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Hydrothermal alteration role on lithium mobility in a geothermal reservoir: Geochemical analyses of deep granite in the Upper Rhine Graben

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ABSTRACT

The Upper Rhine Graben (URG) is a highly promising area for geothermal lithium (Li) extraction. Li concentration in deep geothermal brine circulating in naturally fractured Visean and Triassic reservoirs exceed 150 mg/L and are combined with significant water flows exploited by geothermal plants. However, there are still a lack of knowledge in the fluid-rock interactions leading to present high Li concentration in the geothermal brine. To address the behavior of Li in the crystalline reservoir during hydrothermal alteration, 36 granite rock samples were selected from 3 deep geothermal wells at Soultz-sous-Forêts (GPK-1, GPK-2 and EPS-1) in France. These samples were analyzed both chemically and mineralogically to assess the impact of dissolution/precipitation on major elements together with Li precipitation in mineral phases or solubilization in the brine. In total, 4 different main alteration facies from low to high alteration grades were identified in the 36 granite samples (fresh granite, propylitic alteration, argillic alteration, argillic alteration and fractured) that displayed significant chemical, mineralogical and textural changes. The Li concentration of the total rocks range from 18 to 1938 ppm and could be attributed to secondary mineral precipitation (illite, illite/smectite and chlorite/smectite mixed layers, quartz, carbonates, barite) and hydrothermal alteration by partial dissolution of the main minerals (biotite, chlorite, feldspars) present in the granite. These results highlight the importance of fluid-rock interactions due to hydrothermal circulation in the mobilization of Li in the reservoir and refine the story behind high Li concentration in the URG brine.

1 INTRODUCTION

The global transition to electric vehicles and renewable energy storage has resulted in a significant rise in worldwide lithium demand to produce Li-ion rechargeable batteries. In the European Union (EU), lithium mining and production is currently limited, which have therefore led the EU to add lithium to the list of 30 critical raw materials since 2020 (European Commission, Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs, 2020).

Lithium resources can be divided into three categories: rock deposits, surface continental brines and ‘emerging’ resources, which include deep brines, seawater, and lithium-ion battery recycling.

- The main solid lithium deposits are found in the form of pegmatites (a type of igneous rock with large crystals) that contain lithium minerals of significant economic interest (with lithium content ranging from 1% to 5%), such as spodumene, petalite, lepidolite, amblygonite, and zinnwaldite (Bale and May, 1989; Tadesse et al., 2019; Alessia et al., 2021).
- Surface brines (also known as ‘salar’) rich in lithium (with an average of 1400 ppm for the Atacama salars in Chile, Munk et al., 2016) are the most easily accessible and represent the largest global reserve (approximately 65% of the world’s lithium reserves). However, extracting lithium from these minerals can still be complex and time-consuming (for salars) due to an evaporation period of 1 to 2 years (Alessia et al., 2021).
- Emerging resources are lithium resources that could ensure long-term sovereignty over metal extraction for several countries. However, they are not yet sufficiently developed from a technological standpoint for economic viability, and certain parameters still need to be studied to enhance extraction yields or the sustainability of the resource.

Geothermal brines are naturally occurring saline waters within deep geothermal reservoirs, they are an emerging resource for Li and a promising alternative for the future needs of critical metals in the EU. These geothermal brines offer a dual potential for renewable geothermal energy generation and lithium extraction, making them a strategic resource for regions with geothermal activity (Flexer et al., 2018; Sanjuan et al., 2022). Among these EU geothermal sites, the Upper Rhine Graben (URG) has a great potential for an Li exploitation because of the high concentration of Li in these fluids (>150 mg/L) and the significant water flows exploited by the geothermal power plants in this area (Sanjuan et al., 2016; Bosia et al., 2021; Sanjuan et al., 2022). Furthermore, Li extraction from URG geothermal fluid, at Soultz-sous-Forêts (SsF), under operational conditions (high pressure and temperature) was proved feasible within the EuGeLi project (European Geothermal Lithium). In this research project, the first kilograms of European battery-grade lithium carbonate from geothermal brine were produced from the SsF geothermal plant during exploitation (Fries et al., 2022).

However, to make Li extraction economically viable and sustainable, it is essential to determine the mechanisms of Li recharge in brine and identifying Li-rich geological units. For instance, understanding the source of lithium transported by geothermal brines would provide valuable insights for selecting the optimal drilling depth, thereby enhancing the extraction of lithium concentration. All the deep geothermal projects reaching the Triassic or the Visean basement reservoirs of the URG show high Li concentration in the geothermal brines ranging between 160 and 210 mg/L (Bosia et al., 2021, Figure 1). Although there are many publications on lithium concentration in geothermal fluid (Sanjuan et al., 2022), there are still a limited number of published Li analyses in deep rocks (sedimentary and crystalline) from the URG (Genter, 1989; Ledésert et al., 1993; Plagnes et al., 2000; Dugamin et al., 2024; Jungmann et al., 2025). In this context, one of the critical research goals is to identify the rock formations within the URG that release lithium into the geothermal brines.

This paper aims to address this interrogation by exploring the geochemical composition of 36 core granite samples from deep wells at SsF geothermal site.

2 SITE DESCRIPTION AND BRINE COMPOSITION

2.1 Geothermal site setting

The SsF site is in the URG, which is a Cenozoic rift structure showing a series of thermal anomalies characterized by a thermal gradient up to 100°C/km (Figure 1). Those anomalies are interpreted as the trace of natural brine advection inside a nearly vertical fracture system cross-cutting both deep-seated Triassic sediments and Paleozoic crystalline basement (Genter et al., 2010). The Soultz geothermal site is located on a local horst structure bounded by faults showing an apparent normal off-set of 500 m. Deep geothermal boreholes were drilled to 5000 m depth that penetrated a sedimentary pile of 1400 m thick made of Tertiary and eroded Jurassic and Permo-Triassic sediments (Figure 1). Since 1988, several deep geothermal wells were drilled to develop a new technology for electricity production from tight basement rocks called Hot Dry Rock (HDR). However, natural permeability was systematically observed in fractured zone/faulted zones which was significantly improved by applying various stimulation renamed as Enhanced Geothermal System (EGS). Three wells, named GPK-2, GPK-3 and GPK-4, reached 5000 m deep. However, only shallower exploration wells, named GPK-1 and EPS-1 were partly to fully cored. Most of the cores used in this study were sampled from the EPS-1 well that reached 2230 m. Today, GPK-2 is used as a production well with a flow rate of 30 kg/s at around 150°C, while GPK-3 and GPK-4 serve as injection wells. The binary plant has an installed capacity of 1.8 MWe and is operating since 2016. It is planned of drilled new wells in this area for developing this Soultz production.

