the acidified water samples and we added Suprapur® HNO₃ till to pH < 2, if necessary (Marcovecchio et al., 2014). We used ultrapure water (Millipore, Milli-Q, 16 MΩ cm) to prepare blanks, standard solutions, sample dilutions, and an internal standard, Rh, to correct the ICP-MS instrumental drift. The analytical accuracy of this method ranges between 2% and 5% (Barberio et al., 2017; Nigro et al., 2017). We analysed, after each tenth sample, blank and two standard reference materials (SRM1640a) purchased from the National Institute of Standards and Technology (United States) as water samples. The parameters for water analyses by ICP-MS (X Series II Thermo Fisher Scientific Inc.) are reported in [Supplementary File \(Table S2\)](#). The measurement of uncertainties for all constraints was done and controlled by using a regular laboratory replica of samples and by confirming the precision/calibration of the instrument over regular runs with standard solutions. The recoveries of analytes of interest were in the range of 98.4–106.3%, and the recoveries of the SRM1640a were in the range of 91.2–111.6%. We used the addition of 206Pb, 207Pb, and 208Pb isotopes to measure the concentration of lead (Ricolfi et al., 2020).

We also applied Principal Component Analysis (PCA) to the studied water samples. This multivariate analysis is a statistical tool useful to discover unsuspected relationships, reducing the dimensionality of the data set, while retaining the information present in the data structure. It has been successfully applied to explain hydrogeochemical composition of geothermal waters in different geological settings (Awaleh et al., 2020; Boschetti et al., 2003; Nicholson, 1993). Different codes as OriginPro version 2019b (OriginLab Corporation, Northampton, MA, USA) and SPSS version 16 (released 2019; Armonk, NY: IBM Corp; IBM, 2019) were used for "classic" PCA. Before PCA extraction, the sampling adequacy of the data matrix was checked in terms of "subject-to-variables" ratio (Bryant and Yarnold 1995; Hutcheson and Sofroniu, 1999; Hatcher and O'Rourke, 2013; Garson, 2018), Kaiser-Meyer-Olkin and Bartlett's test of sphericity (IBM, 2019). Results are also compared with Categorical PCA (CATPCA) and Robust PCA (RPCA; Filzmoser and Todorov 2013; Hubert et al., 2016). Other details are discussed below in the dedicated section.

In addition, we used the Change point analysis over the temporal series of chemical data. A change point (CP) is the point in which an ordered sequence of data ($y_1, y_2, \dots, y_n$) changes its statistical properties (Skalska, 2017). Some freely available codes can solve detection and statistical evaluation of changes in the data trends (Skalska, 2017). The Joinpoint Regression Program (JRP), version 4.8.0.1, is a software package that fits data into joinpoint models (Joinpoint Regression Program, 2020). The software enables the user to test whether or not an apparent change in trend is

statistically significant. A sequence of permutation tests (Monte Carlo method) identifies the change points between trends. The procedure is based on a sequential application of likelihood ratio type tests (Kim et al., 2000). This brief description does not attempt to be mathematically or statistically exhaustive; therefore, the reader is referred to the referenced literature for more details. In this study, the operative conditions of the code were the following: i) to obviate the fact that the sampling dates of the trace elements do not have a regular periodicity, a standard error of 5% (i.e., higher than the real 2%) was taken into account for each raw data concentration before elaboration; ii) the Weighted Bayesian Information Criteria (WBIC) was chosen as model elaboration. This latter combines both traditional Bayesian Information Criteria (BIC) and its modification with a harsher penalty (BIC3) using a weighted penalty term based on the data characteristic (Joinpoint Regression Program, 2020).

Concerning seismic data, we considered earthquakes from September 1st, 2010 to December 31st, 2018, ~800 seismic events ($M_w \geq 4$) occurred in Iceland (see Fig. 1; Table S3). These earthquakes were mostly linked to the volcanic activity and caldera collapse of Bárðarbunga (indeed, these earthquakes mainly occurred between August 2014 and February 2015) and to the seismic activity of the Húsavík-Flatey Fault and Grímsey Oblique Rift in northern Iceland (Fig. 1). All selected earthquake data are from the Global CMT (Ekström et al., 2012).

4. Results and Discussion

4.1. Elemental variability of the HA01 groundwater

Before observing the chemical data (Table S1) of the monitored HA01 borehole over the studied time window and against the seismic and volcanic activities in the same period (i.e., the time series), we computed and show all coefficients of variation associated to the HA01 groundwater trace elements in Fig. 2a (Table S4).

The low variability range (coefficient of variation < 0.5) includes Li, B, Al, V, Ga, As, Rb, Sr, and Mo. The intermediate variability range (≥ 0.5 and < 1.0) includes Cr, Co, Cu, Zn, Cd, In, and Cs. The high variability range (≥ 1.0) includes Mn, Fe, Ni, Sb, Pb, and U (Fig. 2a).

Most elements with coefficients of variation > 0.5 have very low average concentrations over the sampling period, namely less than 1 ppb or even below the quantification limit of the instrument (Table S4). For this reason, we excluded these elements (i.e., Co, Cd, In, Cs, Cr, Mn Ni, Cu, Sb, Pb and U) from our subsequent analyses and elaborations. For the same reason, we also excluded Zn. Indeed, this latter element, despite an average concentration of 6.42 ppb, was detected only in 29 out of 166 analyzed samples. Although Fe concentration was often below the instrument detection limit (i.e., in 54 samples out of a total of 166 ones), we considered it the same in the following analyses for its documented role in pre-seismic processes elsewhere (Barberio et al., 2017; Boschetti et al.,

2019). The remaining elements (Li, B, Al, V, Ga, As, Rb, Sr and Mo) are mostly characterized by low coefficients of variation (< 0.5). These low coefficients of variation over a long time series (8-9 years) corroborate the suitability of these elements as good indicators for changes connected with environmental events. In other words, anomalies in groundwater concentrations would be emphasized by the stability of time series expressed also by the low coefficient of variation.

To better understand the statistical distribution of the analyzed populations, we also graphed (Fig. 2b) concentrations of the selected (see above) elements (Li, Mo, As, Sr, Rb, B, V, Ga, Al, and Fe) as box-and-whisker plots. Each box represents interquartile ranges (25th–75th quartiles) and it is separated into two parts by the median. The whiskers are limited by the interquartile range (IQR) with a factor equal to 1.5. All selected elements have small boxes, meaning that the populations are well clustered around the median. Furthermore, all elements except As and Al have outliers (dots in Fig. 2b), which are "anomalous values" compared to the median and the associated box as they exceed the whiskers (Fig. 2b).

