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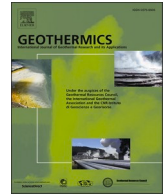
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Atlas of lithium geothermal fluids in Europe

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ABSTRACT

In the last decade, lithium has become a strategic metal leading several European countries to assess their Li-resources. For the first time, a geochemical characterization and assessment of identified Li-rich deep fluids in Europe has been conducted. A total of 182 occurrences have been identified. Geostatistical study suggests that the highest Li concentration values (i.e. 250–480 mg/l) are strongly correlated to B, Rb, K, SO₄, Na, Cl and F whereas the lowest Li concentration values (i.e. 15 to 63 mg/l) are correlated to Mg, Mn, U and NH₄. Moreover, the fluids' ages are either coeval with a widespread emplacement of Li-magmatic bodies or deposition of sedimentary basins in Europe. Both reflecting extensional geodynamic setting. This review addresses main geochemical characteristics of deep fluids and contributes as a first step to the fundamental understanding of the geological processes for Li enrichment in the geothermal fluids.

1. Introduction

Lithium, which is the lightest solid element and an excellent conductor of heat and electricity, has become in the last decade, a strategic metal due to its extensive consumption in electro mobility and stationary energy storage technologies. Consequently, worldwide demand has considerably increased, stimulating European interest in lithium mining and leading several countries to assess their resources/reserves in order to secure their own supplies and reduce their Li imports dependency.

Conventionally, this white metal is extracted mainly from two distinct types of deposits: 1) *brines* from which Li occurs in salts accumulated from saline groundwater in relatively young, arid basins (e.g., the northern Argentina to western Bolivia and northern Chile, [Ericksen and Salas, 1987](#); the Qinghai-Tibet plateau, [Yu et al., 2013](#); [Mao-Yong et al., 2020](#)); and 2) *hard-rock* in which Li occurs in sedimentary and magmatic deposits such as pegmatites (e.g., Greenbushes, Australia), rare metal granite (St Austell, UK) (e.g., [Kesler et al., 2012](#)). Li-bearing minerals are various and include Li-micas, spodumene, petalite etc. However, unconventional resources have also been identified in several sites related to oilfield and geothermal fluids. Although potential

resources are difficult to quantify for these sites because the volume, circulation paths and mixing processes of these fluids are poorly known and thus constrained ([Houston et al., 2011](#)), an EIT (European Institute of Technology) RAW Material project entitled EuGeLi (European Geothermal Lithium Brines) seeks to provide an European innovative Li extraction process for Li-rich geothermal fluids. As a first step of this project, a geographical compilation of the European Li-bearing geothermal fluids has been carried out. In the following, a geochemical characterization of these fluids ([Sanjuan et al., 2022](#)) has been produced and identification of their features has been assessed in order to identify the Li origin and its geological distribution, as well as the physical and chemical processes of Li enrichment for helping prospection of this metal in geothermal fluids.

In parallel, a recent re-assessment of the European lithium resources has been conducted on *hard-rocks* deposits ([Gourcerol et al., 2019](#)). This study has concluded that Li is not rare and is related to various genesis processes. It appears that Li is significantly enriched in two distinct geodynamical contexts: 1) late orogenic process, coeval with a continent-continent collision for endogenous processes; and 2) local crustal thickening, as well as post-orogenic extensional setting for the exogenous processes. Thus, the complementarity of these two studies

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would help to geologically constrain the distribution of the geothermal fluid deposits.

In details, this paper presents for the first time a compilation of the geothermal fluid occurrences in Europe from which $Li \geq 15 \text{ mg/l}$ and discusses the latter using geostatistical tools (e.g., exploratory statistical tools, agglomerative hierarchical clustering). Moreover, a comparison and distribution of the Li-bearing *hard-rock* versus Li-bearing geothermal fluid occurrences is also assessed.

2. Database description

Compilation of Li-bearing geothermal fluids in Europe has been done collecting information from several supports including peer-review publications. Thus, in total 182 occurrences have been identified in which Li is concentrated above 15 mg/l (Fig. 1), mainly distributed into eight geographical region countries (Fig. 2). Knowledge and available datasets from these various occurrences are very heterogeneous and may reflect water sampling at various timeframes (e.g., seasons, years) and conditions (host-rocks), done by different samplers and analyzed for different geochemical analysis packages. Thus, it has to be studied carefully and their comparisons have to be done with caution.

2.1. Water parameters

Based on this compilation, different fluid parameters have been assessed (Fig. 3). Importantly, temperatures and pressures of the well and host-rocks were not considered for the geostatistical characterization due to potential heterogeneity of the data acquisition. For instance, temperature and pressure of the geothermal well (Twell and Pwell) are sometimes measured at the surface and thus, are not representative of the deep reservoir conditions and sometimes not reported.

