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# How Important Is the Hydrothermal Alteration in the Upper Rhine Graben for Geothermal Lithium Assessment?

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## Keywords

*Geothermal lithium, Li-bearing minerals, X-Ray diffraction, laser ablation, Upper Rhine Graben (URG), GLITER project*

## ABSTRACT

The Upper Rhine Graben (URG) benefits from an extensive geothermal history with several industrial projects on stream since the beginning of the 21<sup>st</sup> century. Several deep wells have demonstrated that hydrothermal brines circulate inside a complex network of natural fractures developed in the Triassic sandstones and the altered granitic basement with temperatures up to about 210°C and Li concentrations up to 210 mg/L. More recently, scientific studies have revealed that geothermal lithium could be extracted from this brine. The opportunity for lithium extraction combined with a low CO<sub>2</sub> emission heat gave a second life to the geothermal exploration in the URG. A better knowledge of lithium sources will be based on mineralogical and geochemical characterization of the potential reservoir rocks. Representative samples were collected, i.e., several facies from the base to the top of the Triassic and Permian sandstones and granites of Hercynian basement from quarries in Vosges mountains as well as from deep wells. Micro-analytical techniques were correlated to petrological and geochemical data to discuss the Li resource circulations at the regional scale. Further investigations in other samples of the URG will be compared to attempt to upscale the Li rich rocks assessment at the regional scale and elucidate the Li enrichment in the brines.