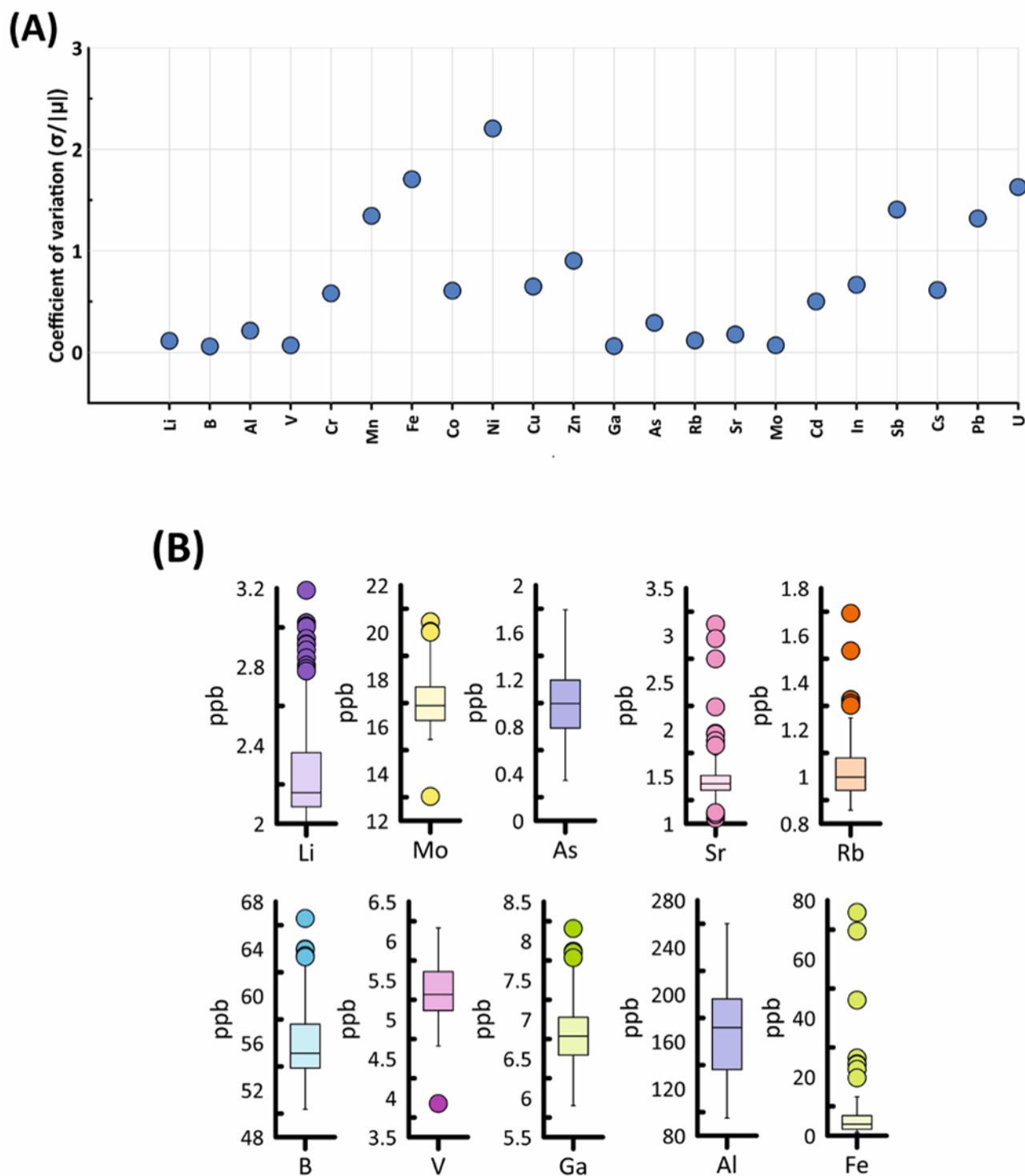


Figure 2 – Variability of elements in the HA01 groundwater. (A) Coefficients of variation for all the trace elements (Table S4). (B) Box-and-whisker plots for the selected trace elements where dots represent “anomalous values” of concentrations (ppb) compared to the median and the associated box as they exceed the whiskers.

4.2. Time series of trace elements in the HA01 groundwater

The time series of previously selected (Li, Mo, As, Sr, Rb, B, V, Ga, Al, and Fe; see previous section) trace element concentrations (Table S1) are shown in Fig. 3. The graphic representation of the time series allows us to appreciate immediately the extraordinary stability found in the concentrations of Li, B, Mo, V, Ga, As, Rb, Sr and Al over nine years (Table S1). This statement is confirmed by the low variability of the sample around the average values (Table S1). Instead, Fe and Zn show a very high standard deviation, symptom of a higher intrinsic variability and/or potential instrumental difficulties in their determination (Fig. 3 and Table S1). In detail, in Fig. 3, it is possible to identify two groups based on the trends of concentration over time. The first group is represented by elements such as Li, Ga, and Mo, while the second one by B, V, and Al. These groups of elements exhibit similar behaviors, in which comparable trends of concentrations are recognized.

Sr, Rb, and Fe concentrations recorded very stable time series around their average values, from which they significantly departed only between January 2018 to the end of sampling (Fig. 3).

The As time series is characterized by very low and variable (but within a very narrow concentration interval of about 1 ppb) concentration values. No clear trends are visible in this narrow distribution within the monitoring period (Fig. 3).

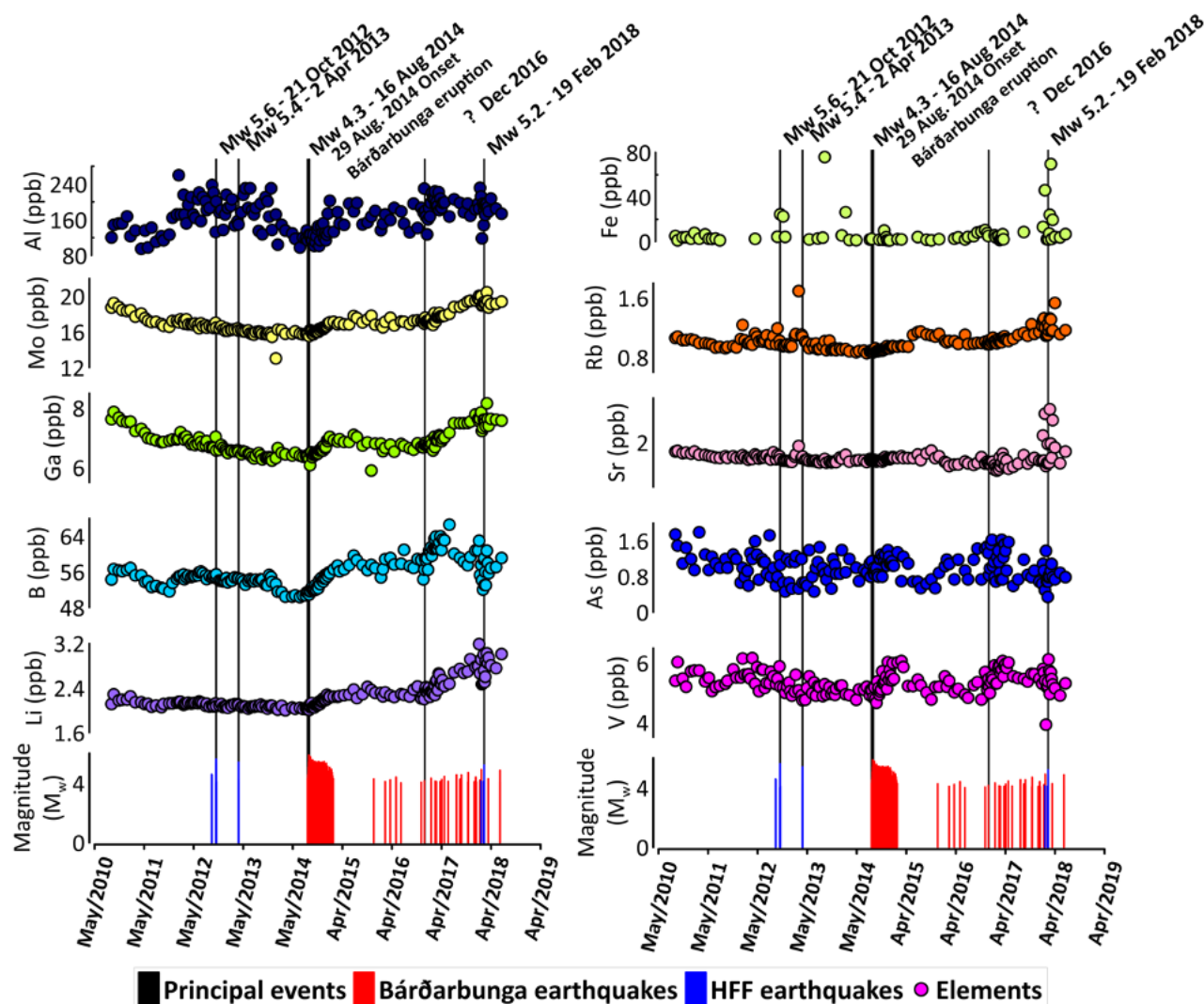


Figure 3 – Time series of trace element concentrations and major earthquakes and volcanic eruptions. Trace elements concentrations in the HA01 groundwater (ppb; September 22nd, 2010 – June 25th, 2018; [Table S1](#)) are shown with circles of different colors. Seismic events ($M_w \geq 4$; January 13rd, 2011 – February 23rd, 2019; [Table S3](#)) related to the Bárðarbunga Volcano and Húsavík-Flatey Fault (HFF) activities are displayed with red and blue bars, respectively. Earthquake data are from the Global CMT ([Ekström et al., 2012](#)).