Lithium content varies from 15 mg/l to 480 mg/l with a mean at 90.7 mg/l and a median at 52 mg/l. The pH values are reported for 159

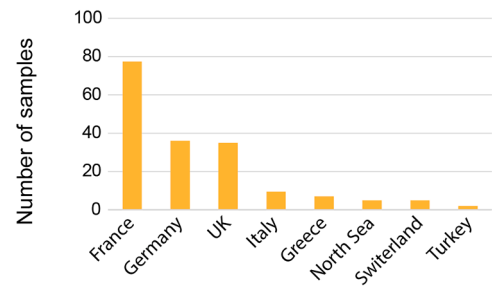


Fig. 2. Bar chart of the compiled number of Li-bearing geothermal brines in geographical regions.

samples and reflect weakly acidic to neutral conditions for most of the dataset (Fig. 3B) varying between 3.2 and 8.7, but with a mean at 6.1 and a median at 6.3.

Importantly, there is no significant correlation regarding pH conditions and Li concentrations. Moreover, as only few observations are recorded for the other physico-chemical parameters (e.g., Eh, flow rates), it appears difficult and too speculative to compare their variations to Li concentrations.

2.2. Geostatistical tools and methodology

In order to assess affinities and dissimilarities (i.e. correlation and anti-correlation) between geochemical parameters from this database, geostatistical tools have been applied. The methodology described below allows identification, classification of element affinity groups and their relationship to lithium-mineralizing processes. It may help to track the element association of Li enrichment at various scales when studying the type of host rock (fluids samples to regional scale).

A first step of this assessment is to normalize the element

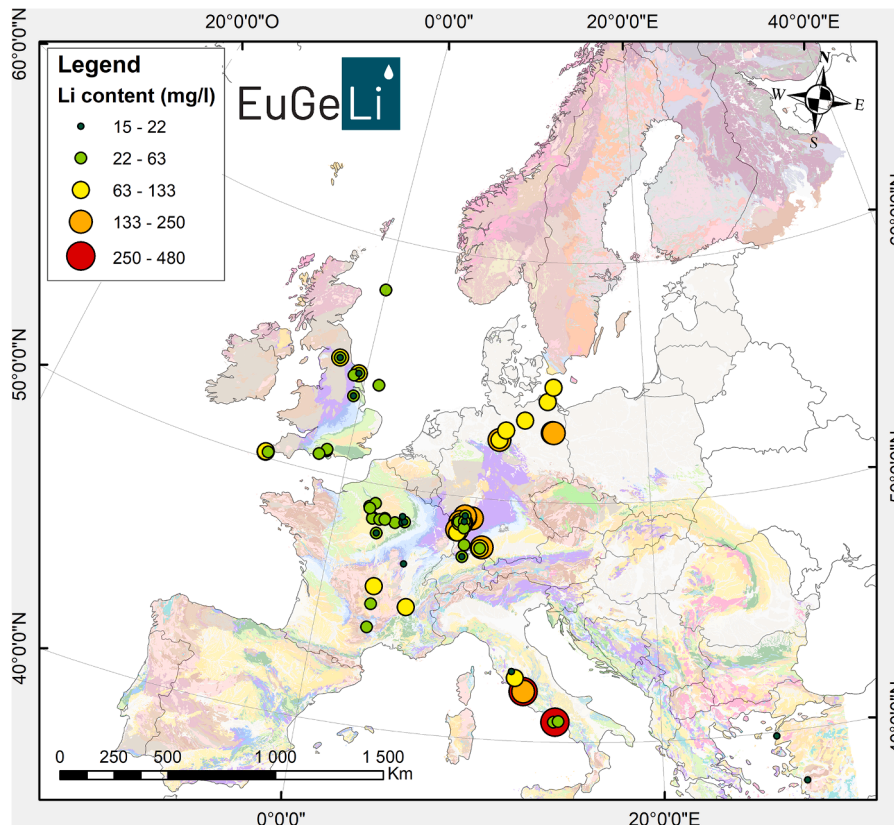


Fig. 1. Distribution map of the Li-bearing geothermal brines in Europe (using the homogenized European geological map, Billa et al., 2008). Cf Appendix 1.