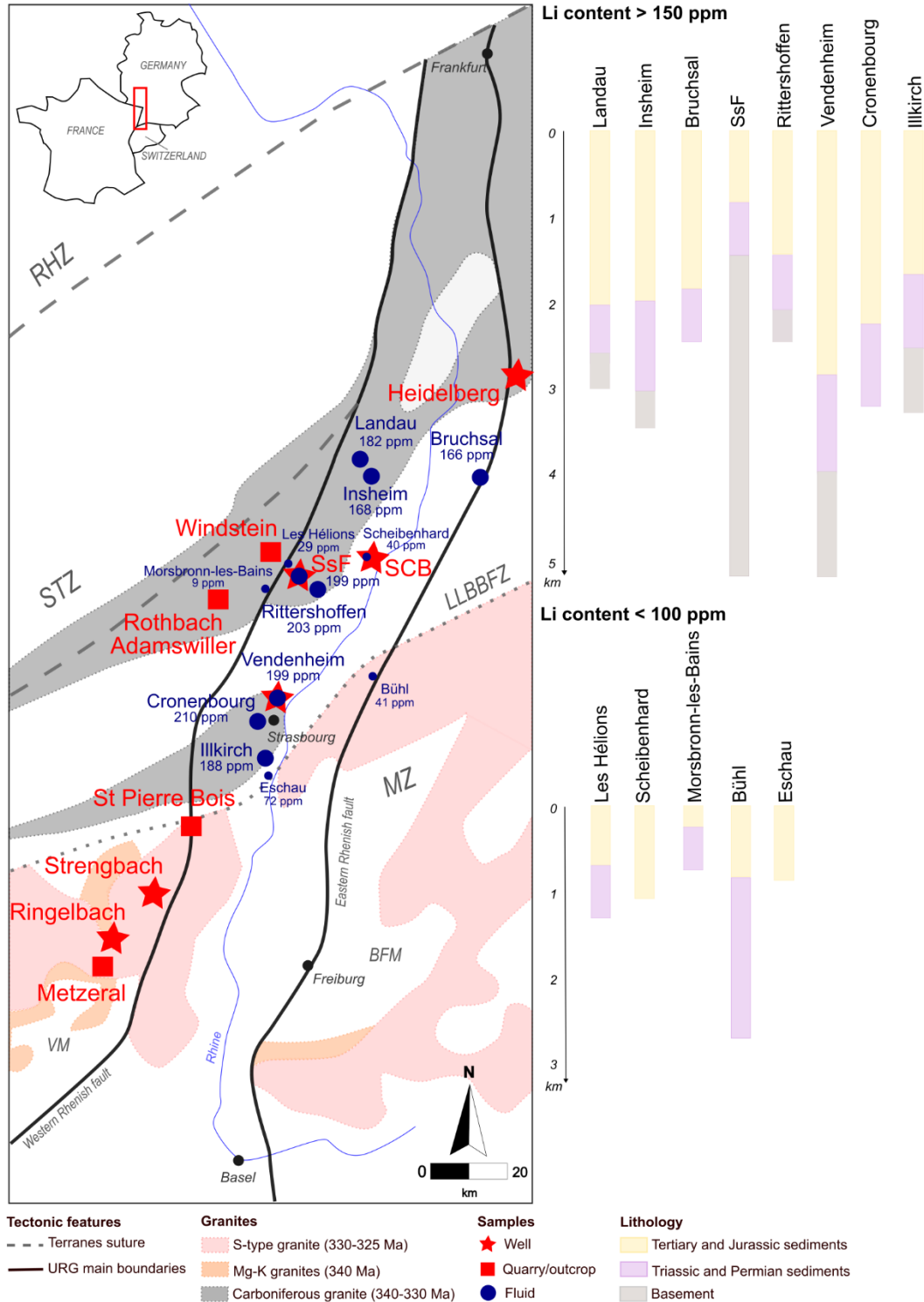
## 1. Introduction

In the 1970s, the discovery of lithium concentrations until 400 ppm in the Salton Sea geothermal field in California attracted curiosity of researchers among the world (Werner, 1970). In the Upper Rhine Graben (URG), a first geochemical analysis of geothermal fluid from the Cronenbourg geothermal exploration borehole near Strasbourg, reveals high lithium levels of 210 ppm (Pauwels et al., 1993). The URG presents unique geological conditions, characterized by elevated geothermal gradient and brines upflow along major faults associated to regional thermal anomalies

that make it an ideal region for geothermal exploitation (Baillieux et al., 2013; Pribnow and Schellschmidt, 2000). Over the year, several reservoirs have been investigated for geothermal projects. Projects with the highest flowrate targeted fracture and fault zones in the granitic basement, while projects targeting the sandstones reservoir remain with lower flowrate (Vidal and Genter, 2018). Today, five high-temperature geothermal plants operate in Alsace (France), in Palatinate and in Baden-Württemberg (Germany), producing heat and power, with lithium concentrations in the deep geothermal brines ranging from 166 to 203 ppm (Bosia et al., 2021; Sanjuan et al., 2016) (Figure 1). Similar Li concentrations were analyzed in the brines from deep geothermal wells recently drilled in the granite basement at Vendenheim (Sanjuan et al., 2021) and Illkirch, in Alsace (Bosia et al., 2021). This ongoing research and development highlights the potential of geothermal lithium as a sustainable resource. In this framework, the GLITER project (Integrative multiscale investigation of heat and lithium source and pathways in Deep Geothermal System in a rift context: Focus on the Upper Rhine Graben), cofunded by the French National Research Agency, investigates, among other things the Li sources and Li fluid concentration processes in the URG. Petrological and geochemical characterisations are conducted on the selected samples of sandstones, and granite of the URG from deep wells, quarries and outcrops in order to determine the major Li-carrier minerals and correlate them to fluids concentration at the regional scale.

A geothermal well, named VDH, from the Strasbourg area is presented in this study. Cuttings from several facies of Triassic and Permian sandstones as well as Carboniferous granitic basement intersected below 3.5 km depth were sampled. These formations reached temperature above 200°C in VDH well and were affected by several hydrothermal events. The well intersected permeable fracture and fault zones that channelize deep circulations in both sandstones and granite. The circulating geothermal brine in VDH well has a high Li content between 162 and 200 ppm and a Total Dissolved Solids around 100 g/L. The Li range observed is explained by different sampling methods under different conditions, with production tests carried out on the early and late development stages of the well and having timelines ranging from few days to several weeks of circulations.