4.3. Preliminary observations on hydrogeochemical changes vs. seismic and volcanic events

To identify possible correlations between trace elements of the analyzed groundwater and geological events such as earthquakes and volcanic activity, we compare our hydrogeochemical time series with times series of seismic events with $M_w \geq 4$ and main volcanic episodes (i.e., from the Bárðarbunga Volcano) for the period of monitoring in selected areas of Iceland ([Figs. 1 and 3](#)). These possible correlations will be further investigated below through statistical methods, i.e. the principal component and change point analyses. In synthesis, we identify the following possible temporal correlations:

- (1) An apparent increase of B, Al, and V concentrations (HA01) started about five months (May, 2012) prior to the M_w 5.6 seismic event that occurred off northern Iceland on October 21st, 2012 at about 75 km from the HA01 borehole. Later (from July, 2012), concentrations of these three elements returned to background values (Fig. 3). Different hydrogeochemical potential precursors for this earthquake were previously identified (Skelton et al., 2014; 2019; Andrén et al., 2016).
- (2) From January, 2014, B, Al, and V exhibited a substantial decrease of their concentrations (HA01) until August, 2014, when a quick inversion and increase of all three elements were recorded. In detail, this increase started about one week prior to the start of the Bárðarbunga seismic sequence and rifting event (August 16th, 2014), which, in turn, heralded the volcanic eruption (started on August 29th, 2014) by about two weeks (Gudmundsson et al., 2016). Hence, the elemental inversion and increase of B, Al, and V (HA01) occurred about three weeks before the onset of the Bárðarbunga eruption, which occurred at about 140 km from the HA01 borehole. Moreover, in September, 2014 (after the onset of the volcanic eruption), Li, Ga, and Mo concentrations started to increase. B, Al, V, Li, Ga, and Mo returned to background values in February, 2015 (Fig. 3).
- (3) All considered trace elements (i.e. Li, B, Ga, Mo, Sr, Rb, and Fe concentrations in the HA01 groundwater) except Al, V, and As exceeded the $+2\sigma$ threshold (Table S1) since January, 2018, about seven weeks prior to the M_w 5.2 earthquake, which occurred off northern Iceland on February 19th, 2018 at about 70 km from the HA01 borehole (Fig. 3). Concentrations from these elements remained high until the end of our study period (June 2018).
- (4) Some hydrogeochemical variations occurred in 2016-2017 (HA01) when no significant seismic and volcanic activities occurred. In particular, Li, Ga, and Mo exhibited a substantial increase in groundwater concentration (HA01) from December, 2016 to November, 2017, whereas B, Al, and V exhibited a substantial increase from January, 2017 to June, 2017 (Fig. 3). In the same period, also the concentration of some major chemical elements in the HA01 water showed anomalous changes (Skelton et al., 2019).

The aforementioned possible correlations between hydrogeochemical trends and seismic-volcanic events will be statistically tested below.

4.4. Trace element hydrogeochemistry and volcanic events

As mentioned above and observed in Fig. 3, hydrogeochemical changes before the 2014 Bárðarbunga activity are the most obvious over the recorded time series. While these time series will be further analyzed below through statistical methods, we here propose some geochemical-

thermodynamic computations to understand the possible sources of trace elements (and their pre-volcanic concentration changes) in Icelandic volcanic environments.

Earthquakes are among the most important signals in forecasting eruptions, due to magma movement enhancing the stress of the surrounding rocks. However, seismic activity in volcanic areas can be characterized by a wide variability, depending on the large range of elastic behavior and rheology of the rising magma and surrounding rocks (Marzocchi and Bebbington, 2012). Among the main volcanic precursors, geochemical signals may be important to forecast volcanic eruptions (Marzocchi and Bebbington, 2012). Monitoring methods based on chemical changes related to volcanic activity have been used to detect changes within the volcanic system. In particular, geochemical monitoring has mainly focused on gas emissions from fumaroles or craters and, less frequently, the studies have addressed changes in remote groundwater geochemistry prior to volcanic eruptions (Armienta et al., 2008). Nonetheless, the application of geochemical monitoring methods to water (springs, streams, etc.) associated with volcanism has proven to be productive in understanding mechanisms related to volcanic activity (Armienta et al., 1995). In an active geothermal system, as is this case study in Iceland, fluids are able to remotely transport or deposit metals that originate from source water, magmatic volatiles, and via rock dissolutions (Kaasalainen et al., 2015; Blomgren et al., 2019). For example, B is highly mobile during water-rock interaction in basaltic hosted geothermal system and therefore is a good indicator of rock leaching. B is one of the chemical species more sensitive to changes in volcanic activity. Indeed, magma displacement can lead to dome or dike emplacement facilitating leaching of the host-rock. For this reason, hydrogeochemical composition of springs varies with the changes of volcanic stress pattern (Armienta et al., 2008; Arnórsson and Andrésdóttir, 1995; Kaasalainen et al., 2015).

The calculation of relative mobility of the trace elements (Aiuppa et al., 2000; Gislason et al., 1996; Koh et al., 2016), i.e. the normalized-to-sodium ratio between the trace concentrations detected in the HA01 borehole and basalt (Kokfelt et al., 2006; Kaasalainen and Stefánsson, 2012; Shorttle et al., 2013) – definitively confirms that B is the most mobile element in the studied area (Supplementary File RM). Therefore, for the above-mentioned volcanic hydro-sensitivity of B, in this study, we have carried out an analysis about the relationship between B and trace element concentrations in the geothermal aquifer fluids of the Hafralækur area (Fig. 4). In detail, we compared our water samples (black dots) with data from previous studies concerning: snow samples from Vatnajökull glacier and the highland NE of the glacier during 2014/2015 Bárðarbunga eruption (white rhombuses; Galeczka et al., 2017), water samples from Jökulsá á Fjöllum River (JFR) during the 2014/2015 Bárðarbunga eruption (light blue squares; Galeczka et al., 2016), Icelandic cold groundwater (green triangles; Kristmannsdóttir and Klemensson, 2007; Kristmannsdóttir and Guðrúnardóttir, 2009;

Kristmannsdóttir, 2011), and Icelandic thermal groundwater (orange triangles; Arnórsson, 1969; Kristmannsdóttir and Klemensson, 2007; Kristmannsdóttir, 2008; Kristmannsdóttir and Guðrúnardóttir, 2009; Kristmannsdóttir, 2011; Kaasalainen and Stefánsson, 2012; Kaasalainen et al., 2015). The transition temperature between cold and thermal waters is 10 °C (Kristmannsdóttir and Klemensson, 2007; Kristmannsdóttir and Guðrúnardóttir, 2009; Kristmannsdóttir, 2011), in agreement with Schoeller's definition of thermal waters (air or surface water temperature increased of 4°C) (Schoeller, 1962). Indeed, in Húsavík, the mean annual temperature of surface water is approximately 5.6 °C. The transition between cold and thermal waters occurs at about $\log B = 1$. The logarithmic values tend to fade away the temporal element variability, particularly in samples with lower coefficient of variation values. However, it is possible to have some indications on the origin of the trace constituents, thanks also to the comparison with the median trace elements concentration in Icelandic basalts (Kaasalainen and Stefánsson, 2012) and with the literature data of Icelandic thermal waters at temperature lower than or equal to 100 °C (Arnórsson, 1969; Kaasalainen and Stefánsson, 2012; Kaasalainen et al., 2015). Geochemical-thermodynamic codes can be used to model equilibria of major and trace elements during water-rock interaction (e.g., reaction-path modeling; Kaasalainen et al., 2015; Marini, 2013). However, the low concentration of trace elements in $T \leq 100$ °C groundwater combined with the difficulty in taking into account other phenomena such as adsorption/absorption in minerals (in particular oxides and hydroxides), the co-precipitation in complex phases (such as the solid solutions or mixed layered clays), and the incompleteness of the thermodynamic data on solution species mean that these models must be used with extreme caution when applied to trace elements (Marini, 2013; Oelkers et al., 2009). This is evident in Fig. 4, where especially in the case of Li and Rb, the borehole waters are positioned below the reaction path model created by Kaasalainen et al (2015). That model was calculated for high temperatures geothermal waters in Iceland; however, the first stretch of the path (low B content) can be compliant for waters at $T \leq 100$ °C, as in the case of HA01 borehole. It is relevant to observe how the HA01 samples are clustered at the switch domain between surface waters of JFR (Galeczka et al., 2016) and the Icelandic thermal waters, which is approximated by the maximum boron content detected in JFR during the 2014-2015 Bárðarbunga eruption ($\log B = 1.8$) (Fig. 4). The samples tend to be closer to the reaction path model in the case of Sr, Al, and Fe, with the first one being not very mobile compared to boron. The HA01 borehole groundwater samples have lower contents in Sr in comparison both to reaction path model and to the Icelandic thermal waters, due probably to the high pH of the HA01 groundwater (i.e., faster calcite precipitation especially close to surface conditions) and/or to co-precipitation in calcic zeolites (Andrén et al., 2016).