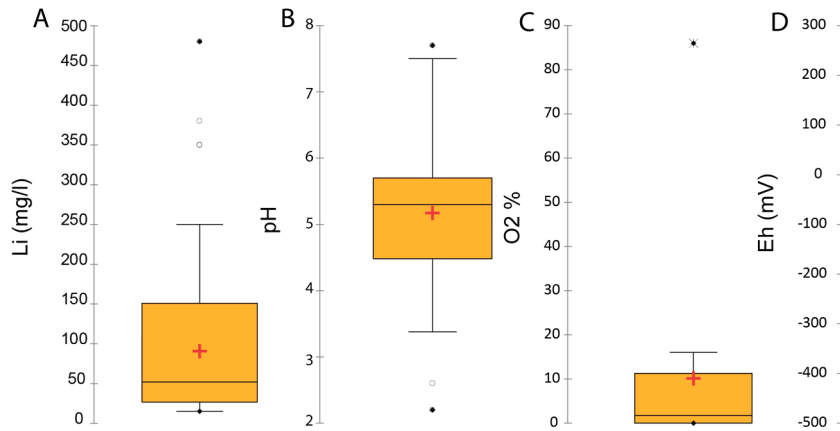


Fig. 3. Bar Box plots of various parameters: A) Li concentrations, B) pH values, C) O2 values and D) Eh potential. The boxes indicate the median (black line), the upper and lower quartiles (25 %; defined the grey boxes), the maximum and minimum values (upper and lower whiskers), the outliers (black circles) and the mean of the dataset (red crosses). See Table 1 for details.

concentrations in order to acquire a matrix of elements versus the Pearson correlation coefficients of the elements (McInnes et al., 2008). Then, an exploratory agglomerative hierarchical clustering (AHC) can be performed. This approach leads to progressive clustering of elements by a single linkage based on their similarity degrees calculated from their respective normalized concentrations and a dendrogram plot illustrates this method (Fig. 4).

Applied to a selection of elements from the dataset, there are three elemental groups (different colors illustrate them in the Fig. 4):

- 1) Th-Cs-Bi-As-Ti-SiO₂-Al-Ni;
- 2) Li-K-B-SO₄-Rb-Fe-Sr-Zn-Pb-F-Ba-Ca-NO₃-Br-Mn-Mg-Cl-Na; and
- 3) Nd-PO₄-Ge-NO₂-Cr-Be-Ag-Sb-Co-Cu-Cd.

Note that colors and identification numbers of the groups do not reflect particular order of importance.

However, it appears that Li-K-B-SO₄-Rb show a strong correlation. Besides, it should be indicated that few elements are missing in this AHC assessment as they are not strongly represented and would dilute the element association signal.

Regarding the correlation matrix (Fig. 5), where most of the elements from the dataset are studied, Li shows a good correlation with Ca, K, Rb, B, SO₄, Ge, Sr, F, Na and Cl whereas it shows an anti-correlation mostly

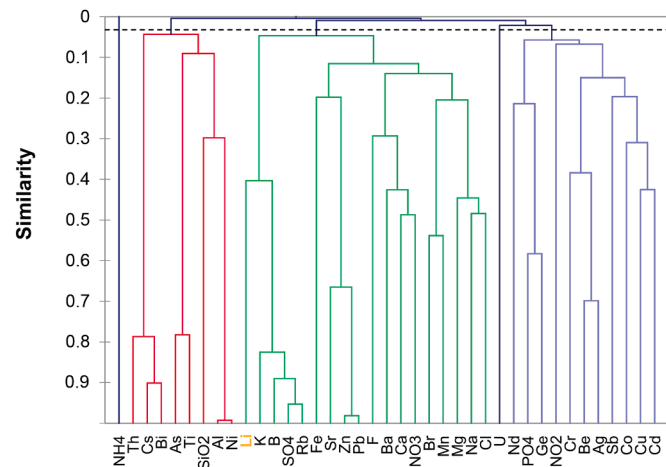


Fig. 4. Bar Dendrogram plot for the agglomerative hierarchical clustering (AHC) statistical analysis applied to the Li-bearing geothermal brine dataset on a relevant element selection. The three distinct colors define the three distinct elemental groups based on their related affinities.

with Mg, Mn, NH₄, U, Ti, As, Al, Th, Bi, Ni and Cs.

We highlight that the AHC method interpretation has to be combined with the study of correlation matrix in order to get a “multidimensional” approach as the AHC only presents the closest element relationship.

Exploratory statistical tools can also be applied to the dataset in order to refine these first observations through various and complementary methods: 1) the principal component analysis (PCA); and 2) the linear discriminant analysis (LDA).