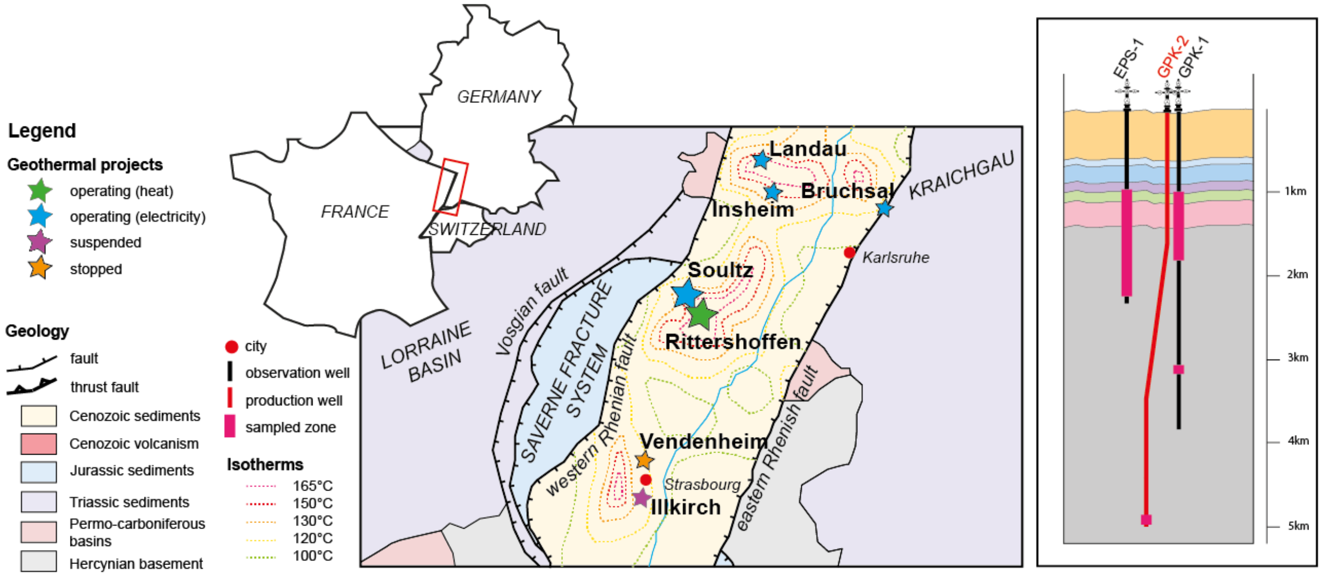

Figure 1: Schematic geological map of the Upper Rhine Graben showing the EGS site location and status between Karlsruhe in Germany and Strasbourg in France (left). Simplified geological cross-section showing three SsF geothermal wells (EPS-1, GPK-1, GPK-2) where core samples were analyzed for a geochemical characterization (right).

2.2 Deep-seated fractured crystalline rocks

Deeper, these boreholes target the geothermal reservoir in the Carboniferous crystalline basement, characterized by a porphyritic monzogranite (Figure 2, sample 1) at the top which comports grey to pink mega crystals of potassium feldspar, plagioclase, quartz, biotite, hornblende and accessory minerals (magnetite, titanite and apatite). Based on detailed mineralogical studies done by Gardien et al. (2016) it appears that the primary magmatic quartz of the facies contains two fluid inclusion types: an early one (primary fluid inclusions) formed at relatively high temperature (>350°C) and containing CO_2, and the latest assemblage (secondary fluid inclusions) generated at low temperature (<210°C) and enclosing only water.

Below, between 4800 m depth and the bottom depth, a fine-grained two-mica granite takes place. The granitic basement, which is unconformably overlain by Mesozoic formations; was affected by pre-Cenozoic tectonics, particularly the Hercynian orogeny. Hence, a dense fracture network is distributed in the granitic basement. During the Cenozoic, a series of compressive and extensive tectonics events took place generating a multi-scale network of fractures and faults. Post-Paleozoic sediments in this Tertiary basin host oil field widely exploited in the past by wells or galleries in which abnormal high temperature gradients were measured. Also, large faults intersect the Jurassic, Triassic, Permian and Carboniferous formations. As in many petrological studies of crustal-rock, hydrothermal alteration activity corresponds to an early pervasive propylitic alteration phase overprinted by successive hydrothermal veining and argillic alteration related to tectonic events. The early propylitic alteration event is related to the emplacement of the granitic basement under temperatures higher than 350°C (Stussi et al., 2002).

The granite batholith was affected by a propylitic alteration during its emplacement, only visible at microscopic scale. Then the batholith was impacted by brittle tectonic events, which caused the formation of fractured zones associated with intense hydrothermal alteration visible at macroscopic scale. They represent the main pathways for natural circulating fluids and provoke the subsequent argillic hydrothermal alteration which is superimposed on the propylitic one and significantly changed the granite mineralogy (Genter, 1989).

The former propylitic alteration corresponds to the lowest hydrothermal alteration grade encountered in the porphyritic monzogranite and is widely distributed in the granite matrix as well as in small-scale fractures (carbonate, locally chlorite). It is mainly characterized by the alteration of primary biotite and plagioclase (Figure 2, samples 2 a,b). Generally, in the monzogranite matrix, primary biotite (phlogopite) is locally kinked and transformed into chlorite (brunsvigite), calcite and other secondary minerals (hematite, leucoxene, epidote, hydrogrenat). Primary plagioclase (oligoclase) is characterized by a secondary mineralogic assemblage made of corrensite (a trioctahedral mixed layer chlorite/smectite), calcite, illite and locally prehnite or epidote. K-feldspars, several centimeters in length, occur as euhedral megacrysts and contain up to 1% of BaO in their core zone. These K-feldspars are relatively insensitive to this propylitic hydrothermal event. Propylitic alteration facies are characterized by a green color brightness of the granite matrix due to the local transformation of plagioclase (Figure 2, sample 2a) locally associated to the occurrence of small-scale fractures sealed with carbonates (Figure 2, sample 2b). The fine-grained two mica granite, which is deeper than the porphyritic monzogranite, undergone also propylitic alteration characterized by the occurrence of secondary chlorite or chamosite (Jungmann et al., 2025). Primary biotite and secondary chlorite are the main minerals bearing lithium in the fresh granite. Their hydrothermal alteration released lithium in the geothermal fluid (Dugamin et al., 2024).