The Al and partially Fe concentrations in HA01 groundwater show the best agreement with the trend of JFR samples towards the Icelandic thermal waters. These two elements are geochemically similar; indeed, they can be classified as “immobile” trace elements ([Supplementary File RM](#)), probably due to their tendency to form oxide-hydroxide colloids. However, Fe has the greatest variability in parity of B concentration, probably due to variable redox conditions and/or due to the fact that iron resides in the structures of nano- to micron-scale clay mineral particles undergoing cycling between Fe(II) and Fe(III) ([Ilgen et al., 2019](#)). Differently, Mo is the second more mobile trace element after B ([Supplementary File RM](#)). Its concentration in the HA01 groundwater is also noteworthy because close to that of basalts, much higher than surface waters, and slightly shifted toward higher concentrations in comparison with other Icelandic thermal waters ([Fig. 4](#)). Mo is an element not very concentrated in basalts, but it tends to accumulate in water proportionally to the time and temperature of interaction ([Arnórrson and Óskarsson, 2007](#)). This confirms that the HA01 groundwater is ancient, probably originated by glacial melting, and roughly datable to the pre-early Holocene time as suggested by the low stable isotope ratio value of hydrogen, $\delta^2\text{H}(\text{H}_2\text{O})$ ([Skelton et al., 2014](#)). It is therefore clear that the analogy of the B contents between the waters of the JFR and the borehole HA01 prior to and during the 2014-2015 volcanic crisis is a mere coincidence, even if the position of the borehole HA01 on the “growth trend” of the trace elements in the waters is compatible with an origin from glacial melting. Indeed, the early Holocene (12–8.2 cal ka) deglaciation and pulsed warming was associated in Iceland with two major generations of “jökulhlaups” (glacier outburst mega-floods) around the Vatnajökull ice-cap, at ca 11.4–11.2 cal ka and ca 10.4–9.9 cal ka, and major tephra emissions from the Grímsvötn and Bárðarbunga subglacial volcanoes ([Van Vliet-Lanoë et al., 2020](#)).

In addition, we indicate the evolution of the JFR during the 2014-2015 event (purple arrow) and also a less marked line representative of the correlation of the samples typical of the thermal waters of north Iceland (among which there is also the borehole HU01; [Kristmannsdóttir, 2008](#)) ([Fig. 4](#)). As well as the HA01 borehole, these samples show a more basic pH (median equal to 9.7) compared to others (8.37 [Kristmannsdóttir and Klemensson, 2007](#); [Kristmannsdóttir and Guðrúnardóttir, 2009](#); [Kristmannsdóttir, 2011](#); 8.66 in NaCl waters [Kaasalainen and Stefánsson, 2012](#)). It is noteworthy that basic pH values are typically measured from water originating from glaciers and are caused by the isolation of groundwater atmospheric CO_2 ([Vigier et al., 2006](#)). The correlation line (green line) is always close to the HA01 samples ([Fig. 4](#)). Therefore, this line can be representative of the evolutionary trend of the waters in Hafralækur area. However, water samples from the HA01 borehole represent the transition between JFR and the thermal waters (vertical red line), evident especially in Al and Fe graphs. Moreover, trends of HA01 samples and other “basic”

samples are similar for elements with geochemical affinity, such as (Fig. 4; Supplementary File RM): Al and Ga (different mobility but similar dissolved species behavior due to the pH; Elmi, 2009), As and Mo (similar high mobility and affinity with sulphides), and Li and Rb (similar moderate mobility and parallel trend to the ratio B / alkali metal in basalts). Finally, a special mention is necessary for the alkali metals Li, Rb, and Cs. In geothermal fluids, the concentration of these elements increases with increasing temperature (Kaasalainen et al., 2015). This also explains why the trend is different from the high temperature geochemical model (dotted line), given that the HA01 borehole has a deep T equal to ca. 100 °C (Fig. 4). In Fig. 5, most of the HA01 borehole samples are clustered between the mean composition of meteoric water and a Li/Rb = 2.26 weight ratio, which is between that of basaltic glass (Li/Rb = 2.33, Berger et al., 1988, which is in turn also similar to MORB, Li/Rb = 2.26, Gale et al., 2013) and the median ratio of Icelandic tholeiitic basalts, (Li/Rb = 2.18; Kaasalainen and Stefánsson et al., 2012), the latter being more Cs enriched as well (Fig. 5). Generally, processes related to the distribution of these elements in thermal waters are particularly evident at high temperatures in the following range: $150 < T < 350$ °C (Kaasalainen et al., 2015; Giggenbach, 1991; Seyfried and Bischoff, 1979; Seyfried, 1987). In such a temperature range, the absorption of Li on quartz or Cs on zeolites is more pronounced (Giggenbach, 1991).

In synthesis, the calculation of relative mobility of trace elements confirms that B is highly mobile during water-rock interaction in basaltic hosted geothermal system (Supplementary File RM). In particular, the analysis about the relationship between B and trace element concentrations in the geothermal aquifer fluids of the Hafralækur area allows us to confirm that water samples from the HA01 borehole represent the transition between JFR and the thermal waters (Fig. 4). Furthermore, the noteworthy concentration of Mo confirms that the HA01 groundwater is ancient, probably originated by glacial melting, and roughly datable to the pre-early Holocene time (Arnórsson and Óskarsson, 2007; Skelton et al., 2014).