The preliminary results of the mineralogical and geochemical studies conducted on these samples are compared to existing literature, but also other analyses acquired in the framework of the GLITER ANR project; core samples at the sediments-basement interface from the EPS1 well at Soultz-sous-Forêts as well as sandstones samples from Adamswiller and Rothbach quarries in the western border of the URG (Figure 1). By synthesising these data, the goal of the project is to elucidate where the brines are enriched in depth and how they make it possible to mobilize the lithium available in the rock formations.



**Figure 1: Map of Li distribution in fluids of the URG superimposed to the granite and granitoids emplacement. Li contents in fluids are from Bosia et al. (2021), Pauwels et al. (1993) and Sanjuan et al. (2016). Granites emplacements are extrapolated from the geological map and interpretative signature of the basement from Edel and Schulmann (2009). RHZ = Rhenohercynian zone, STZ = Saxothuringian zone, MZ Moldanubian zone, LLBBFZ = Lalaye-Lubine fault zone, VM = Vosges Mountains, BFM = Black Forest Mountains**

## 2. Sampling and methodology

Cuttings were sampled in representative formations intersected by the VDH well at Vendenheim: Voltzia sandstones in the Upper Buntsandstein, Vosgian sandstones in the Middle Buntsandstein, Permian sandstones, the hydrothermalized granitic basement. The goal was to conduct analysis on fresh and fractured and altered levels to compare the impact of alteration on Li resource. In EPS-1 well at Soultz-sous-Forêts, Permian sandstones as well as the first few hundred meters of biotite-amphibole granite described in Dezayes and Lerouge (2019) were sampled. Voltzia sandstones were sampled from Adamswiller quarry while Vosgian sandstones are from Rothbach quarry. Other rock samples identified on Figure 1 will be presented in further studies to correlate the results of this paper.

For VDH well, mineral phases were identified by binocular (Figure 2) and quantified using X-ray diffraction on bulk rock and Rietveld refinement (Figure 3). XRD were performed on powder mounts using a D8 Advance Bruker AXS diffractometer (CuK $\alpha$ , from 2° to 70°2 $\theta$  with a step-scan 0.02° increments per second, counting time 1s per increment, 30 mA, 40 kV) at IC2MP laboratory at the University of Poitiers. Then, bulk rock geochemistry was analyzed by Multi Collector Inductively Coupled Plasma Mass Spectrometer from major and trace elements in cuttings samples of representative formations.

