

Modeling of brine-rock interactions in German geothermal systems for future lithium recovery

Felix Jagert¹, Katharina Alms¹

¹ Fraunhofer IEG, Fraunhofer Research Institution for Energy Infrastructures and Geothermal Systems,
Am Hochschulcampus 1 / IEG, 44801 Bochum, Germany

felix.jagert@ieg.fraunhofer.de

Keywords: PHREEQC, Lithium, Exploitation, Brine, reservoir, Germany.

ABSTRACT

Presented is the framework of the modeling part of the project "Li-Fluids". For this purpose, electrolyte models are presented that can be used for a modeling of lithium-bearing minerals. The identification of sources of lithium and their integration into the hydrogeochemical calculation programme PHREEQC allow the simulation of lithium release from geothermal reservoirs in principle. However, there are also challenges: Brines can only be calculated validly with the Pitzer approach, which limits the number of minerals considered. There are other databases that are suitable for high ionic strengths, but more research is needed for appropriate Li-mineral modeling in the future.

1. INTRODUCTION

The German Mineral Resources Agency (DERA) expects global demand for lithium to double or even triple between 2017 and 2025 (Schmidt 2017). The use of lithium in rechargeable batteries, especially in e-mobility, has been identified as a key driver for this development. Due to this strongly increasing demand for lithium, the co-production of lithium at geothermal power plants is currently being discussed worldwide and has already been implemented locally in isolated cases, as increased lithium contents in deep hydrothermal fluids have already been proven at various locations worldwide.

The aim of the joint project "Li-Fluids" is to create the necessary basis for the development of a raw material strategy for lithium extraction from hydrothermal fluids in Germany. A reason for enhanced interest are measured elevated lithium concentrations in hot deep waters in the North German Basin (NDB) and the Upper Rhine Graben (ORG) in Germany of several hundred mg/l lithium (Alms et al., this issue).

The common goal of experiments and modeling is to determine equilibrium concentrations for lithium in deep fluids on the one hand and to gain an understanding of the kinetic reaction rates on the other.

Only with this knowledge is it possible to assess the long-term economic recovery of lithium from geothermal reservoirs in a circulating geothermal operation.

For the modeling part within this project, the basic time scales and hydrogeochemical reactions of lithium-bearing minerals and dissolution processes between rock and fluid are to be clarified with the help of modeling investigations (Fraunhofer IEG) and laboratory experiments (partner Federal Institute for Geosciences and Natural Resources: BGR).

2. LITHIUM-BEARING MINERALS WORLDWIDE

The supply of lithium (chemical element "Li") globally is derived mostly from brines and hard-rock deposits (around 50% for each provenance, Lithium Australia NL 2022). The resources of lithium are from different sources: Enrichment took place in magmatic melts, so that pegmatites are an important hard-rock source (Linnen et al. 2012).

An additional and well-known source of lithium are salars, which are evaporites in deserts, concentrated by solar evaporation from brines (Warren 2016). Lithium-containing brines are magmatic in origin and generally associated with volcanic events (Lithium Australia NL 2022).

A third source represents less than 3% of the global lithium resources. They are a kind of sediment-hosted deposit (Dessemond et al. 2019). Lithium, which occurs in a clay mineral itself (and is not present as impurity in the sample under investigation), is most likely incorporated into the crystal structure during the formation of the clay, for example by contacting Li-bearing deep groundwaters. Hydrothermal alteration can also lead to the incorporation of lithium into these crystal structures (Starkey 1982; Norton and Schlegel 1955).

Another Li-candidate in this kind of source are micas. An enrichment of lithium in micas may be interpreted as being caused by isomorphic replacement (Foster 1960).

2.1 Hard rocks as source

Important hard-rock deposits to produce lithium from are pegmatites containing high-grade the Li-bearing minerals spodumene and petalite. Conventional hard-rock mining techniques are used and operating costs are high (Lithium Australia NL 2022).