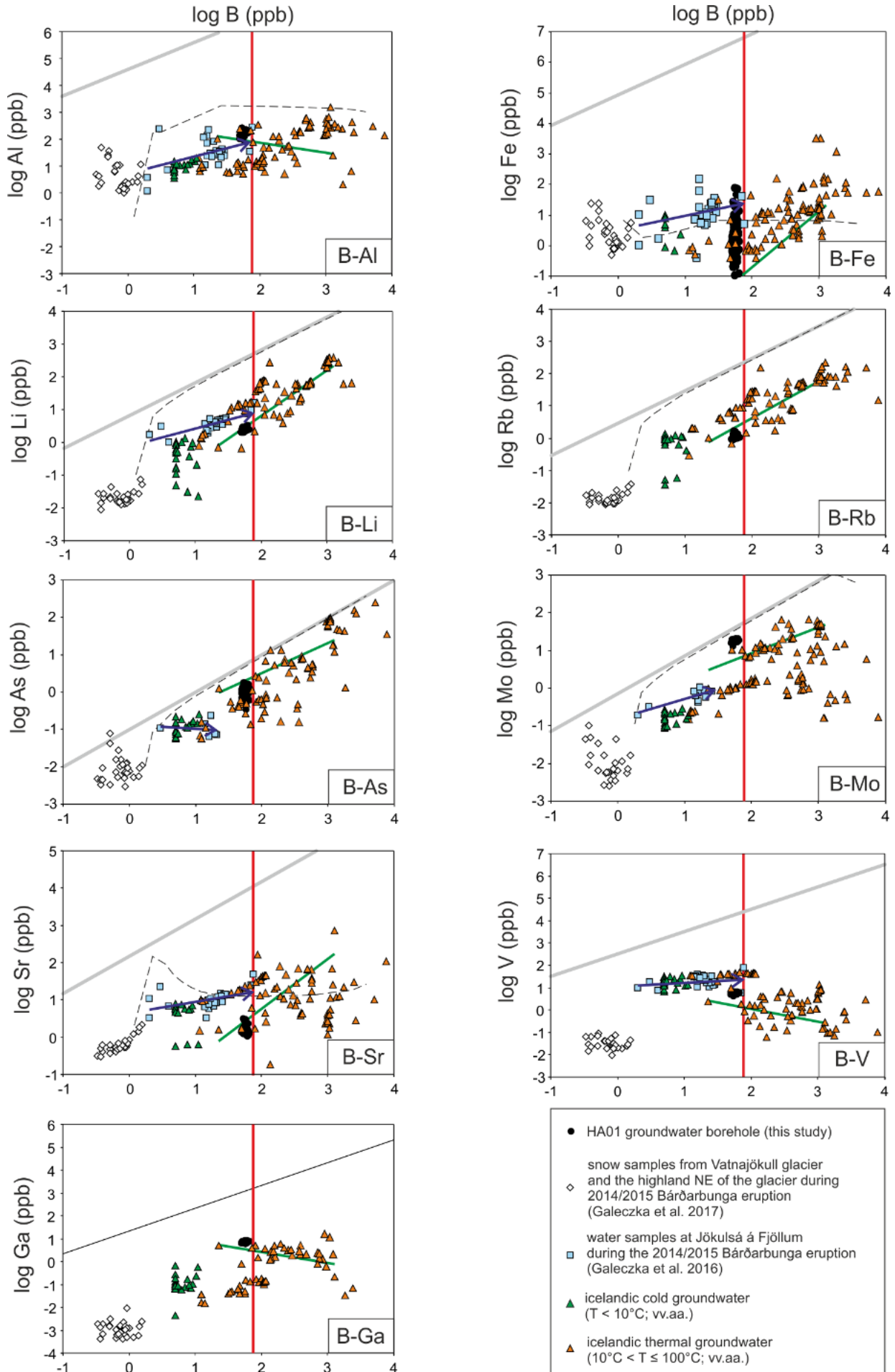


Figure 4 – Relationships between B and trace element concentrations in the HA01 groundwater. Solid black line depicts the boron/element ratios according to Kaasalainen and Stefánsson (2012, and references therein), except for Ga (median Ga value from Arnórsson, 1969; De Argollo, 1978; Willis, 1979; Reimann and De Caritat 1998). Purple arrow shows the trend line of the trace elements in the Jökulsá á Fjöllum River samples (white squares) during 2014-2015 Bárðarbunga eruption (Galeczka et al., 2016); vertical red line shows the maximum boron concentration detected in the river during that period ($\log B = 1.8$). Snow samples during the same periods are also shown for comparison (white diamonds; Galeczka et al., 2017). Dashed lines depict the reaction-path modeling for high temperature geothermal water (meteoric water – basalt interaction at 260°C; Kaasalainen et al., 2015). Green and orange triangles are icelandic cold ($T < 10^\circ\text{C}$) and thermal waters ($10^\circ\text{C} < T \leq 100^\circ\text{C}$) (see the main text for a complete reference list), respectively; green line depicts the best fit of high-pH thermal waters in northern Iceland.

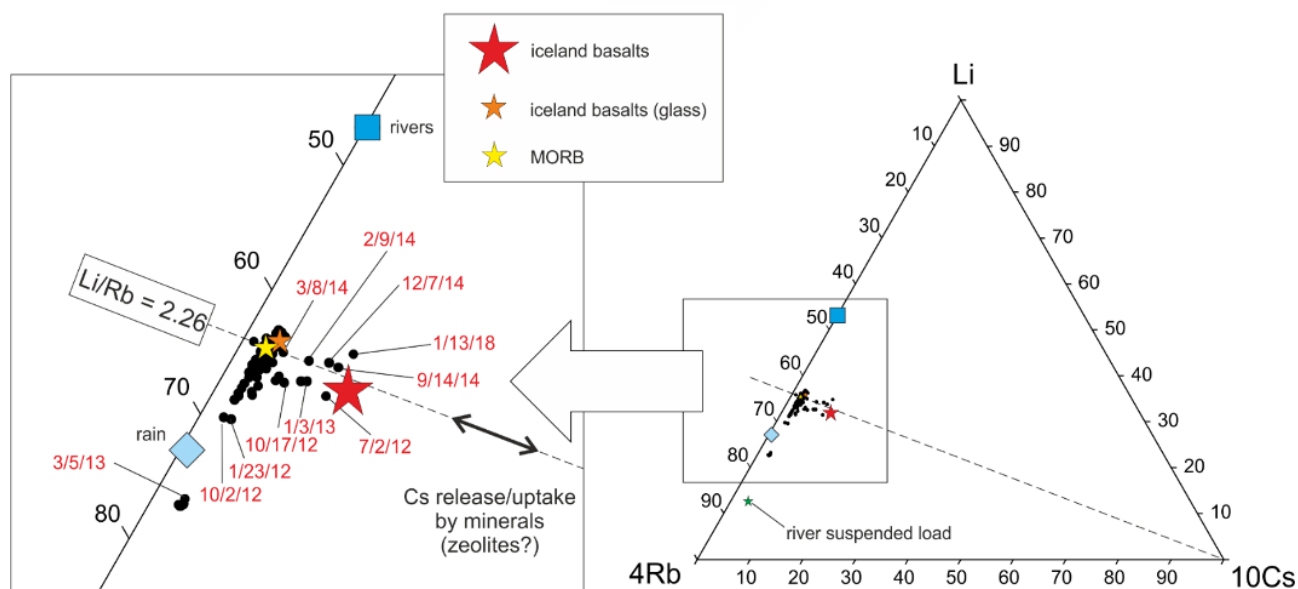


Figure 5 – Li-Rb-Cs ternary diagram. Element percentage from ppb (waters) or ppm (rocks) concentration values are reported over the diagram sides. Black dots show HA01 borehole monitoring trace dataset (this work, Table S1; $\text{Li/Rb} = 2.26$ is the median value of that dataset). Median basalt (Kaasalainen and Stefánsson, 2012), basaltic glass (Berger et al., 1988), MORB (Gale et al., 2013), river and rain waters (Kaasalainen and Stefánsson, 2012) are also shown for comparison. Black dots with sampling date labels as MM/DD/YY.

4.5. Principal Component Analysis (PCA)

In this study, some previously investigated major constituents such as Ca, Na, Si, K (Skelton et al., 2014, 2019) were added to the trace elements database (Li, B, Al, V, Ga, As, Rb, Sr, Mo) to bring out as much information as possible from PCA. This also helps to compensate for the lack of some trace elements, not inserted in the PCA processing as below the quantification limit. In this manner, a data matrix of 13 variables (the elements) and 156 subjects (the samples) was obtained, which agree both with the “subject-to-variables” ratio of Bryant and Yarnold (1995), $STV > 5$ and to other rules of thumb related to the dimension of the subjects (Garson, 2018): subjects = variables x 5 or subjects > 100 (Hatcher and O'Rourke, 2013); subjects > 150 (Hutcheson and Sofroniu, 1999). The principal components were extracted by OriginPro code, using the correlation matrix (Supplementary File 1). Quite similar results were obtained by SPSS code, which has the additional option to rotate the extracted components using Varimax (IBM, 2019). With this latter code, both Kaiser-Meyer-Olkin measure of sampling adequacy ($KMO = 0.746$) and Bartlett's test of sphericity (significance level $<< 0.05$) indicate that PCA is useful for the interpretation of the dataset. As suggested by the scree plot's elbow, the right number of components was four, which explains 75% of the cumulative variance of the data (OriginLab, 2019; Supplementary File 1). However, considering that variance associated to fourth component, (PC4), is less than 10% and that the third component, (PC3), was mainly associated to one trace element (As, see the 3D vector plot of the first three components in the Supplementary File 1), the PCA results are interpreted using a binary plot which shows both the variable eigenvectors and the PC1 and PC2 scores related to the samples (Fig. 6). In that plot, As is represented on the centroid of the diagram. Three main association of the other variables are evident: i) a correlation between Na and Si vectors, mainly represented by the positive side of PC2 (Y axis); ii) the relationship between K and Ca vectors, oriented towards the negative quadrant of Fig. 6; iii) the grouping of the trace elements vectors on the positive side of PC1. Moreover, the sample scores show a counterclockwise distribution starting from 2010 (up/right quadrant, Y axis, PC2). After that, the 2012-2013 samples are distributed just above the positive side of PC2 mainly represented by Na and Si variable vectors. This agrees with the chemical variations detected during the swarm events of that period (Skelton et al., 2014), which were related to the labradorite-analcime reactions reported in Andrén et al. (2016). The subsequent clustering of the samples is onto the negative (left side) of PC1, which seems to be related to a period of lower chemical concentration of most of the trace elements described by PC1 (from June 2013 to June 2014). After that, the chemical variability of samples collected in the second half of 2014 is progressively shifted towards the K vector. In particular, the samples collected after the seismic swarms at Bárðarbunga volcano (August 2014) seem not only related to that seismic events, but to also the heat flow variations in that area (Reynolds