The PCA method is a dimension-reduction technique applied to the correlation matrix (Grunsky and Smeed, 1999) and is presented as correlation-circle plots. In this latter process, elements are distributed as a function of their similarities (i.e. positive correlations) and dissimilarities (i.e. negative correlations) with respect to two factors, which represent the main variables of the dataset. Thus, this method mainly confirms the positive correlation with SO₄, K, B and Rb and negative correlation with Mg, Mn, NH₄, U, Ti, As, Al, Th, Bi, Ni and Cs (Fig. 5).

The LDA method (Fisher, 1936) is similar to the PCA but differs by a classification of the dataset as a function of predefined concentration categories (e.g., Venables and Ripley 2002, Grunsky et al., 2013, Gourcerol et al., 2018). Indeed, this method displays elements in a two dimensional diagram based on their discrimination scores as a function of their behavior with a selected variable such as Li concentrations. This method allows assessment of an element’s variations as a function of Li concentration categories. Applied to the dataset, this method states that the highest Li concentration values (i.e. 250–480 mg/l) are strongly correlated to B, Rb, K, SO₄, Na, Cl and F (Fig. 7). The moderate values (133–249.9 mg/l) are correlated to the Ca, Ge, Sr, PO₄ element association (Fig. 7). Finally, the lowest Li concentration values (i.e. 15 to 63 mg/l) are correlated to Mg, Mn, U and NH₄.

Fig. 6.

3. Discussions

3.1. Geochemical assessment of the fluid

This study demonstrates a strong correlation between the (highest) Li and SO₄, Na, Cl, K, Rb, B, and F contents, which is in good agreement with the main physical and chemical properties of the geothermal Li-rich fluids. Indeed, it indicates that high salinity (Na-Cl brines) and high temperature (characterized by high dissolved concentrations of K, Rb, B and F) are, at least, two necessary conditions to concentrate high Li content in solution (Sanjuan et al., 2022); the third condition being the nature of the rocks and minerals in interaction with the brines. For this latter, the element association of Li, Rb, SO₄ and B probably illustrates late hydrothermal alteration through fluid circulation, of older

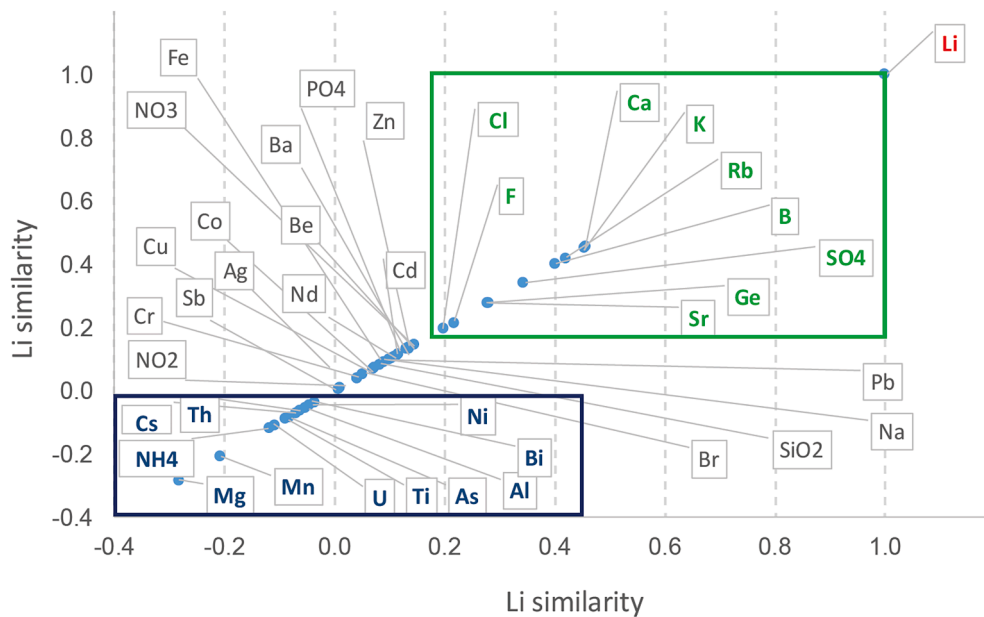


Fig. 5. Representation of the correlation matrix using the Pearson coefficient. Blue dashed square represents the elements showing anti-correlation with Li whereas green dashed square illustrates the positive correlation with Li concentration.