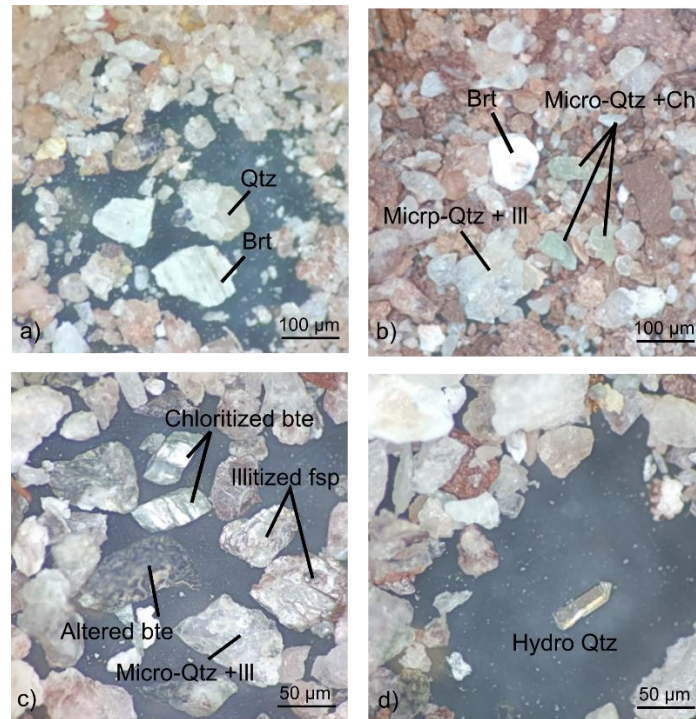
In all samples from wells and quarries, analyses of major elements ( $^{23}\text{Na}$ ,  $^{24}\text{Mg}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ,  $^{39}\text{K}$ ,  $^{48}\text{Ti}$ ,  $^{56}\text{Fe}$ ) and lithium ( $^7\text{Li}$ ) in minerals were performed using a UVl laser-ablation micro-sampler CETAC® Excite (193 nm) coupled to an Agilent triple quadrupole plasma mass spectrometer at the French Geological Survey laboratory in Orléans (France), according to the laser configuration of Monnié et al. (2018). Ablation spots 35  $\mu\text{m}$  in diameter were performed at 8 Hz frequency with energy of  $\sim 6 \text{ J/cm}^2$  for quartz and  $\sim 4 \text{ J/cm}^2$  for other silicates. Analysis time for each spot was 60 s, including 20 s of background measurement with the laser off and 40 s of analysis time with the laser on. Quantification was performed with Glitter® software. All data were calibrated against the external standard NIST SRM 612 (Pearce et al., 1997), and the internal standard of the Si value in the mineral.

## 3. Results

### 3.1 VDH deep well from Strasbourg area

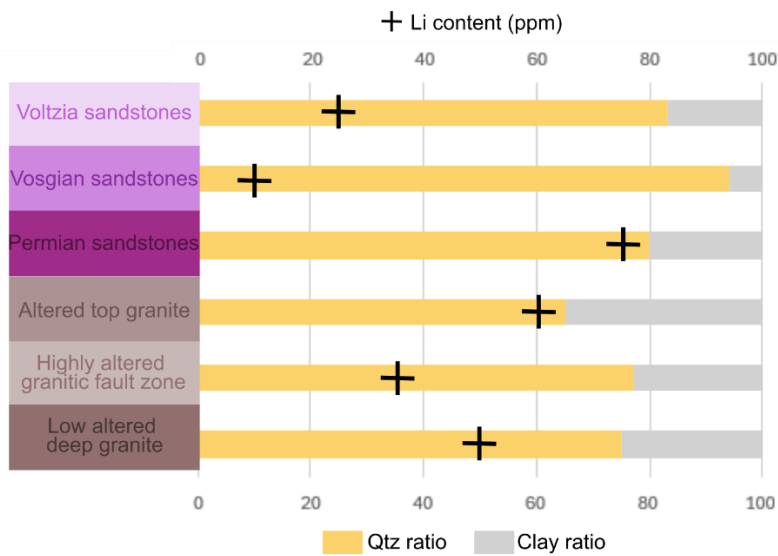
The Voltzia sandstones are micaceous sandstones presenting a very low matrix porosity and permeable levels associated to fractures. Fracture filling of the all Permo-Triassic sequence intersected is mainly barite (Figure 2). Li measurements on illite and muscovite range between 30 and 50 ppm (Table 1).

The Vosgian sandstones are quartz-rich sandstones with heterogeneous porosity mainly due to variation of grain size and occurrences of fractures. Li average content of illite is higher ( $127 \pm 57$  ppm) than in the Voltzia sandstones (Table 1). Li contents of scarce biotite (143 ppm) and chlorite (317 ppm) are also higher than that measured in the Voltzia sandstones (13 and 96 ppm respectively). However, the bulk rock geochemistry reveals similar Li content of 20-25 ppm in the Triassic sequence (Figure 3).