The subsequent argillic hydrothermal alteration are well known according to previous studies and core observations on the SsF geothermal wells in the granite (Traineau et al., 1991; Ledésert et al., 1999; Sausse et al., 2006; Meller and Kohl, 2014; Meller et al., 2014; Meller and Ledésert, 2017) and can be easily linked with the grades observed on cuttings samples (Glaas et al., 2018; Vidal et al., 2018).

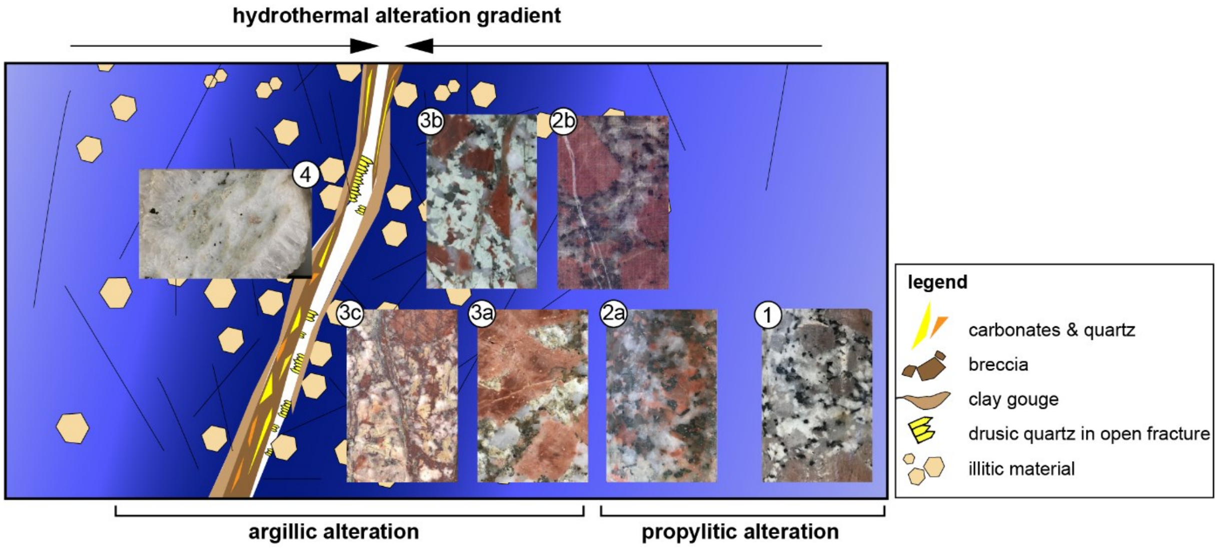

Figure 2: Schematic fracture zone in granite of URG showing the hydrothermal alteration and fracture density gradients. 1. Fresh granite: low propylitic alteration, 2a. Intense propylitic alteration, 2b. Intense propylitic alteration with low deformation, 3a. argillic alteration with low deformation, 3b. intense argillic alteration with low deformation, 3c. intense argillic alteration with high deformation, 4. Quartz vein in open fracture.

Post-magmatic brittle tectonic episodes generated fractured zones which are accompanied by the precipitation of hydrothermal dioctahedral clays (illite), carbonates, secondary automorphic quartz (Figure 2, sample 4), sulphides (galena, pyrite), sulphates (barite, natro-jarosite), and by severe peripheral alteration of the wall rock surrounded the main fault core (Figure 2, samples 3a and 3b). In such peripheral zone, argillic alteration of biotite and plagioclase, hematization of K-feldspar, and locally dissolution of primary quartz are the main characteristics of the wall rock alteration. K-feldspar becomes reddish and is also transformed into illite when brittle deformation is highly developed (Figure 2, sample 3c). Locally, an interstratified chlorite-smectite clay bearing lithium takes place and displays an alveolar structure (Ledésert et al., 1999). It is a regular dioctahedral mixed layer chlorite/smectite, called tosudite, which occurs mainly in relics of plagioclases grains (Figure 2, sample 3b) and crystallized ahead a fibrous illite/calcite/quartz assemblage associated with organic matter (Bartier et al., 2008; Ledésert et al., 1999). Tosudite appears similar under the microscope to kaolinite with a low birefringence. Based on X-ray diffraction analyses on core samples, kaolinite was observed only once at SsF on the peripheral part of a hydrothermally fractured zone in the GPK-1 well around 1604 m depth (Genter, 1989). Kaolinite has also the well-known property to adsorb lithium (Li and Liu, 2020). Based on XRD measurements on core and cutting samples, tosudite occurrence was observed in EPS-1 well at 1455, 2158 and 2159 m depth and in GPK-1 well at 2520 m depth. Primary plagioclases react with rich CO_2 fluid circulating into the fractured granite and carbonates crystallize into matrix and fractured zone. Argillic alteration is related to high fluid rock ratio and corresponds to temperatures ranging between 130 and 200°C. In this argillic alteration grade, the presence of very high amount of secondary drusy quartz is characteristic (Figure 2, sample 4). Based on microthermometric studies on SsF cores, Gardien et al., (2016) show that geodic quartz contains small fluid inclusions that homogenized the liquid phase during heating. Fluid inclusions display temperatures ranging between 116°C and 143°C and equivalent salinities from 0.9 to 28 wt.% eq. NaCl, in agreement with previous results by Dubois et al. (1996) and Smith et al. (1998) on similar SsF core samples. In the fractured zones that are present-day permeable, higher quantities of illite/smectite mixed layers are observed than in paleo-permeable zones (Glaas et al., 2021).

2.3 Geothermal brine at Soultz-sous-Forêts

Geothermal water sample are often collected at the production well GPK-2 and the injection well GPK-3 to assess the chemical composition and the stability of the fluids during the period of the exploitation (Bosia et al., 2021). A new collection of geothermal fluids was made in April 2024 and sent to laboratory for major and minor elements together with gases analyses. All the results are displayed in Table 1.