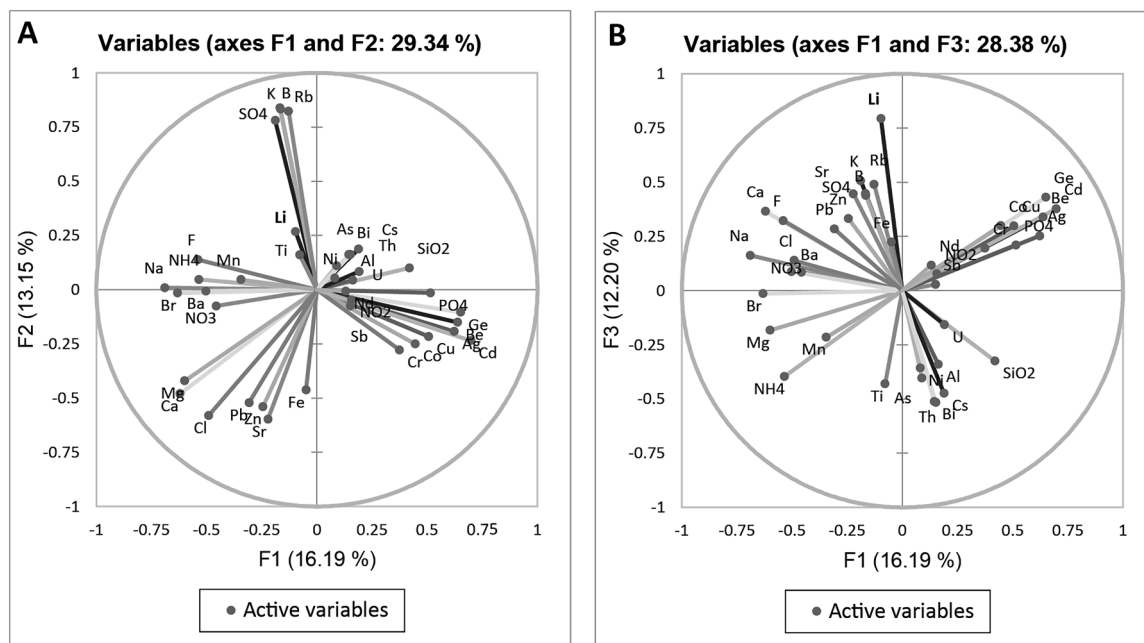


Fig. 6. Principal component analysis (PCA) plots of relevant selected elements as a function of: A) F1 and F2, and B) F1 and F3. Note that the variables are the elements.

sedimentary units such as evaporites. Indeed, these elements and metals are strongly recognized in salt lakes (e.g., Ma et al., 2020) where lithium precipitates from solution as sulfate complex LiSO_4^- explaining the positive correlation between those two ions despite that high temperatures involve decreasing of the SO_4 content in the fluid. Importantly, the higher SO_4 values are illustrated in several areas where the aquifer is hosted in sedimentary rocks such as fluvio-deltaic sandstones (Paris basin, France) or limestones (e.g., Riniken borehole, Switzerland) showing variable Li content and reported $T_{\text{well}} > 200^\circ\text{C}$ (Table 1; note that temperature is not assessed in this study due to potential heterogeneity of the dataset).

The negative correlation between high Li and Mg concentrations is

also in good accordance with the temperature effect and the alteration of clay minerals because it is known that Mg can substitute Li in clay minerals at high temperature (e.g., Kharaka and Mariner, 1989; Vigier et al., 2008). At these temperatures, the Mg contents in the geothermal fluids are very low and close to zero, whereas the Li concentrations increase significantly.

The behavior of dissolved SiO_2 , Cs and SO_4 fate is somewhat surprising because high dissolved silica and cesium concentrations and low sulfate concentrations are known to be generally associated with high temperatures and therefore, would have to be correlated with high Li concentrations. The other correlations and anti-correlations can probably be explained by the nature of the rocks and minerals in interaction