**Figure 2: Mineralogical observations of cuttings samples in (a) Vosgian sandstones (b) Permian sandstones (c) altered granitic basement (d) fault zone in granitic basement. Qtz = quartz, Hydro Qtz = hydrothermal quartz, Bte = biotite, Brt = barite, Chl = chlorite, Fsp = feldspar, Ill = illite**

The Permian sandstones contain a low clay ratio similar to Voltzia sandstones. However, the Li content of the bulk rock ranges between 65 and 75 ppm, the highest values measured in the well. The Li content in minerals was not yet measured in the sample. It would be relevant as a major permeable fracture zone was intersected in this formation.



**Figure 3: Clays and quartz ratio (in %) estimated from XRD as well as distribution of Li content (in ppm) measured in bulk rock. Clays include muscovite, illitic minerals (illite and illite-smectite mixed layers), biotite and chlorite.**

**Table 1: Li contents (in ppm) measured in minerals by laser ablation. Bte = biotite, Chl = chlorite, Ill = illite and illite-smectite mixed layers), Qtz = magmatic quartz, Amp = amphibole, ave = average, sd = standard deviation**

Lithology	Sample	Bte		Chl		Ill		Qtz		Amp	
		ave	sd	ave	sd	ave	sd	ave	sd	ave	sd
Voltzia sandstones	VDH well	13	6	96	28	39	8	-	-	-	-
	Adamswiller quarry	~320		-	-	321	541	-	-	-	-
Vosgian sandstones	VDH well	143	3	317	86	127	57	14	8	-	-
	Rothbach quarry	-	-	-	-	109	143	-	-	-	-
Permian sandstones	EPS1 well	-	-	-	-	219	339	-	-	-	-
Altered top granite	VDH well	105	32	439	67	108	48	47	83	67	39
	EPS1 well	501	124	504	103	55	5	10	2	10	3

In the Hercynian basement, petrographic observations provide evidence of biotite, amphibole, quartz, feldspars, chlorite, illite, carbonates in cuttings of granite, suggesting that it consists of a biotite-amphibole granite affected by an intense weathering marked by the abundance of clay minerals including illite, chlorite, and the presence of hydrothermal microquartz and carbonates (Figure 2).

The Li contents of bulk rock vary considering the grade of alteration. The whole Li content is around 50-60 ppm in zones where chlorite and residual biotite prevail, and around 30-35 ppm in zones where illite, carbonates and hydrothermal quartz are dominant (Figure 3). The Li contents of minerals vary a lot:  $105 \pm 32$  ppm in altered biotite,  $67 \pm 39$  ppm in amphibole,  $439 \pm 67$  ppm in chlorite or chloritized biotite,  $108 \pm 48$  ppm in illitic minerals (Table 1). Quartz analyzed with laser ablation in granite is mainly magmatic one ( $47 \pm 83$  ppm) as hydrothermal quartz in fault zone is more difficult to target.

### 3.2 Additional work on EPS1 deep well from Soultz-sous-Forêts

Core samples in Permian sandstones intersected by EPS1 well indicate very heterogeneous Li content of detrital micas ranging between 3 and 1444 ppm.

Some samples from the first few hundred meters of biotite-amphibole granite present preserved magmatic biotite showing high Li content ( $501 \pm 124$  ppm) compared to amphibole ( $10 \pm 3$  ppm). Chlorite associated to the diffuse propylitic alteration observed in the less altered samples shows similar high Li content ( $504 \pm 103$  ppm) to that of biotite. In the most intense altered samples, illite in fractures ( $55 \pm 5$  ppm) and in the granite wallrock ( $< 40$  ppm) has significantly lower Li contents than ferromagnesian minerals. It is noteworthy that hydrothermal quartz fills in fractures exhibits high Li content ( $353 \pm 152$  ppm) compared to magmatic quartz ( $10 \pm 2$  ppm).

### 3.3 Sandstone quarries

Voltzia sandstones from Adamswiller quarry exhibit a large range of Li concentrations in illitic minerals (1-2247 ppm, median = 86 ppm) and contain scarce biotite flakes (around 320 ppm). Vosgian sandstones from Rothbach quarry present a large range of Li concentrations in illitic minerals too (1-717 ppm, median = 62 ppm).