Geothermal water at SsF is mainly enriched in chlorine (Cl), sodium (Na), calcium (Ca) and potassium (K) with significant amount of Li which is the 5th most abundant element in the liquid (around 25 mmol/L). The geothermal fluid chemistry at SsF is very close to other locations in the URG (Landau, Insheim, Rittershoffen, Bruchsal, Figure 1) suggesting that despite the slight differences in total salinity and isotopes ratios most the fluids have a common origin (Sanjuan et al., 2016). Understanding the mechanisms behind Li enrichment in the brine at SsF could therefore help understand Li origins in the URG deep geothermal brine.

Table 1: Chemical composition of the geothermal fluids sampled at Soultz-sous-Forêts the 10/04/2024. All field measurements (pH and conductivity) and samples were collected at a temperature of 50°C (± 2°C). Cations and anions were analyzed using ion chromatography (DIN EN ISO 14911 and DIN EN ISO 10304-1), and gases using gas chromatography (QMA 504-2/15)

	Well name			Well name	
	GPK-2	GPK-3		GPK-2	GPK-3
	mg/L			mg/L	
Na^+	24400	-	Cl^-	57000	58520
Ca^{2+}	8800	8600	Br^-	255	-
K^+	3400	-	SO_4^{2-}	240	240
Mg^{2+}	154	-	HCO_3^- (Alk)	177	-
Fe^{2+}	35,9	35,6	P	1,59	0,67
Sr^{2+}	480	-	B	42	-
Mn^{2+}	19,1	-	Pb	0,319	0,325
NH_4^+	20	-	Sb	0,062	0,062
As^{3+}	9,3	9,2	Nm^3 of gas / Nm^3 of fluid	0.831	-
Zn^{2+}	2,2	-	CO_2 (%)	87,70	-
Ba^{2+}	22,5	23,9	N_2 (%)	9,77	-
Cs^+	15	-	CH_4 (%)	2,11	-
Rb^+	25	-	He (%)	0,30	-
Li^+	171	170	H_2 (%)	0,07	-
Si	98	-	H_2S (%)	0,0005	-

3 MATERIALS AND METHODS

Based on the geological heritage of the geothermal sites preserved, particularly in terms of cores, a rock sampling strategy was initiated to explore the whole geochemistry of the crystalline basement on the SsF site. Indeed, this study is the first to propose so much geochemical characterization of crystalline rocks including lithium dosage. The objective of the sampling was to recover representative samples of granite at different depths and in two different granitic facies (monzogranite, fine-grained 2-mica granite). Three wells containing basement cores between 1375 m and 5058 m deep, representing a cumulative thickness of 3.5 km on the same vertical, were sampled. As a result, porphyritic monzogranite, fined-grained 2-mica granite as well as several samples taken in hydrothermally altered and fractured areas were collected for rock characterization (Figure 1 right). The sampling of the rock samples for this study was meticulously done to ensure that each granite type was represented by at least 4 samples: 6 samples of fresh granite (Figure 2, sample 1), 4 samples in the propylitic alteration (Figure 2, samples 2a and 2b), 15 samples in the argillic alteration (Figure 2, samples 3a and 3b) and 11 samples in the fractured argillic alteration (Figure 2, samples 3c and 4; Figure 5).

The geochemical analyses for the selected rock samples were carried out at the Service d'Analyse des Roches et des Minéraux of the Centre de Recherches Pétrographiques et Géochimiques in Nancy, France. Before analyses, all the rock samples were grinded to reach a particle size of solid samples lesser than 80 µm. Major and minor elements (SiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, TiO_2) were analysed by ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry) ICAP 6500 following the methodology and preparation described in Carignan et al., (2001). Loss of ignition (LOI) was determined by gravimetric analyses at 1020°C. Cl analyses were performed by UV visible spectrophotometry and Li concentration were measured by flame atomic absorption spectrometry.

4 RESULTS

The chemical composition of major elements and LOI analyzed in the sampled granite rocks are illustrated in Figure 3. Chemical variations of the different alteration facies are described separately:

- Fresh granite (6 samples, Figure 2, sample 1)

This alteration facies includes all the granites that are the least impacted by propylitic alteration and are therefore identified as fresh granite. The fine-grained two mica granites (n = 2) mainly consist of SiO_2 (71.6%) followed by Al_2O_3 (14.7%), K_2O (4.6%), Na_2O (4.0%), Fe_2O_3 (1.7%) and CaO (1.3%). The monzonite granites (n = 4) have a close chemical composition dominated by SiO_2 (62.5 to 71.3%) followed by Al_2O_3 (13.1 to 16.9%), K_2O (3.7 to 7.6%), Na_2O (3.6 to 4.3%), Fe_2O_3 (1.5 and 4.5%) and CaO (1.8 and 2.9%). These geochemical data are close to previous measurements made by several authors on fresh granite from SsF (Cocherie et al., 2004; Dugamin et al., 2024; Genter, 1989; Stussi et al., 2002). LOI, which can be used for determining moisture and volatile materials present in the rock, ranges from 0.8 and 1.8% in both rock types.