et al., 2019). Indeed, the November 2014 samples, which corresponds to the maximum thermal power in the cauldrons produced by magmatic intrusion (Reynolds et al., 2019), are exactly at the top of the K vector (closer look to the Fig. 6; Supplementary File 2). The samples collected from late 2014 to late 2017/early 2018 migrate gradually towards the lower right quadrant, near the apex of the B and Li vectors, and subsequently (January-February 2018) towards the upper-right quadrant of Fig. 6. Most likely, this could be connected to further thermal power events, which continued until 2017 with a lower intensity but that were related to the increase and shrank of the cauldrons (Reynolds et al., 2019). Accordingly, the time-series variation of the deep temperatures inferred by Na/K (Verma and Santoyo, 1997) and Na-K-Ca (Fournier and Truesdell, 1973; Fournier and Potter, 1979; Fournier, 1989) geothermometric equations applied to the HA01 samples show a maximum temperature at the end of 2014 and other minor jumps in the second half of the 2016 (Supplementary File 3). Finally, the progressive temporal shifting of the samples towards the trace elements vectors, mainly related to positive side of PC1 (Fig. 6), agree with the fact that the pre-seismic/seismic events related to 2018 (e.g., M_w 5.2 earthquake, February 19th, 2018) are detectable only with trace elements.

A second PCA analysis was performed using the correlation matrix of the trace elements only with the aim to better interpret their behavior. The KMO (0.721) and Bartlett's test (significance level $<< 0.05$, respectively) results certify once again the suitability of the data for structure detection. The main characteristics of this analysis are: i) the two main components that explain the 60% of cumulative variance confirm the V, B, Al and Li, Ga, Mo clustering mentioned in the previous section, the latter group being mainly explained by PC1 axis; ii) at the extreme of the negative side of PC1, samples collected prior to Bárðarbunga eruption are grouped, confirming their concentration decrease before that event; iii) on the opposite side of PC1, early 2018 samples are well distinguished as outliers not only by Li, Ga, Mo but also by Rb. The samples collected during the 2012-2013 seismic swarms are indistinguishable from the others because they fall in the centroid of the diagram, confirming that the seismic events occurred during that period are not highlighted by trace elements. Considering that PC1 explains most of the cumulative variance, it could be used as single variable encompassing all trace elements and reducing the unnecessary background information. Both the Varimax rotation and alternative methods of components extraction as Categorical PCA (CATPCA; Ma et al., 2016) or Robust PCA (RPCA; Jung et al., 2014) do not increase either the percentage of variance explained by PC1 or the discrimination capacity of its scores (Supplementary File 4). Indeed, it is evident how the scores related to the PC1 extracted by “classic” PCA have the higher peak close to the date of the 2014 Bárðarbunga eruption and the lower on late 2017/early 2018 events in comparison with those obtained by Varimax-rotated, CATPCA or ROBPCA (Supplementary File 4).

In synthesis, the Principal Component Analysis (PCA) indicates that the seismic events occurred during 2012-2013 were not preceded by significant changes in trace element concentrations, while the 2018 seismic events were preceded only by trace element changes (and not by major element changes). Furthermore, the chemical variability of the groundwater samples collected after the pre-eruptive seismic swarm of the Bárðarbunga volcano (August 2014) seems not simply related to that seismic event, rather to the heat flow variations in that area connected with the rifting event and Bárðarbunga eruption (Reynolds et al., 2019).

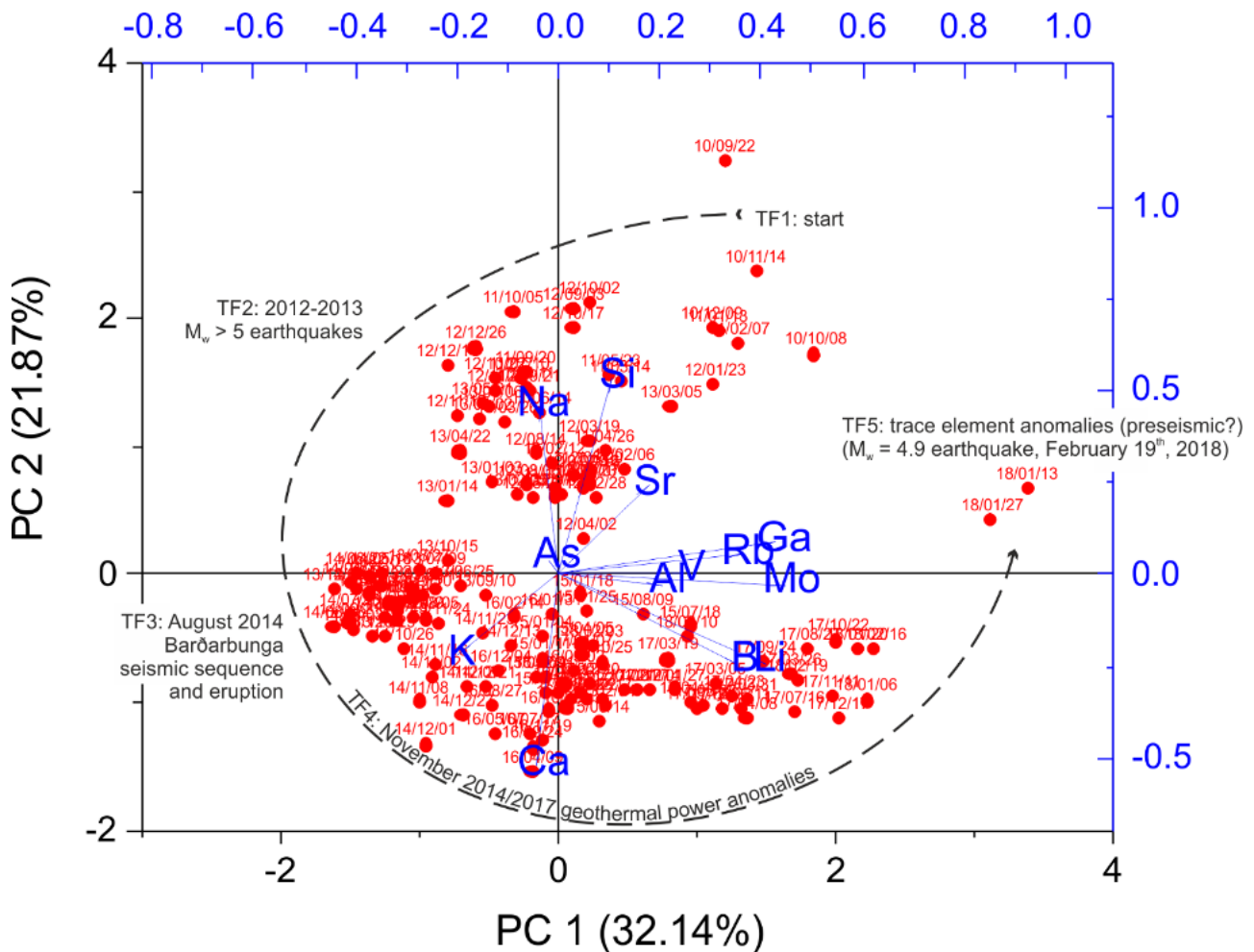


Figure 6 – Principal Component Analysis (PCA) plot. Both the loadings of the variables (eigenvectors, in blue) and the scores assigned to the sampling points (red dots with sampling date labels as YY/MM/DD) are shown, in relation to the first two component (PC1 and PC2). Preliminary data (e.g., correlation matrix) and full results of the PCA are in the [Supplementary File 1](#). The dashed curve depicts an approximated temporal evolution path of the distribution of the sample scores, which seems marked by 5-time frames (TF#). A closer look to the diagram is reported in the [Supplementary File 2](#), showing a magnification of time frames and labels of the sampling data.