#### 4. Discussion

In sandstones, illitic minerals with minor detrital chlorite, muscovite, and biotite are the primary Li-carrier minerals. Micro-analytical measurements on cuttings samples are likely less reliable than those on rock materials. Analyses of clays and mica in sandstones show a wide range of Li contents, suggesting significant heterogeneity in the sources. One mica flake can present a very high Li content, while a neighboring one may have a very low content. The overall Li content of Middle Buntsandstein sandstones, ranging from 20-25 ppm, is consistent with literature values: 20-40 ppm from a deep well in Bruchsal (Kölbel et al., 2023) and 13-17 ppm from a quarry in the Black Forest (Orywall et al., 2017). The highest Li content in Permian sandstones up to 70 ppm, or even 80 ppm in Bruchsal (Kölbel et al., 2023), might be due to a proximal source of dismantled granitic bedrock in the Permian basin, whereas the Middle Buntsandstein's extensive fluvial context transported weathering products over several thousand kilometers.

The granite intersected in the VDH well from the Strasbourg area consists of biotite-amphibole granite. The first few hundred meters show intense alteration, with at least two stages identified: 1) diffuse propylitic alteration marked by biotite chloritization, and 2) fracture wallrock alteration associated with hydrothermal circulations, marked by prevalent matrix illitization, carbonate fills in fractures, and hydrothermal quartz fills in permeable levels. The Hercynian basement intersected by the VDH well is similar in terms of magmatic rock and alterations to that intersected at Soultz, aged from Carboniferous (330-340 Ma) (Genter, 1989).

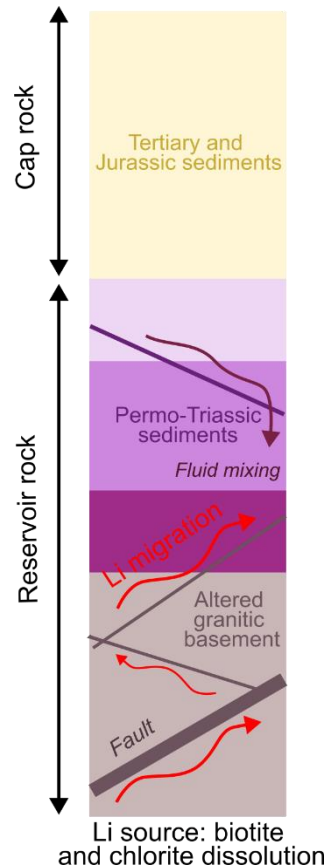
In the VDH well, the granitic basement shows heterogeneous Li distribution mainly due to the type and intensity of alteration. The highest whole-rock Li contents correspond to zones where propylitic alteration (biotite chloritization) prevails and residual primary magmatic biotite remains. Lower values are found in fractured zones affected by matrix illitization and carbonate and quartz fills in fractures. These results are consistent with bulk rock data from Soultz; 25 ppm for illitized facies vs 37 ppm for facies dominated by propylitic alteration (Genter, 1989). High Li contents in biotite and chlorite and low ones in illite, measured in VDH and EPS1 wells, are similar to findings by Dugamin et al. (2024). The high Li contents measured in hydrothermal quartz in the EPS1 well and some quartz spots in the Strasbourg well confirm data from Dugamin et al. (2024) (623-1043 ppm). These high Li contents were also identified in a major fault outcropping in the St Pierre Bois quarry on the western shoulder of the URG (Dezayes et al., 2021).

These preliminary results, correlated with existing literature, suggest that ferromagnesian primary minerals of the Carboniferous granitic basement could be a possible source of lithium. The dissolution of Li-bearing ferromagnesian minerals during brine circulations in fracture and fault zones could lead to brine Li-enrichment (Figure 4). Simple seawater evaporation during the Triassic cannot explain the Li content observed in present-day fluid (Dugamin et al., 2024). Li resources migrate in the Permo-Triassic and Carboniferous reservoir rocks through fracture and fault networks where water-rock interactions are intense.