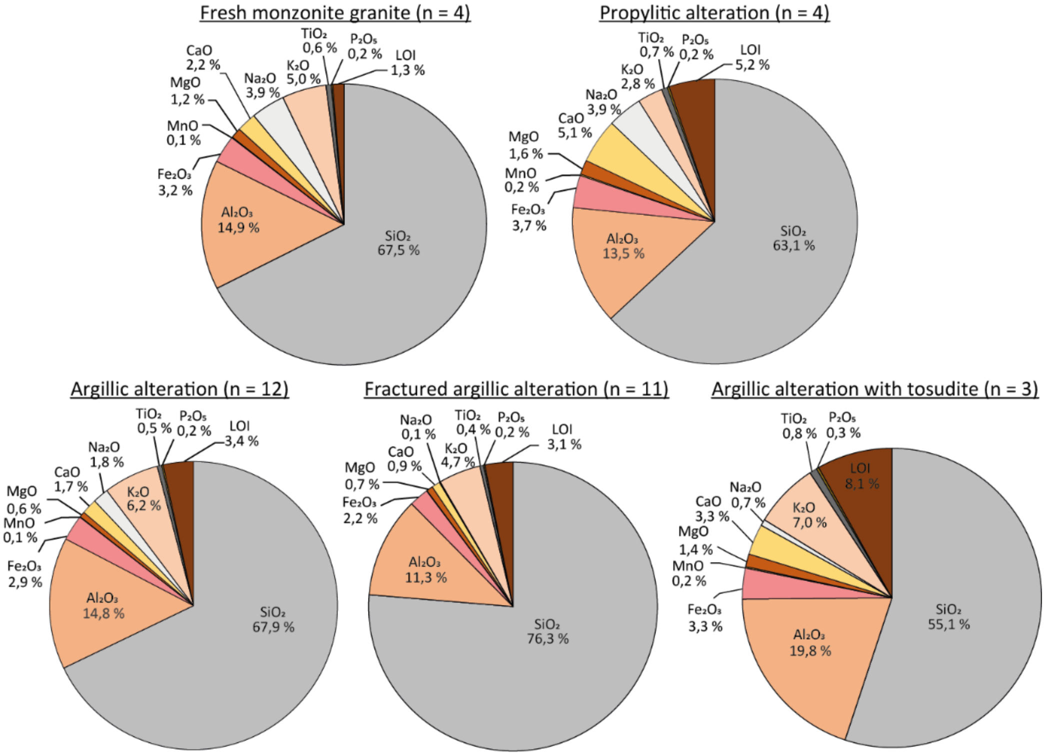

Figure 3: Average concentration of major chemical elements measured in the different alteration facies for rock samples from the URG. The chemical composition of fresh granite (low propylitic alteration) is representative of the monzonite granite only. Argillic alteration composition is represented with the tosudite minerals identified in previous study (n = 3) and without (n = 12).

In the monzonite and the fine-grained granite, Cl concentration ([Cl]) measured in the fresh samples range from 170 to 300 ppm (averaging at 230 ppm for monzonite granite) and are the first geochemical data of Cl presented in the literature for the deep rocks at SsF (Figure 4). These values are comparable with [Cl] analyzed in granites from north Wales and Scotland (Fuge, 1979) and close to the average of granitic rocks measured in different countries (220 ppm; Kuroda and Sandell, 1953).

Li concentration ([Li]) range from 36 to 74 ppm with an average at 53 ppm in monzonite granite (median at 51 ppm; Figure 4). In comparison, the samples of fine-grained granites have lower [Li] of 35 and 38 ppm. These values are close to previous [Li] measured in fresh facies granite rocks at SsF that ranged from 29 to 64 ppm (Dugamin et al., 2024; Genter, 1989; Ledésert, 1993; Plagnes et al., 2000). The median of Li in fresh granite from this study is also comparable with published worldwide granite values (n = 137; median Li = 34.5 ppm compilation in Sun et al., 2016). Due to the difference of chemical composition between the fine-grained and the monzonite granite, and to provide a better comprehension of alteration gradient at similar depth (fine-grained samples were collected at ~5058 m) only the monzonite granite chemical composition is used as fresh granite for further comparison in the study.

- Propylitic alteration (4 samples, Figure 2, samples 2a and 2b)

The average chemical composition of granite more impacted by propylitic alteration is close to the fresh granite composition with a majority of SiO_2 (55.1 to 68.2%) followed by Al_2O_3 (8.8 to 15.3%), K_2O (1.8 to 3.7%), Na_2O (2.8 to 4.5%), and Fe_2O_3 (2.4 and 5.0%). CaO (1.9 to 8.9%) and LOI (1.6 to 9.9%) have important variations and are higher in average compared to the fresh granites.

Cl concentration measured in these granites range from 175 to 320 ppm (averaging at 223 ppm) and do not differ from measurements made in the fresher granites. The propylitic altered granites have a [Li] comprised between 45 and 67 ppm with an average at 55 ppm which is identical than in fresh granite (median at 55 ppm).

- Argillic alteration (15 samples, Figure 2, samples 3a and 3b)

In three samples collected between 2158,4 and 2159.3 m depth from EPS-1 well (Figure 2, sample 3b), important chemical discrepancies are noticeable compared to others granite impacted by argillic alteration. This zone corresponds to the presence of tosudite minerals that were identified in previous studies (Ledésert et al., 1996, 1999). These granites with tosudite have lower SiO_2 content (46.8 to 64.2%) and higher Al_2O_3 (16.2 to 22.0%) and K_2O (5.5 to 9.5%) compared to the rest of the granites analyzed (Figure 3). An average LOI of ~8.1% is also significantly higher than the rest of the granite impacted by argillic alteration and similar chemical characteristics were observed in Ledésert et al., 1999.

Granites affected by argillic alteration outside of this tosudite zone have a chemical signature that is close between all granites regardless of the spatial origin (wells and/or depth). These granites (n = 12) have a chemical composition with a majority of SiO_2 (64.2 to 71.6%) followed by Al_2O_3 (12.9 to 16.0%) which are almost identical to the fresher granites. The main changes are linked with an important increase of K_2O (3.1 to 10.9%) and LOI (2.0 to 5.8%) together with a significant decrease of Na_2O (0.2 to 3.6%) and MgO (0.3 to 1.4%).

Cl concentration measured in argillic altered granites outside the tosudite zone range from 200 to 1180 ppm (averaging at 748 ppm) which is three times more than in the fresher granites. In the granites with tosudite, [Cl] range from 1420 to 2420 ppm (averaging at 1847 ppm) which are the highest concentration measured in the sampled rocks.

These highly altered granites (without tosudite) have a [Li] comprised between 18 and 237 ppm (averaging at 43 ppm). The [Li] median of these granites (24 ppm) is two times lower than the fresher granites. Most of the sample have lower [Li] compared to the fresher granites (propylitic alteration and fresh granite; Figure 4). The [Li] average is only driven toward higher value due to one sample collected at 1604 m depth from GPK-1 ([Li] = 237 ppm). This specific sample was collected at the depth where kaolinite was identified in GPK-1. Granites with tosudite have the highest [Li] in all the rock sampled, ranging from 900 to 1938 ppm (averaging at 1318 ppm). High [Li] were analyzed in granite with tosudite at the same depth with concentration reaching 1447 ppm (Ledésert, 1993).

- Fractured argillic alteration (11 samples, Figure 2, samples 3c and 4)

Granites impacted by this alteration are predominantly characterized by SiO_2 (61.7 to 86.9%) followed by Al_2O_3 (6.3 to 15.7%), K_2O (2.3 to 6.8%), Fe_2O_3 (0.6 and 3.7%), and LOI (1.4 to 6.0%). Compared to granites affected solely by argillic alteration without fracturing or deformation, these fractured granites exhibit a reduction in CaO (0.1 to 2.5%) and an almost complete absence of Na_2O (0.1 to 0.3%) and MnO.

Cl concentration measured in highly altered and fractured granites range from 295 to 880 ppm (averaging at 511 ppm) which is more than 2 times the value analyzed in the fresher granites.