The bulk continental crust contains 16 ppm lithium. In comparison, pegmatite can contain extreme high concentrations of lithium, e.g. ores in the Tanco pegmatite (Manitoba, Canada) contain up to 13,900 ppm lithium. Chemical-grade Li refers to spodumene that is converted to lithium carbonate or lithium hydroxide. Lithium has also been produced from petalite in complex-type pegmatites (Linnen et al. 2012).

LiAlSi₂O₆ (Spodumene, 3.73% Li)

LiAlSi₄O₁₀ (Petalite, 2.27% Li)

(Two well-known lithium-aluminosilicates)

Traditionally, spodumene is crushed, heated and contacted with sulphuric acid. The resulting lithium sulphate is leached by water and can be precipitated or transformed into lithium chloride or lithium carbonate. There are also alternative processes with different reagents for lithium extraction patented (Dessemond et al. 2019).

2.2 Brines as source

The lithium of this source occurs either as a brine component or as lithium-bearing mineral in saline clays, like e.g. hectorite (compare section 2.3). Low-grade lithium from brines is concentrated by solar evaporation. The capital input for the extraction of lithium from brines is high, but the subsequent operating costs are low (Warren 2016; Lithium Australia NL 2022).

By far the most important lithium enriched brine deposits (in terms of resources) are Salar de Uyuni, Bolivia and Salar de Atacama, Chile. For Salar de Uyuni typical sediment thickness is 121 m, consisting of halite beds separated by mud and sand. The brine under the surface contains about 80 - 1,150 ppm of lithium. Elevated Mg contents makes the Li-extraction more difficult. For Salar de Atacama, Chile the sediment thickness is more than 950 m of intercalated halite and lacustrine muds. Lithium concentrations range between 1,000 - 4,000 ppm (Warren 2016).

Also an important site for lithium brine processing is Salar de Hombre Muerto, Argentina: Its brines origin from lithium-containing hot springs and seeps, fed by groundwaters that leached surrounding volcanoclastics (Li-concentration about 520 ppm) (Warren 2016 and references therein).

2.3 Sediment-hosted deposits

Lithium, in low grades, is widespread in clay minerals and mines for this type of production are currently in

development. Lithium can be extracted from e.g. hectorite, a lithium-bearing trioctahedral smectite (Lithium Australia NL 2022; Starkey 1982; Norton and Schlegel 1955).

Dessemond et al. (2019) highlights hectorite and jadarite for this type of deposit. But Foster (1960) described some additional minerals focussing on micas: Lepidolite and muscovite are often associated, so that lithium is widespread in micas. She specifically describes isomorphic substitution for muscovite, by replacement of octahedral Al by Li, or for siderophyllite, by the replacement of Fe⁺² by Li.

Starkey (1982) points out, that lithium may be weathered out from micas and is incorporated again in adjacent newly formed clays. Lithium from hydrothermal waters may be incorporated into preexisting clays.

3. PHREEQC MODELING

Published geothermal fluid analyses collected from various wells in NDB (Tab. 1) and other areas in Germany were modeled to evaluate saturation states of minerals using the hydrogeochemical modeling software PHREEQC 3 (Parkhurst and Appelo 2013).

The criterion for reliable modeling is a consistent water analysis with a low charge balance error, which consists of the temperature, acidity as pH, alkalinity (as bicarbonate), main elements and if possible trace elements (anions and cations).

Since aluminosilicates are considered for modeling, Al and Si (H₄SiO₄) must have been determined in the sample analysis. However, this is rarely the case for water analyses within a literature review. And if it is, conventional ICP-OES is often not sufficient to correctly determine Al in concentrations of µg/l to mg/l within the fluid-matrix, so the appropriate analytical equipment must be given.

Furthermore, lithium must have been determined in the lab, which is not self-evident, since saltwater or brine usually has an extreme excess of Na⁺, Cl⁻, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, K⁺ and therefore missing minor cations are not evident in charge balance errors.