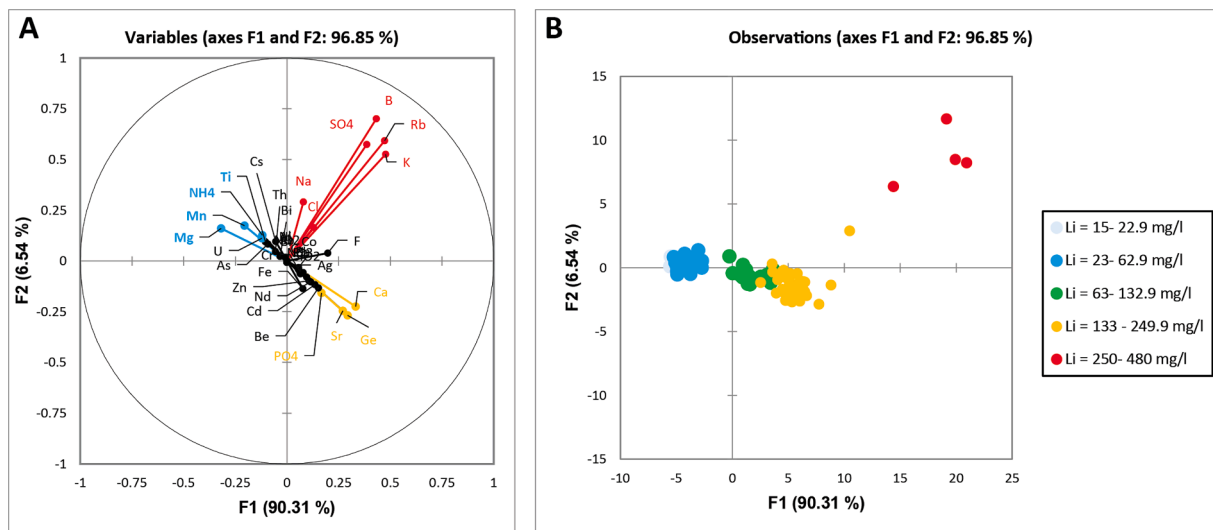


Fig. 7. Linear discriminant analysis (LDA) plots of relevant selected element from the Li-bearing geothermal brines dataset. The data have been discriminated by Li concentrations (mg/l) for the function factors of 1 and 2 representing 97 % of the dataset. A. Note that in this case, elements close to the center of the circles correspond to a ‘true similarity’ with the hypersphere.

Table 1
Statistical details of selected parameters and Li concentrations. See Fig. 3 for the corresponding box plots.

	Twell (°C)	Pwell (bar)	T (°C)	pH	O2_%	Eh (mV)	Li (mg/l)
Observations	101.00	18.00	100.00	165.00	16.00	54.00	201.00
Minimum	9.50	18.20	9.50	3.20	0.00	-490.00	15.00
Maximum	450.00	520.00	83.00	9.99	86.00	264.00	480.00
1er Quartile	86.50	18.40	19.80	5.50	0.00	-80.30	26.78
Median	150.00	22.31	26.30	6.30	1.70	-6.00	54.12
3rd Quartile	168.75	294.00	35.00	6.78	11.25	52.50	148.00
Mean	162.89	163.51	29.32	6.23	10.11	-18.48	88.23
Variance (n-1)	12,213.00	34,861.40	171.83	0.96	475.85	16,104.59	5874.04
Standard Deviation	110.51	186.71	13.11	0.98	21.81	126.90	76.64

with the geothermal brines.

3.2. Comparison of hard-rock deposit and Li-bearing brine deposits in Europe

Six particular host-rock’ ages (i.e. Devonian, Carboniferous, Permian, Triassic, Jurassic and Paleogene) have been reported in the

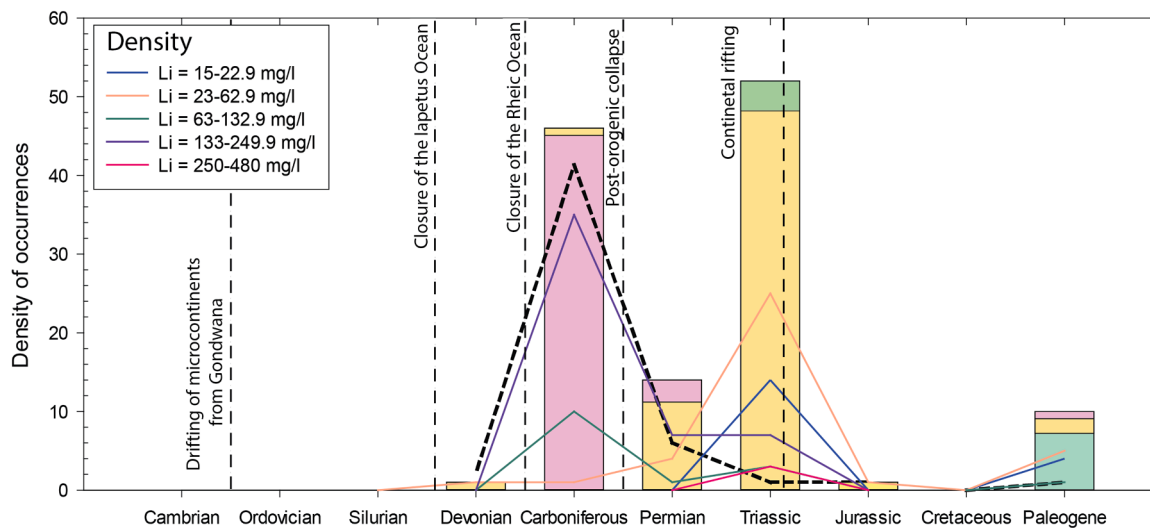


Fig. 8. Classification of Li-bearing geothermal brine host rocks by their ages. Pink represents granitic host-rocks, yellow for sedimentary and green for metamorphic host-rocks. Li concentrations and various major geological events are reported. The dashed black line represents density of dated Li hard-rock occurrences in Europe according to Gourcerol et al., 2019.

literature concerning the Li-bearing brine database (Fig. 8). These ages can be contextualized regarding major European geological events and be compared to ages of Li-bearing hard-rock deposits (Gourcerol et al., 2019).