These fractured and altered granites have a [Li] comprised between 38 and 156 ppm (averaging at 80 ppm). The [Li] median of these granites (56 ppm) is close to the granite impacted by propylitic alteration and the fresh granites. The highest [Li] were only identified in the granites that present a drusy quartz vein (Figure 5). In EPS-1, these samples (n = 4) with quartz veins have [Li] ranging from 99 to 156 ppm, and one sample in GPK-1 has a [Li] of 81 ppm which is significantly higher than the rocks that are impacted by argillic alteration without fracturing ([Li] median = 113 ppm). If drusy quartz veins are absent of the sample, the [Li] median of these granites is 45 ppm and is still more concentrated in Li than the rocks with an argillic alteration facies without fracturing or deformation. In other words, when the granitic rock texture is preserved from any tectonic deformation (fracturing, shearing), Li concentrations are lower.

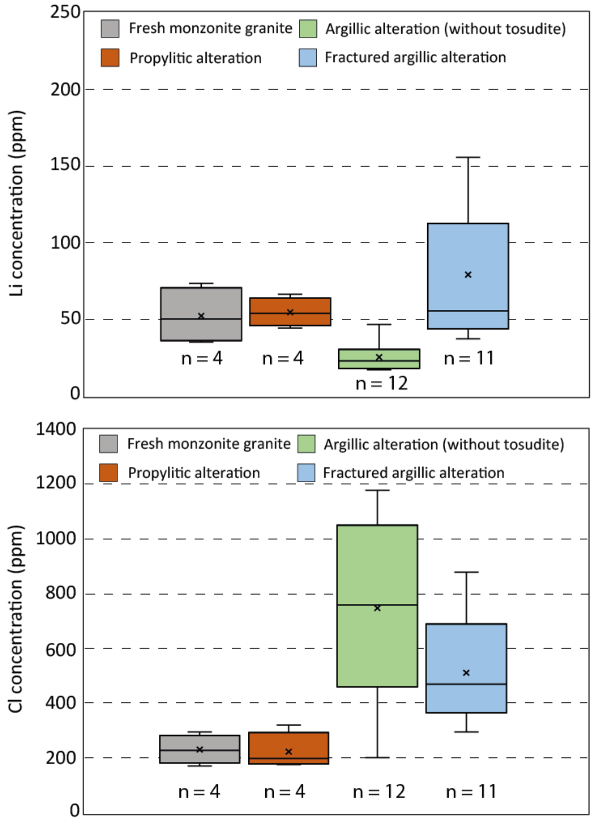

Figure 4: These boxplot diagrams illustrate the distribution of [Li] and [Cl] in the whole rocks across the different granite alteration facies identified in this study. The box represents the interquartile range (IQR), encompassing the middle 50% of the data. The horizontal line within the boxes indicates the median concentration, and the cross indicates the average concentration. Whiskers extend to the smallest and largest values within 1.5 times the IQR from the lower and upper quartiles, respectively. One sample from argillic alteration is beyond the [Li] range (247 ppm) is considered as an outlier and is not depicted as an individual marker.

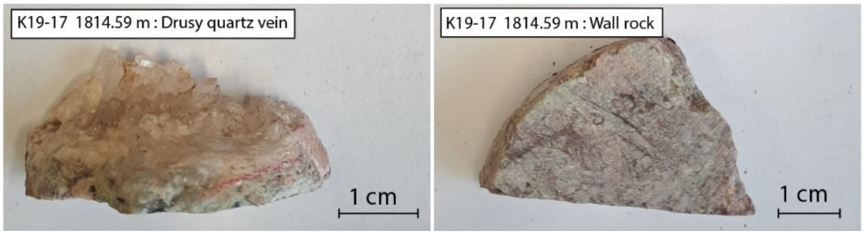

Figure 5: Highly altered and fractured granites from GPK-1 well around 1815 m. The initial primary minerals of the granite are completely transformed. The sample on the left present a drusy quartz with [Li] = 155 ppm, while the wall rock at the same depth on the right has a [Li] = 48 ppm.

5 DISCUSSION

5.1 Major elements and hydrothermal alteration gradient

In all the granites selected, whole rock chemistry can differ significantly due to the abundance of one mineral compared to another in the sample analyzed. For instance, two fresh granites (K12-5 and K13-8) sampled around 1435 m from GPK-1 well have significant chemical changes due to different mineralogy (Figure 6). In sample K12-5, MgO and Fe_2O_3 (respectively 1.1 and 3.1%) are two times higher than in K13-8 certainly due to a higher proportion of primary biotite (ferromagnesian minerals). Similarly, K_2O content in sample K13-8 (7.6%) is two time higher than in K12-5 because of the presence of a phenocrystal of primary K-feldspars ($KAlSi_3O_8$) contained in the core sample. Despite the mineralogical differences, the fresher granites have a Na_2O content with limited variations which could be attributed to a more stable proportion of minerals from the sodic pole of plagioclase ($NaAlSi_3O_8$; albite and oligoclase).

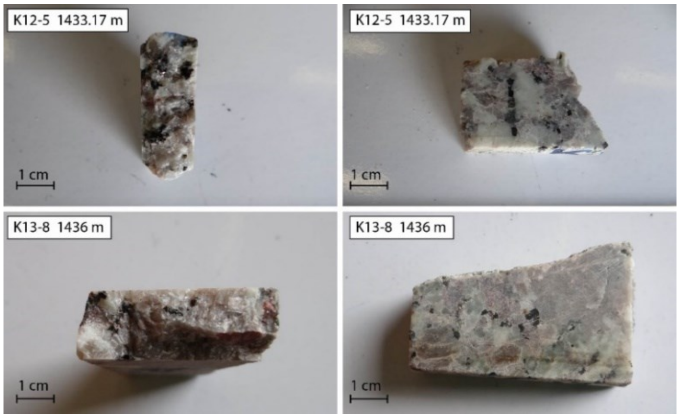

Figure 6: Fresh monzonite granite K12-5 (two pictures on top) and K13-8 (two pictures on the bottom) sampled from GPK-1 well. The sample K12-5, richer in primary biotite, has a [Li] of 74 ppm and K13-8 a [Li] of 39 ppm.