A recorded redox state in water analyses is also important, but is rarely determined and often not measured correctly because redox electrodes in the field have delays in measurement, leading to incorrect results. If necessary, the redox state can be calculated via redox couples within PHREEQC. Lithium as a monovalent cation has no redox partner, therefore only associated mineral reactions while modeling (e.g. Fe²⁺, Fe³⁺, H₂S, S²⁻, for pyrite oxidation, etc.) require redox measurements.

Table 1: Two fluid analyses of geothermal wells in Northern Germany. Note the lack of Al and Si measurements.

	Horstberg Z1	Groß Schönebeck
location	75 km north-east of Hanover	50 km north-east of Berlin
year	2004	2001
depth (m b.g.l.)	~3800	4235
temp. (°C)	~90	~150
pH	4,9	5,7
cations / anions (mg/l)		
Na ⁺	65975	38400
Mg ²⁺	1628	430
Ca ²⁺	35700	54000
K ⁺	6225	2900
Ba ²⁺	52	34
Sr ²⁺	1908	1900
Fe ²⁺	179	114
Mn ²⁺	258	270
Pb ²⁺	153	180
Zn ²⁺	325	74
Li ⁺	179	204
Cl ⁻	175000	167300
SO ₄ ²⁻	888	140
HCO ₃ ⁻	32	18,9
BO ₂ ⁻	365	-
Br ⁻	1188	300
SiO ₂	58	-
Literature	Hesshaus et al. (2010)	Huenges and Wolfgramm (2004)

3.1 Selection of appropriate databases

Due to a large spread of either ionic strengths (deep groundwater, saltwater, brines) or temperatures, different thermodynamic databases were selected for modeling (examples in Tab. 2). Brackish waters and saltwaters were modeled with the PHREEQC or MINTEQA databases, which are based on the extended Debye-Hückel approach (theory of ion dissociation), whereas higher salinities up to brines are modeled with the Pitzer approach (ion interaction approach) or the ThermoChimie database (SIT: specific ion interaction theory). There are considerably more databases. For example, Carbfix.dat (Voigt et al. 2018), which is a further development from Core10.dat (Neveu et al. 2017). Many mineral solubilities were determined only under laboratory conditions at 25 °C and 1 bar. Pitzer is more suitable for different pressure and temperature conditions, but it can be used to model rather few

mineral phases (Appelo et al. 2014). A disadvantage in the calculation of aluminosilicates is that the high ionic strengths of some wells (Tab. 1) can actually only be calculated with Pitzer. However, no Al is integrated in this database, which is why one is forced to switch to less valid databases.

3.2 Mineral phases

The databases supplied with PHREEQC contain a large number of mineral phases, but only a few of them contain lithium. These mineral phases must then be integrated from other databases into the database used. Often minerals have already been defined for radioactive repository research, deep geothermal energy or CO₂ capture and storage in PHREEQC and can therefore be found.

For example, Carbfix.dat (Voigt et al. 2018) already contains the mineral phases LiCl, eucryptite, petalite and spodumene. In addition, Zhang et al. (2019) published a PHREEQC RATES block for spodumene, among other minerals, which in turn uses parameters from Palandri and Kharaka (2004).

However, Boschetti (2022) is the most important recent source: He has recognized the great importance of missing lithium-bearing minerals in the available databases and has transformed and compiled thermodynamic parameters from various sources (Mineral phases: bikitaite, cookeite, elbaite, ephesite, hectorite, lepidolite, Li-mica, petalite, polyolithionite, taeniolite, zinnwaldite). Thus, great aids are available for modeling, but the availability of kinetic rates for diverse Li minerals still needs to be developed.

3.3 General thoughts about Li-extraction modeling from a geothermal reservoir

First basic knowledge of the associated pore fluid or thermal water at pressures between 1 and 1000 bar as well as temperatures between 25°C to 200°C (Appelo et al. 2014), depending on the depths considered, can thus be obtained. The reaction processes are modeled via simulated batch experiments as well as 1D transport experiments to test the interaction of rock-forming minerals, such as spodumene, mica or clay minerals in the presence of water. They provide a theoretical framework for predicting the occurrence of lithium-bearing deep waters in geothermally relevant regions.