The decrease in Li contents from the propylitic alteration to an intense hydrothermal alteration (illite-carbonates-quartz) and the Li content in hydrothermal quartz suggest lithium mobilization from the granite into the hydrothermal fluids. This underscores the need for further analysis of other granite types in the URG and graben shoulders, such as Mg-K granite or S-type granite (Tabaud et al., 2015). The latter are peraluminous granites known as sources of Li, and



understanding differentiation processes during granitic intrusion and granitoid emplacement could help elucidate Li distribution at a regional scale (Figure 1).



**Figure 4: Conceptual model of the geothermal lithium play in the URG**

## 5. Concluding remarks and perspectives

These preliminary results highlight the high-level content in ferromagnesian minerals from the Carboniferous granite making them potential sources of lithium during brine's enrichment. When the brine suffers disequilibrium and precipitate it can lead to Li-rich newly formed quartz. As the Permo-Triassic rocks result from granite's dismantling, the sedimentation context and grade of alteration of the minerals will impact the Li distribution in the reservoir rocks. The Li content of the reservoir rocks associated to an illite-facies is lower than a biotite-chlorite-facies.

The lithium behavior in alteration processes is only partially understood due to the lack of data on the lithium distribution in fresh minerals and their alteration products. Further analysis will be conducted in different sites and rock formations of the URG to strengthen the understanding of lithium enrichment in brines.

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## REFERENCES

- Baillieux, P., Schill, E., Edel, J.-B., Mauri, G., 2013. Localization of temperature anomalies in the Upper Rhine Graben: insights from geophysics and neotectonic activity. *International Geology Review* 55, 1744–1762. <https://doi.org/10.1080/00206814.2013.794914>
- Bosia, C., Mouchot, J., Ravier, G., Seibt, A., Jähnichen, S., Degering, D., Scheiber, J., Dalmais, E., Baujard, C., Genter, A., 2021. Evolution of Brine Geochemical Composition during Operation of EGS Geothermal Plants (Alsace, France), Proceedings of 46th Workshop on Geothermal Reservoir Engineering. Stanford University, California, USA.
- Dezayes, C., Lerouge, C., 2019. Reconstructing Paleofluid Circulation at the Hercynian Basement/Mesozoic Sedimentary Cover Interface in the Upper Rhine Graben. *Geofluids* 2019, 4849860. <https://doi.org/10.1155/2019/4849860>
- Dezayes, C., Lerouge, C., Innocent, C., Lach, P., 2021. Structural control on fluid circulation in a graben system: Constraints from the Saint Pierre Bois quarry (Vosges, France). *Journal of Structural Geology* 146, 104323.
- Dugamin, E.J.M., Boiron, M.-C., Cathelineau, M., Richard, A., Peiffert, C., Lebreton, A., Banks, D.A., Despinois, F., 2024. Brine-granite interaction and lithium leaching in a continental rift (Soultz-sous-Forêts, Rhine Graben, France). *Lithos* 478–479, 107604. <https://doi.org/10.1016/j.lithos.2024.107604>
- Edel, J.-B., Schulmann, K., 2009. Geophysical constraints and model of the “Saxothuringian and Rhenohercynian subductions – magmatic arc system” in NE France and SW Germany. *Bulletin de la Societe Geologique de France* 180, 545–558. <https://doi.org/10.2113/gssgfbull.180.6.545>
- Genter, A., 1989. Géothermie roches chaudes sèches: le granite de Soultz-sous-Forêts (Bas-Rhin, France). *Fracturation naturelle, altérations hydrothermales et interaction eau-roche* (PhD thesis). Université d’Orléans, France.
- Kölbel, L., Kölbel, T., Herrmann, L., Kaymakci, E., Ghergut, I., Poirel, A., Schneider, J., 2023. Lithium extraction from geothermal brines in the Upper Rhine Graben: A case study of potential and current state of the art. *Hydrometallurgy* 221, 106131. <https://doi.org/10.1016/j.hydromet.2023.106131>
- Monnier, L., Lach, P., Salvi, S., Melleton, J., Bailly, L., Béziat, D., Monnier, Y., Gouy, S., 2018. Quartz trace-element composition by LA-ICP-MS as proxy for granite differentiation, hydrothermal episodes, and related mineralization: The Beauvoir Granite (Echassières district), France. *Lithos* 320-321, 355–377. <https://doi.org/10.1016/j.lithos.2018.09.024>
- Orywall, P., Drüppel, K., Kuhn, D., Kohl, T., Zimmermann, M., Eiche, E., 2017. Flow-through experiments on the interaction of sandstone with Ba-rich fluids at geothermal conditions. *Geothermal Energy* 5, 20. <https://doi.org/10.1186/s40517-017-0079-7>
- Pauwels, H., Fouillac, C., Fouillac, A.-M., 1993. Chemistry and isotopes of deep geothermal saline fluids in the Upper Rhine Graben: Origin of compounds and water-rock interactions. *Geochimica et Cosmochimica Acta* 57, 2737–2749. [https://doi.org/10.1016/0016-7037\(93\)90387-C](https://doi.org/10.1016/0016-7037(93)90387-C)