During a more advanced stage of propylitic alteration, important variations of CaO and LOI compared to fresher granite highlight that the calcic pole of plagioclase minerals (anorthite; $CaAl_2Si_2O_8$) is impacted by hydrothermal alteration. In the bulk rock chemistry, these variations are only visible when carbonates (mostly $CaCO_3$) have precipitated in fractures of the core sample which increase the CaO and LOI content (Figure 2, sample 2b). The close chemical composition between the propylitic altered granite and the fresh granite suggests that the transformation occurs under nearly isochemical conditions with relatively low fluid/rock ratios (Nishimoto and Yoshida, 2010).

K_2O/Na_2O ratios are lower (0.6 to 0.8) in granites impacted by propylitic alteration (with and without fracture filled with carbonates) compared to fresh monzonite granite (1.0 to 2.0). Together with variations of CaO, the evolution of K_2O/Na_2O towards lower values could indicate albitization of calcic plagioclase in the altered rocks with an increase of Na_2O compared to K_2O (Figure 7). This effect is highlighted by the Na_2O median of altered granite (4.2%) that is 0.5% higher than the Na_2O median of fresh granite indicating a possible albitization. The lower K_2O/Na_2O values is also likely a combined effect with the chloritization of biotite ($K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$) in the propylitic alteration facies. The chemical transition from biotite to chlorite ($(Mg,Fe)_5Al_2Si_3O_{10}(OH)_8$) releases K from the minerals and could justify the lower K_2O/Na_2O in this alteration facies. Supporting this idea, the average Fe_2O_3 and MgO increase in the propylitic altered granite due to the relative increase in magnesium (Mg) and iron (Fe) in the chlorite structure.

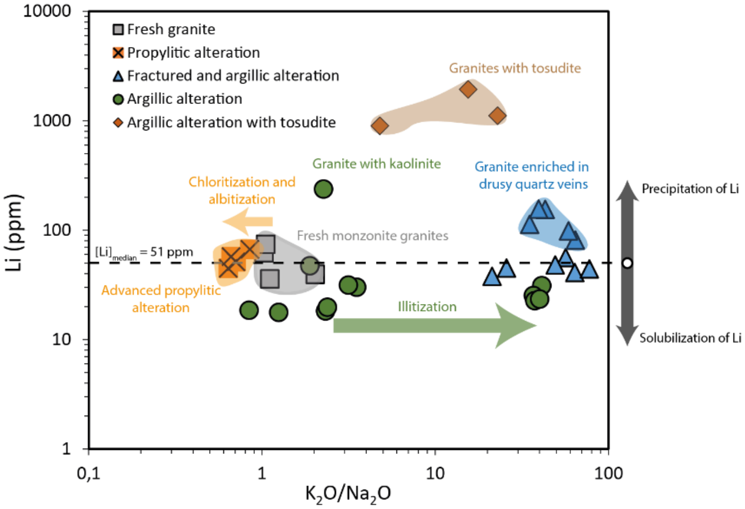

Figure 7: Evolution of the K_2O/Na_2O ratio and [Li] in the SsF granites (logarithmic scale). The [Li] median of 51 ppm represented by the dotted line is the calculated median of fresh monzonite granites. Samples located below the dotted line in the graph have lost Li compared to the fresh granite and samples above the dotted line have accumulated Li.

K_2O/Na_2O ratio of granites impacted by argillic alteration have the largest differences of all granites ranging from 0.8 to 41.2 (Figure 7). These K_2O/Na_2O variations are explained by the progress of hydrothermal alteration (Ledésert et al., 1999; Nishimoto and Yoshida, 2010; Drüppel et al., 2020; Jungmann et al., 2025). Plagioclase minerals are dissolving (higher K_2O/Na_2O due to the loss of Na_2O) while biotite minerals still experience chloritization (lower K_2O/Na_2O due to the loss of K_2O). These two combined processes are maintaining the K_2O/Na_2O to a certain level until the precipitation of illite (expressed as muscovite, $KAl_3Si_3O_{10}(OH)_2$)) that drives the K_2O/Na_2O towards higher values. These reactions evolve until the biotite and plagioclase are completely altered leaving the rocks with an abundant quantity of K-feldspar and illite ($K_2O/Na_2O > 10$). In the final stage, the Na_2O present initially in the fresh granite is completely leached (Figure 8) and hydrothermal quartz veins are precipitating leading to an increase of SiO_2 in the fractured and altered granite samples (Figure 3).

The variability in elemental concentration of these fractured samples could be the results of rock deformation, or different stage of intense hydrothermal alteration where secondary minerals are continuously precipitating or mobilized during more important fluid/rock interactions (Nishimoto and Yoshida, 2010).

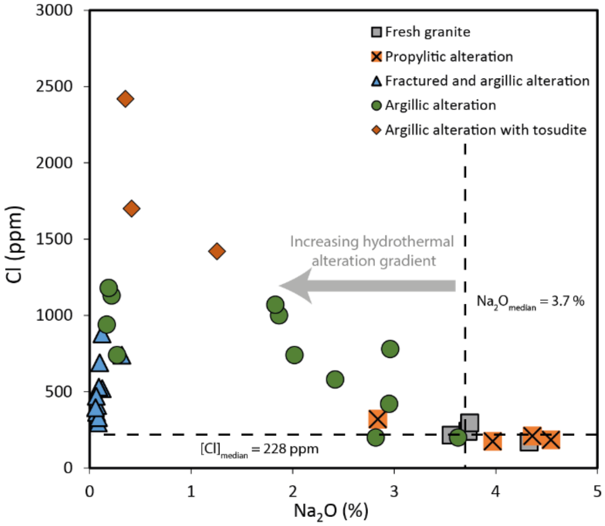

Figure 8: Evolution of [Cl] and Na_2O in the granites. The [Cl] and Na_2O median of respectively 228 ppm and 3.7% represented by the dotted lines are the calculated median of fresh monzonite granites.

5.2 Behavior of [Li] and [Cl] from fresh to highly altered and fractured granite

In monzonite granites, lithium is primarily found in phyllosilicates, with the highest concentration present in biotite with [Li] of several hundreds of ppm while [Li] in quartz, plagioclase, and K-feldspar remain confined to only few ppm (Drüppel et al., 2020; Dugamin et al., 2024; Edmunds et al., 1985; Jungmann et al., 2025). In the fresh monzonite granites (Figure 6), the abundance of biotite seems to increase the [Li] (74 ppm in K12-5) compared to a granite with lower biotite presence (39 ppm in K13-8). Chlorine can also be found in the biotite of granite (Edmunds et al., 1985), however, the abundance of biotite in the sample K12-5 appears to have a limited impact on the [Cl] compared to the [Li] which suggests that Cl is not principally controlled by the amount of biotite. Teiber et al., (2014) have found that amphibole rich sample can be a main contributor to whole rock's Cl which could explain the differences between [Cl].