4.6. Change Point (CP) detection in time-series

The change point (CP) detection in time-series data of the six trace element clusters detected by the PC1 axis (B, Al, V, Li, Ga, and Mo; [Fig. 7](#)) reveals that each of them has at least one CP within a central period, which is characterized by the seismic events occurred prior to and during the Bárðarbunga eruption ([Fig. 7](#); [Supplementary File CP](#)). Compared to the first earthquake, the main eruption and following seismic events, the period marked by CPs has a broader date range. The dates marked by CPs span from November 10th, 2013, for Al until November 22nd, 2015, for Ga, with the start of pre-volcanic seismicity (August 16th, 2014) and eruptive events of the Bárðarbunga (August 29th, 2014) approximately at the middle of the time series ([Fig. 7](#)). The CPs of Al should be taken with caution because Al is an element with low mobility. However, the first Al CP is followed by a CP in boron (the most mobile of all trace elements) on December 1st, 2013. This latter CP marks the beginning of a declining trend in concentration, which then reverses on March 8th, 2014. It is difficult to explain, element-by-element, the causes of these variations. However, it is interesting to note how the first CPs are coeval with the stress accumulation detected in the north Iceland BRE seismic station. That station is located immediately above the fault-plane of the Húsavík-Flatey transform fault, and it monitors the shear-wave splitting ([Hong et al., 2020](#)). At BRE, the stress accumulation connected to the Bárðarbunga event was related to the microfractures' fluid overpressure. It began in August 2013, a year before the first pre-volcanic seismic shock at Bárðarbunga ([Hong et al., 2020](#)). Therefore, the first detected CPs here described could be linked to the fluid overpressure in the microfractures before the main seismic event. Differently, late thermal variations connected to the Bárðarbunga eruption, which persist until the end of 2015 ([Reynolds et al., 2019](#)), seem to be marked by the CPs of V and Ga, by the K in the PCA ([Fig. 7](#)), and by the geothermal analysis using the main chemical constituents as described in the previous section.

The second period, characterized by at least a CP in all elements but Ga, is positioned just before the M_w 5.2, February 19th 2018 earthquake ([Fig. 7](#)). Before that seismic event, mobile elements have two (Mo) or three (B, Li) CPs. In particular, after an increasing trend, B starts a declining concentration on April 23rd, 2017, approximately one month earlier than other elements. Then, both B and Li start an abrupt decline on January 1st, 2018, followed by an increase on February 3rd, 2018, i.e. two weeks before the seismic event. It should be remarked that the alkali elements ternary diagram ([Fig. 5](#)) also shows an outlier on January 13rd, 2018. The precursor trends and related CPs, although not supported by all trace elements (5-6), could be due to a more significant role of the water-rock interaction, particularly of the different solubility -and chemical composition- between the glass and

crystalline phase of the rock (Fig. 5), or to the role of adsorption/desorption carried out by the secondary mineral phases in the aquifer fractures (clays, zeolites).

Finally, Mo and Ga have a CP on July 10th, 2011, while Al shows two CPs, the first on October 5th, 2011, and the second on January 23rd, 2012, respectively (Fig. 7). Not being confirmed by other highly mobile elements such as B and Li, that supposed time frame has a "low significance" or "low probability" (4 CPs in 3/6 elements; Fig. 7). This was confirmed by PCA, which does not have found any structure in the trace elements data of that period (Fig. 6). From October 2008 to September 2012, abrupt changes were also detected in $\delta^{18}\text{O}$, accompanied by steadily decreasing concentrations of main constituents (Na, Si, Ca) (Skelton et al., 2014). These were connected to a progressive decrease in the proportion of groundwater affected by water-rock interaction (Skelton et al., 2014). Therefore, in the absence of a better explanation on their origin, these CP could be classified as "false positive" or not directly related to seismic events.

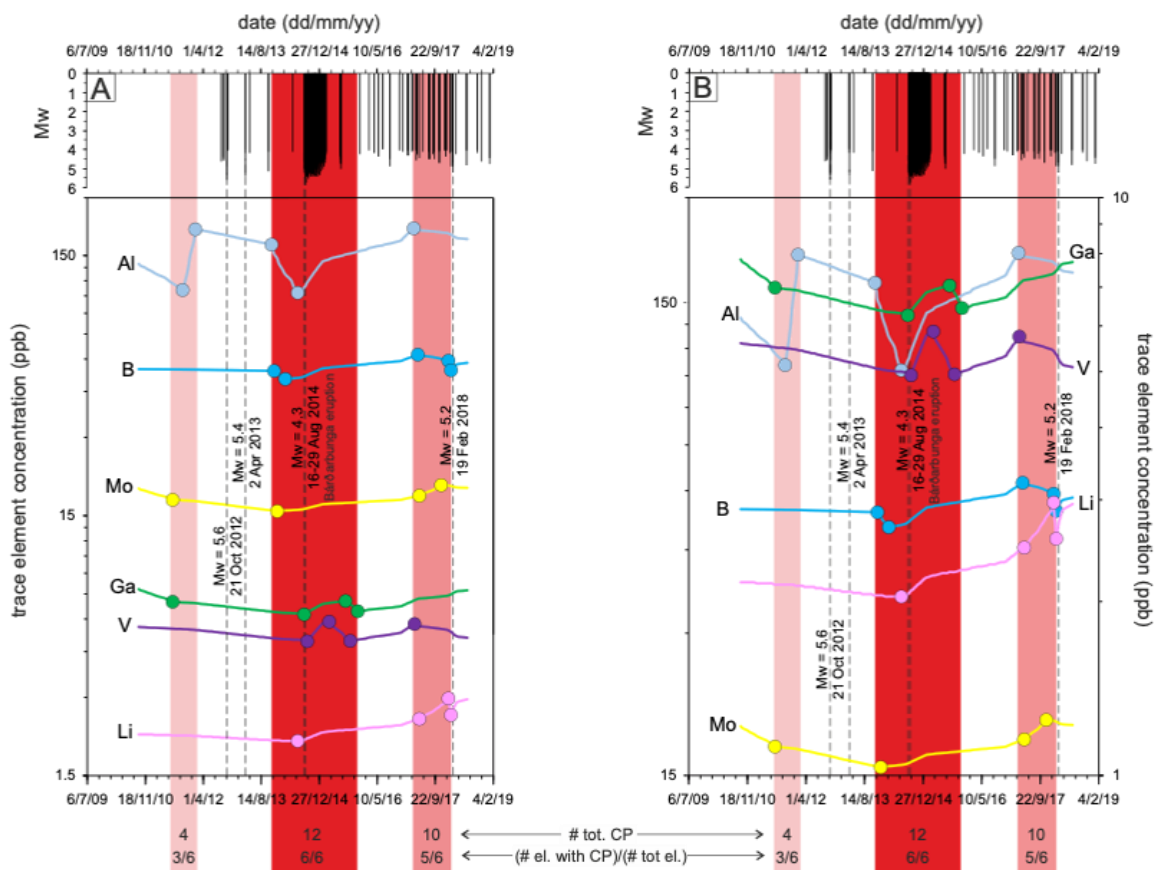


Figure 7 – Change Point (CP) diagram. Comparison between earthquake dates (top of the diagrams, vertical black bars and dashed lines; magnitude moment scale Mw) and the statistically significant change points (CPs) and trends analyzed by the JRP code (colored circles and paths, respectively; Joinpoint Regression Program 2020) related to the six elements clustered on PC1 (Al, B, Ga, Li, Mo and V). In (A), the ppb concentration scale of the elements is referred to the left log₁₀ axis. In (B), to

better show the slope of each element trend between the CPs, the elemental concentration within the first decade were splitted to the secondary axis on the right. Along the paths, elbows not marked by circles are statistically not-significant variations in the trends. In both diagrams, the vertical periods shaded in red highlight three different time frames having a different density of change points (bottom of the diagrams): the greater the number of change points (# tot CP) or the elements with CP to the total (# el. CP/6), the darker the red tone.