- Pearce, N.J., Perkins, W.T., Westgate, J.A., Gorton, M.P., Jackson, S.E., Neal, C.R., Chenery, S.P., 1997. A compilation of new and published major and trace element data for NIST SRM 610 and NIST SRM 612 glass reference materials. *Geostandards and Geoanalytical Research* 21, 115–144.
- Pribnow, D., Schellschmidt, R., 2000. Thermal tracking of upper crustal fluid flow in the Rhine Graben. *Geophysical Research Letters* 27, 1957–1960. <https://doi.org/10.1029/2000GL008494>
- Sanjuan, B., Millot, R., Innocent, Ch., Dezayes, Ch., Scheiber, J., Brach, M., 2016. Major geochemical characteristics of geothermal brines from the Upper Rhine Graben granitic basement with constraints on temperature and circulation. *Chemical Geology* 428, 27–47. <https://doi.org/10.1016/j.chemgeo.2016.02.021>
- Sanjuan, B., Négrel, G., Le Lous, M., Poulmarch, E., Gal, F., Damy, P.-C., 2021. Main geochemical characteristics of the deep geothermal brine at Vendenheim (Alsace, France) with constraints on temperature and fluid circulation, in: *Proceedings World Geothermal Congress 2020+1*. Reykjavik, Iceland
- Tabaud, A.-S., Janoušek, V., Skrzypek, E., Schulmann, K., Rossi, P., Whitechurch, H., Guerrot, C., Paquette, J.-L., 2015. Chronology, petrogenesis and heat sources for successive Carboniferous magmatic events in the Southern–Central Variscan Vosges Mts (NE France). *Journal of the Geological Society* 172, 87–102. <https://doi.org/10.1144/jgs2013-123>
- Vidal, J., Genter, A., 2018. Overview of naturally permeable fractured reservoirs in the central and southern Upper Rhine Graben: Insights from geothermal wells. *Geothermics* 74, 57–73. <https://doi.org/10.1016/j.geothermics.2018.02.003>
- Werner, H.H., 1970. Contribution to the mineral extraction from supersaturated geothermal brines Salton Sea Area, California. *Geothermics, Proceedings of the United Nations symposium on the development and utilization of geothermal resources* 2, 1651–1655. [https://doi.org/10.1016/0375-6505\(70\)90492-X](https://doi.org/10.1016/0375-6505(70)90492-X)