During propylitic alteration, chloritization and albitization have a limited impact on the solubilisation of Li (Figure 7). Despite the chemical transformation of biotite into chlorite, Li is still contained in the chlorite minerals and is not released in the solution. This is supported by the studies of Dugamin et al., (2024) and Jungmann et al., (2025) who compared the [Li] of biotite and chlorite minerals and found similar concentration. Alike [Li], the average [Cl] of granite impacted by propylitic alteration is not different from the fresh granite, and appears to be unaffected by chloritization and albitization processes.

Granites impacted by argillic alteration have lower [Li] (Figure 7) and higher [Cl] (Figure 8) compared to propylitic altered and fresh granites due to progress of hydrothermal alteration. The higher [Cl] could be explained by a higher fluid/rocks interaction. Indeed, the geothermal fluid at SsF is enriched in [Cl] (Table 1) and can be a contributor of the Cl present in the rocks. The increasing fluid/rock ratio would therefore trigger the illitization of the minerals in the granites and solubilize alcalin elements such as Li and Na driving K_2O/Na_2O and [Li] towards lower values (Figure 7 and Figure 8). Following this statement, granites where tosudite minerals were identified have the highest [Cl] and therefore should have the highest fluid/rock interactions. This statement is also consistent with the highest LOI found in the granites with tosudite compared with the rest of the granites analyzed (Figure 3). However, compared to the rest of the granite impacted by argillic alteration that have lower [Li], granites with tosudite have the highest [Li] (Figure 7). In this specific case, [Li] is mainly influenced by the presence of organic matter that trigger tosudite formation (Ledésert et al., 1996) rather than increasing fluid/rock interaction. Interestingly, organic matters could increase [Cl] because Cl ions might be electrostatically attached to the positive charges present on the Al-Fe-organic colloids (Öberg, 1998; Viers et al., 2001). The difference in anions exchange capacity between clay minerals could explain the higher Cl content in granite tosudite (Figure 8). Chloride adsorption capacity appears to be limited in illite clays (Gebhardt and Coleman, 1974) and therefore [Cl] could not be explained only by this unique process.

In the fractured and highly altered granites, Li can precipitate in quartz veins (Figure 5 and Figure 7) which therefore increase the [Li] of these granite. Important [Li] were analyzed in newly-formed quartz (Dugamin et al., 2024) or in quartz with abundant fluid inclusion (up to 1590 ppm; Drüppel et al., 2020), which could justify the higher [Li] in rocks where drusy quartz veins precipitate. The precipitation of secondary minerals in the fracture network could reduce the fluid/rock interaction which therefore could explain the lower [Cl] in fracture and argillic altered granite compared to the argillic altered granites without fracturing.

5.3 Geology of the URG and lithium mobility

Fresh granites which are bearing lithium due to the occurrences of ferro-magnesian minerals like primary biotite or propylitic chlorite, correspond to low lithium concentration crystalline rocks (Jungmann et al., 2025). Similarly, hydrothermally altered granites, characterized by argillic alteration due to the presence of illite, are also depleted in lithium, as are the fractured or deformed altered granite facies. Therefore, the fresh granites as well as the hydrothermal altered granites could contribute to a source of lithium for the brines due the couple fracturing and hydrothermal alteration related to the successive polyphasic tectonic history of the Rhine graben.

Hydrothermally altered granites (with or without tosudite) spatially correspond to wall-rock of large fractured zones showing an internal architecture highly deformed with a fault core where shearing movements induced cataclastic facies like breccia to microbreccia or cataclased to fractured granites. Within hydrothermally altered facies, the rock texture is still visible whereas in the cataclastic facies, the porphyritic rock texture is lost due to the comminution associated with brittle deformation and shearing (Genter et al., 2000). Thus, all those crushed facies are depleted in lithium which probably migrated into the brine. On the contrary, some rare hydrothermally altered granites, relatively depleted in macroscopic fractures, are trapping lithium in particular secondary clay minerals. Therefore, only some hydrothermally altered granite facies characterized by the occurrences of tosudite or kaolinite ([Li] = 247 ppm in the granite with kaolinite; Figure 7) as well as secondary drusy quartz veins, are lithium-rich rock facies. Those late drusy quartz veins were interpreted as present day permeable features in the deep geothermal wells of the URG (Vidal et al., 2019, 2024). The occurrences of tosudite minerals were interpreted as a fluid-rock interaction involving organic matter interaction due to the neighboring overlying Pechelbronn oil field (Ledésert et al., 1999). It turns out that automorphic quartz veins correspond to late opening mode fractures and are in contact with the present-day permeable brine. Therefore, those quartz vein precipitations could probably deplete the present-day brine in dissolved lithium. Both fractured altered facies, hydrothermally altered granites with or without tosudite as well as quartz veins indicate high fluid-rock ratio conditions.

6 CONCLUSION

Hydrogeochemical characterization of the geothermal brines from the URG was done several times from the 90s with a lithium concentration of the geothermal fluid ranging from 160 to 210 mg/L. However, the lithium concentration in the crystalline reservoir rock formations of this area is poorly documented. Therefore about 40 crystalline rock facies from fresh porphyritic biotite-rich monzogranite and fine grained two micas granite to hydrothermally altered or fractured granite samples were analyzed in terms of major and trace elements focusing on lithium content measured from the Soultz-sous-Forêts cores.

It turns out that the growing interest in extracting lithium from geothermal brines in the URG is motivating research into the origin of lithium in the geothermal water reservoir. The higher [Li] in fresh granites compared to granites impacted by argillic alteration indicates the solubilization of Li from deep rocks, supporting a significant contribution of crystalline reservoir rocks to Li enrichment in the brine. The solubilization is triggered by more important fluid/rock interactions which is supported by higher [Cl] in the facies that are more hydrothermally altered. Spot enrichments of Li and Cl are found in granites with tosudite with the highest [Li] and [Cl] recorded in a rock sample from SsF. However, these tosudite minerals act more as a trap of Li than a source. A similar Li enrichment is noticeable in drusy quartz veins, but this Li is also not a contributor of the [Li] in the brine.

This project only looked at samples from the granite at SsF site, but it would be worthwhile replicating it at sedimentary cover of the reservoir that includes Triassic clastic rocks of the URG.

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