Thus, it appears that the first recorded Li-bearing geothermal brine occurs in a Devonian sedimentary host rock in the North Sea. This might be related to localized episodes of lithospheric extension during the Early Devonian (Brown et al., 2008). This geological event is related to the end of the Caledonian orogeny and more particularly to a widespread calc-alkaline magmatism event (ca. 425 to 380 Ma; Miles et al., 2016) illustrated by LCT pegmatite formation in Ireland and Scotland (Barros and Menuge, 2016; Gourcerol et al., 2019).

Forty-six carboniferous host-rocks for Li-bearing geothermal brines have been identified and reported in France, Germany and North Sea area. These rocks are mainly granites and might be correlated to extended fractionated magmatic event through the European area related to post-collisional stage ending the Variscan orogeny (e.g., Cuney et al., 2002; Neace et al., 2016). This is coeval to a widespread emplacement of Li-magmatic bodies (LCT pegmatites, rare metal granites and related greisens) and their close relationship can be illustrated in the Li-rich ca. 305 ± 5 Ma St Austell granite (Cornwall, UK) where Li-bearing geothermal fluids occur (Neace et al., 2016).

The Permian-Triassic-Jurassic ages record widespread Li-bearing geothermal brine sedimentary host-rocks. This period corresponds to the formation of several large-scale intracratonic European basins (i.e. Northern and Southern Permian basins) from North Sea, Scotland, Germany, France and Poland. These basins are formed from active tectonic subsidence mechanisms induced by a crustal extension due to relaxation of the Carboniferous thermal anomaly (e.g., Ziegler, 1990; van Wees et al., 2000; Maystrenko et al., 2008) related to the Variscan Orogeny and are of economic interest for their oil and gas resources.

Finally, during the Paleogene, the earlier basins are reactivated through the European Cenozoic Rift System forming the Upper Rhine Graben (Schumacher, 2002) in France and Germany, which host few Li-bearing geothermal brines (e.g., Landau and Strasbourg areas; Fig. 8).

This assessment confirms that lithium enrichment is related to extension settings observed for *hard-rock* Li occurrences and potential weathering of Li-rich hard-rocks by brines in specific geochemical environments (Sanjuan et al., 2022).

3.3. Limitation of this study and perspectives

Importantly, this inventory reflects only published and recognized Li-bearing geothermal fluids. Thus, others occurrences (not yet identified and/or reported) may occur in Europe and their forthcoming identification would strengthen this database. Moreover, few areas are very well represented by several wells compared to others such as in the Upper Rhine Graben leading to a wealth heterogeneity of data quantity and quality regarding their geographical distribution. Thus, to go deeper on the fluid assessment, it would be necessary to study each geographical area independently.

Furthermore, and as mentioned above, the knowledge on the various occurrences is heterogeneous and may reflect sampling waters at various timeframes (e.g., seasons, years), done by different samplers and analyzed for different geochemical analysis packages. Thus, consistency of sampling may represent a key aspect for the next inventory, which could represent a valuable asset.

4. Conclusions

This review of Li-bearing geothermal fluids has identified 182 occurrences in Europe from which Li content is above 15 mg/l. Assessment of the various water parameters points out that Li concentration values (i.e. 250–480 mg/l) are strongly correlated to B, Rb, K, SO₄, Na, Cl and F. The moderate content values (133–249.9 mg/l) are correlated to the Ca, Ge, Sr, PO₄ element association and finally, the lowest Li concentration

values (i.e. 15 to 63 mg/l) are correlated to Mg, Mn, U and NH₄. Thus, these elements can be used as a proxy for Li enrichment in the sampled geothermal fluids. The strong correlation observed between the highest Li concentrations and the Na, Cl, K, Rb, B, and F concentrations is in very good agreement with the main physical and chemical properties of the geothermal Li-rich fluids, which indicates that high salinity (Na-Cl brines) and high temperature (characterized by high dissolved concentrations of K, Rb, B and F) are, at least, two necessary conditions to have high Li concentrations in solution (Sanjuan et al., 2022), the third condition being the nature of the rocks and minerals in interaction with the brines. Like lithium, rubidium and boron probably come from the hydrothermal alteration of clay minerals. As previously shown, the negative correlation between high Li and Mg concentrations is also in good accordance with the temperature effect and the hydrothermal alteration of clay minerals.