In a first step, PHREEQC simulations were performed using an equilibrium approach with the help of above mentioned established thermodynamic databases for elevated ionic strengths. In a second step, cation exchange as well as kinetic reaction rates were modelled over different time scales. Coupled kinetic mineral reactions are still being under consideration. The databases were extended by those mineral phases which represent the mineralogy for the corresponding site:

For the NDB, a sediment-hosted deposit is assumed. As example, the geology of the Groß Schönebeck well site consists of sedimentary rocks (siliciclastic rocks, e.g.

Rotliegend sandstone), so that the subsurface of the well is considered a sedimentary geothermal reservoir (Legarth et al. 2005). However, Permo-Carboniferous volcanic rocks have also been mentioned, which could be an additional natural deposit of lithium together with micas and clays in the sediments. During the process of the project, other geothermal provinces, e.g. ORG, will be considered in parallel with the NDB.

Theoretically, lithium release could be stimulated via the operation of the geothermal plant. For example,

cation exchange with 2Li^+ could be provoked by Ca^{2+} , so that dissolved lithium is enriched in the water. Furthermore, pH values (cation exchange depends among other factors on pH) or temperatures could be changed to release more lithium from the reservoir.

Estimating leaching rates bring clarity, whether the rock acts as Li-deposit at all or whether the geothermal fluid in the reservoir is depleted in lithium after some time of Li-extraction.

Table 2: Some thermodynamic databases within PHREEQC and recommended ranges of application in terms of ionic strengths, temperatures and pressures.

Database (*.dat)	Model concept	Recommended Range of Application				Reference
		Ionic strength (mol/l)	Salinity	Temp. (°C)	Pressure (atm)	
Phreeqc	extended Debye-Hückel / Debye-Hückel	< 0.7	up to saltwater	25; 0 - 200	1 - 1000	Appelo et al. (2014); Appelo (2015)
WATEQ4F	WATEQ Debye-Hückel, Davies	< 0.7	up to saltwater	25; 0 - 100	1	Ball and Nordstrom (1991)
MINTEQA	extended Debye-Hückel / Davies	< 0.7	up to saltwater	25; < 100	1	Felmy, A., R. et al. (1984)
SIT (ThermoChimie)	Specific Ion Interaction Theory (SIT)	0.1 - 3	up to saltwater and beyond	15 - 90	1	Giffaut et al. (2014); Grivé et al. (2015)
Pitzer	Pitzer equations	> 1	up to saltwater and beyond	0 - 200	1 - 1000	Appelo et al. (2014)

4. PRELIMINARY RESULTS

Preliminary modeling so far has shown the following:

I) The stability of the mineral phases important to the reservoir decreases with increasing temperature, i.e., with increasing depths in the reservoir, the minerals are altered and serve as a source of lithium. The lithium then appears to migrate into the fluid.

II) Increasing the lithium content in the geothermal fluid via stimulation of cation exchange is not possible, at least with conventional cations. Sodium release dominates over lithium release.

III) Initial leaching models with distilled water at 25°C for (detrital) spodumene show little increase in dissolved lithium concentration. Thus, it can be confirmed (see 2.3) that sediments contain lithium but cannot release it at high concentrations. These statements still need to be verified, especially by calibration and extended pH and temperature considerations.

5. CONCLUSION AND OUTLOOK

So far, this study has been able to locate the geological sources of lithium, including unconventional deposits. The most important lithium-bearing mineral phases could be integrated into PHREEQC based on the studies of other authors, so that it is now possible to

model alteration processes and to evaluate lithium release rates.

The general availability of fully documented geothermal fluids or formation waters (including Al and Si) on the one hand and the completeness of databases suitable for high salinities, pressures and temperatures on the other hand has to be considered as moderate. However, this is expected to improve significantly with increasing interest in lithium.