4.7. Pre-eruptive and pre-seismic hydrogeochemical changes: a closer look to the results obtained by statistical analyses

The hydrogeochemical changes recorded before and immediately after the onset of the 2014 Bárðarbunga eruption are the most evident over the recorded time series (Fig. 3), as also shown by the PCA and CP statistical analyses (Figs 6 and 7, respectively). In particular, B and Al concentrations show significant decreases, along with a Mo trend flattening due to its concentration stabilization, since about eight months prior to the Bárðarbunga eruption (Fig. 7). Later, the same elements starts a concentration increases before the rifting event and the following volcanic eruption. Moreover, also for Li, V and Ga concentrations a similar temporal pattern has been recorded, with the inversion of concentrations occurring circa two months (Li) or one day (Ga) before the start of the rifting event and one month (V) after it (Fig. 7). We interpret these hydrogeochemical signals as connected with the large Bárðarbunga rifting event and eruption and therefore the changes in B, Al, Mo and Li, V, Ga concentrations are considered as potential remote volcanic precursors.

As mentioned above, previous studies documented the hydrogeochemical sensitivity to earthquakes of the HA01 borehole groundwater, at least for some major constituents (mainly Na and Si) and stable isotope ratios of water molecule (Skelton et al., 2014; Skelton et al., 2019). In this study, neither PCA nor CP analyses were able to detect significant concentration anomalies or trend variations before and after the October 21st 2012 M_w 5.6 seismic event.

Differently, pre-seismic hydrogeochemical changes occurred before the 2018 M_w 5.2 earthquake (February 19th). All considered trace elements except Al, V, and As (i.e. Li, B, Ga, Mo, Sr, Rb, and Fe) significantly increased their groundwater concentrations from about seven weeks prior to the earthquake (Fig. 3). A similar element clustering and increasing trend marked by significant change points have been statistically demonstrated by PCA and CP analyses, respectively (Figs 6 and 7). It is noteworthy that no major chemical elements nor oxygen-hydrogen stable isotope ratio of water (i.e., $\delta^{18}\text{O}$, and $\delta^2\text{H}$) significantly changed their groundwater concentration prior to this earthquake (Skelton et al., 2019). This evidence is a significant clue that trace elements may be hydrogeochemically sensitive to pre-seismic crustal deformation, particularly for intermediate magnitude earthquakes such as the one occurred on February 19th, 2018, off northern Iceland (M_w

5.2). However, major elements and isotopes of groundwater are fundamental in order to obtain a complete overview. Further evidence is indeed necessary in the future to support or refute this idea also because, in the case of the 2013 M_w 5.4 earthquake, pre-seismic hydrogeochemical anomalies in major element concentrations were recorded (Skelton et al., 2014; Skelton et al., 2019; Andrén et al., 2016), whereas any anomaly in the same samples regarding trace elements was found (Fig. 3). The deviation from the equilibrium between labradorite and analcime was invoked by Andrén et al. (2016) to explain the Na and Si variations during the 2012-2013 seismic events. This process was triggered by new input of Holocene groundwater (Skelton et al., 2014; Skelton et al., 2019), which probably has a lower trace element content than the two other members involved in the mixing (a pre-Holocene meteoric water and an ^{18}O -enriched component due to interaction with fresh basalt; Skelton et al., 2014). Therefore, the variations in the stable isotope ratios documented before the 2012 earthquake (Skelton et al., 2014) and the generalized and smoothed decrease in concentration of trace elements (Fig. 3), but marked by change points of Al, Mo and Ga during July 2011 (Fig. 7), are probably related to these hydrological/permeability changes. Indeed, it should be noted that the depleted ^{18}O -water component, i.e. low affected by water-rock interaction, showed a significant input from April 2011 to May 2012 (Fig. 3b in Skelton et al., 2014). The geochemical relations between Al and Ga, also highlighted by similar trends in Fig. 7, and how Mo is not concentrated in a modern-day groundwater component were already previously underlined.

On the contrary, significant pre-eruptive anomalies in the trace elements are recorded during 2014 (Figs. 6 and 7) without significant anomalies concerning major elements (Skelton et al., 2014, 2019). The complex role and sensitivity of potential hydrogeochemical precursors as well as the role of influencing factors such as type, distance, and magnitude of the causative geological events (e.g. earthquakes, volcanic eruptions or else) in addition to the subsurface geological setting (site-specificity) it is only at the beginning of the understanding process.

Moreover, our interpretation of the recorded hydrogeochemical changes as potential seismic or volcanic precursors is questioned by the observation that, in 2016-2017, some hydrogeochemical variations occurred when no significant seismic and volcanic activities were recorded. In particular, two elemental triplets (i.e. Li, Ga, Mo, and B, Al, V) exhibited a substantial increase in groundwater concentration in periods of 2016 and 2017, respectively (Fig. 3). PCA analysis have demonstrated that the grouping of trace elements with K occurred from late 2014 to late 2017/early 2018 could be related to the thermal phase that marks the transition between the post eruptive phase of the Bárðarbunga and the seismic event occurred during 2018 (Fig. 6). In the same periods, also the concentration of some major chemical elements in the HA01 water showed anomalous changes

(Skelton et al., 2019), possibly caused by a rupture of a hydrological barrier due to fluid overpressure and/or slow deformation.

4.8. Potential precursor interpretation

From the aforementioned results, we speculate that the following hydrogeochemical changes in trace element concentrations could contribute to reliable forecasting of future geological events. In particular, we interpret:

(1) the hydrogeochemical changes in B, Al, Mo and Li, V, Ga concentrations recorded, respectively, before and immediately after the onset of the 2014 Bárðarbunga eruption as potential remote volcanic precursors and postcursors, respectively.

(2) the hydrogeochemical changes in Li, B, Ga, Mo, Sr, Rb, and Fe concentrations, which occurred prior to the 2018 M_w 5.2 earthquake, as potential earthquake precursors, indicating that trace elements may be hydrogeochemically sensitive to pre-seismic crustal deformation, particularly for earthquakes of intermediate-strong magnitude.

Our interpretations have to be further confirmed and validated by future hydrogeochemical monitoring, which must always include the analyses of major elements and isotopes of groundwater to obtain a complete overview.

5. Conclusions

Long term hydrogeochemical monitoring of trace elements has confirmed to be a promising method to identify potential precursors to significant geological events such as $M_w \geq 5$ earthquakes and remote volcanic eruptions. This method should be integrated by further hydrogeochemical monitoring such as concentrations of major elements and isotopes in groundwater. The role of each element (major, trace, and isotope) as a potential precursor can be different and remains to be clearly identified and understood as a function of many influencing factors such as site specificity (i.e. subsurface geology) and type, distance, and magnitude of geological events (e.g. earthquakes or volcanic eruptions).

The obtained results confirm that B is highly mobile during water-rock interaction in basaltic hosted geothermal system. Therefore, this trace element shows a relevant volcanic hydro-sensitivity as it is a good indicator of rock leaching.

Principal Component Analysis (PCA) can help to identify the specific role of elements in different events, highlighting that about 115 events are better explainable with major constituents (e.g., 2012 and 2013 $M_w > 5$ earthquakes; 2014 to 2017 thermal power anomalies) and other with trace elements (e.g., 2014 Bárðarbunga eruption; 2018 M_w 5.2 earthquake). The Change Point analysis (CP) on a

specific cluster of elements identified by the PCA helps to statistically validate the trend variability in the time-series. The trace elements show different behaviors both between volcanic- and tectonic-earthquakes, and between the $M_w > 5$ tectonic-earthquakes occurred in 2012-2013 and 2018. In particular, the contributions of modern-day groundwater -low affected by water-rock interaction- that occurred one year before the 2012 earthquake seem to be coeval with the change points detected in the concentration trends of Al, Mo, and Ga.

Pre- and post-eruptive hydrogeochemical changes in the groundwater from HA01 borehole, which is located farther than about 140 km from the Bárðarbunga volcano, should not be surprising. All seismically-active faults have envelopes of critically-high-pressure pore fluids. Indeed, an increase of stress-accumulation was detected at Húsavík-Flatey fault system before the start of the Bárðarbunga volcanic episode seismic crisis ([Hong et al., 2020](#)). Consequently, although both stations monitoring shear-wave splitting and HA01 borehole in North Iceland are well-over 100 km from Bárðarbunga, they seem so sensitive to stress changes that are expected to record stress-accumulation and chemical variations before Bárðarbunga eruptions.

Certainly, the diffusion of long term hydrogeochemical monitoring sites and networks over seismic and volcanic territories (e.g., [Franchini et al., 2021](#)) will allow scientists to make significant progress in the science of geological risk precursors.

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