Moreover, it has been demonstrated that Li-bearing geothermal brines are coeval with the emplacement of Li-magmatic bodies (LCT pegmatites and granites) as well as the emplacement of large sedimentary basins in Europe suggesting an extensional setting as observed for Li-rock hard-rock deposits.

Significance statement

In the last decade, lithium has become a strategic metal due to its physical and chemical properties. Indeed, it represents a crucial metal in the development of technologies and energy storage devices needed to decarbonize the European energy systems and reach the EU Green Deal goals. Therefore, several European projects have been focused on it in order to assess their own resources and to identify a potential Li-industry. This manuscript presents for the first time a compilation of the geothermal fluid occurrences in Europe from which Li ≥ 15 mg/l and discusses the latter using geostatistical tools (e.g., exploratory statistical tools, agglomerative hierarchical clustering). Moreover, a comparison and distribution of the Li-bearing hard-rock versus Li-bearing geothermal fluid occurrences is also assessed.

Author statement

We are delighted to present this collaborative work that represents a collective exploration in the field of lithium from geothermal brines in Europe. Our team, comprised of passionate researchers, worked closely to develop an integrated database that served as the central pivot for this manuscript.

This project would not have been possible without the active and dedicated contribution of each team member. Each person brought unique expertise, both in the collection and organization of data, as well as in critical thinking and manuscript writing.

The process of crafting the manuscript was a joint endeavor. Animated discussions, critical revisions, and team working sessions helped build a robust text that reflects the depth of our exploration and discoveries.

CRediT authorship contribution statement

Blandine Gourcerol: Conceptualization, Data curation, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Bernard Sanjuan:** Conceptualization, Data curation, Project administration, Writing – review & editing. **Romain Millot:** Project administration, Conceptualization, Data curation, Writing – original draft, Writing – review & editing. **Detlev Rettenmaier:** Conceptualization, Data curation. **Elodie Jeandel:** Conceptualization, Data curation, Writing – original draft. **Albert Genter:** Data curation, Writing – original draft. **Clio Bosia:** Conceptualization, Data curation, Writing – original draft. **Aurélien Rombaut:** Conceptualization, Data curation, Writing – original draft.

Declaration of competing interest

There is no conflict of interest and that all the funding sources have been cited in the manuscript.

Data availability

Data are in the manuscript

Acknowledgments

This study is conducted through the EuGeLi (European Geothermal Lithium Brines) project, which aims to provide Europe with lithium extracted from geothermal brines located at the French/German border. This activity has received funding from the European Institute of Innovation and Technology (EIT), a body of the European Union, under the Horizon 2020, the EU Framework Program for Research and Innovation. The European Union and its Innovation and Networks Executive Agency (INEA) are not responsible for any use that may be made of the information any communication activity contains. The content of this publication does not reflect the official opinion of the European Union. Responsibility for the information and views expressed in the therein lies entirely with the author(s).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.geothermics.2024.102956](https://doi.org/10.1016/j.geothermics.2024.102956).

Appendix A

Location and available geochemical data for the identified geothermal waters from which $\text{Li} \geq 15 \text{ mg/l}$. (from Aquilina et al., 1997; Baldi et al., 1982; Berthier et al., 1982; Bruce, 1990; Bruni et al., 1983; Buonasorte et al., 1993; Calamai et al., 1975; Carella and Guglielminetti, 1983; Caritg et al., 2013; Cathelineau et al., 1993; Corsi and Di Falco, 1980; Dezayes et al., 2018; Downing et al., 1985; Edmunds et al., 1985; Fontes and Matray, 1993; Fouillac, 1983; Fytikas et al., 2005; Holdorf et al., 1992; Karabelas et al., 1989; Koutinas, 1989; Makower et al., 1980; Manning et al., 2007; Matray, 1988a,b; Michard et al., 1996; Millot et al., 2011; Millot and Ph, 2007; Minissale et al., 1997; Pauwels et al., 1991, 1993, 2007; Regenspurg et al., 2010; Sanjuan et al., 2004, 2006b, 2014, 2016; Şimşek, 1984; Stober, 2014; Stober and Bucher, 2004; Vaute, 1998; Warren and Smalley, 1994; Sanjuan et al., 2001; Sanjuan et al., 2006a)

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