REFERENCES

- Alms, K.; Jagert, F.; Blömer, J.; Gehrke, I.: Co-production of geothermal energy and lithium from geothermal waters. In : European Geothermal Congress 2022, Berlin, Germany | 17-21 October 2022, Abstract 351.
- Appelo, C. (2015): Principles, caveats and improvements in databases for calculating hydrogeochemical reactions in saline waters from 0 to 200 °C and 1 to 1000 atm. In *Applied Geochemistry* 55, pp. 62–71. DOI: 10.1016/j.apgeochem.2014.11.007.
- Appelo, C.; Parkhurst, D. L.; Post, V. (2014): Equations for calculating hydrogeochemical reactions of minerals and gases such as CO₂ at high pressures and temperatures. In *Geochimica et Cosmochimica Acta* 125, pp. 49–67. DOI: 10.1016/j.gca.2013.10.003.

- Ball, J. W.; Nordstrom, D. K. (1991): User's manual for WATEQ4F, with revised thermodynamic data base and text cases for calculating speciation of major, trace, and redox elements in natural waters. Edited by U.S. GEOLOGICAL SURVEY. Menlo Park, California (Open-File Report, 91-183). Available online at <https://doi.org/10.3133/ofr91183>.
- Boschetti, T. (2022): A revision of lithium minerals thermodynamics: Possible implications for fluids geochemistry and geothermometry. In *Geothermics* 98, p. 102286. DOI: 10.1016/j.geothermics.2021.102286.
- Dessemond, C.; Lajoie-Leroux, F.; Soucy, G.; Laroche, N.; Magnan, J.-F. (2019): Spodumene: The Lithium Market, Resources and Processes. In *Minerals* 9 (6), p. 334. DOI: 10.3390/min9060334.
- Felmy, A., R.; Girvin, D., C.; Jenne, E., A. (1984): MINTEQA-A COMPUTER PROGRAM FOR CALCULATING AQUEOUS GEOCHEMICAL EQUILIBRIA. Edited by U.S. Environmental Protection Agency, Washington, D.C. Battelle, Pacific Northwest Laboratories Richland, Washington 99352 (EPA-600/3-84-032). Available online at <https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=9101VXPk.txt>.
- Foster, M. D. (1960): Interpretation of the composition of lithium micas. Relations of lithian muscovites and lepidolites, and of siderophyllites, protolithionites, zinnwaldites, and lepidolites, based on published analyses. WASHINGTON (GEOLOGICAL SURVEY PROFESSIONAL PAPER, 354-E). Available online at <https://doi.org/10.3133/pp354E>.
- Giffaut, E.; Grivé, M.; Blanc, P.; Vieillard, P.; Colàs, E.; Gailhanou, H. et al. (2014): Andra thermodynamic database for performance assessment: ThermoChimie. In *Applied Geochemistry* 49, pp. 225–236. DOI: 10.1016/j.apgeochem.2014.05.007.
- Grivé, M.; Duro, L.; Colàs, E.; Giffaut, E. (2015): Thermodynamic data selection applied to radionuclides and chemotoxic elements: An overview of the ThermoChimie-TDB. In *Applied Geochemistry* 55, pp. 85–94. DOI: 10.1016/j.apgeochem.2014.12.017.
- Hesshaus, A.; Hauswirth, H.; Jatho, R.; Tischner, T.; Schellschmidt, R.; Junker, R.; Sulzbacher, H. (2010): Verbundprojekt GeneSys: GeneSys Horstberg II – Methoden und Konzepte zur Erdwärmegewinnung aus gering permeablen Sedimentgesteinen. Abschlussbericht zum Vorhaben FKZ 0329996. Edited by Bundesanstalt für Geowissenschaften und Rohstoffe. Hannover.
- Huenges, E.; Wolfgramm, M. (2004): Sandsteine im In-situ-Geothermielabor Groß Schönebeck: Reservoircharakterisierung, Stimulation, Hydraulik und Nutzungskonzepte. Deutsches GeoForschungsZentrum GFZ. Potsdam (Scientific Technical Report, STR04/03), checked on <https://doi.org/10.2312/GFZ.B103-04036>.
- Legarth, B.; Huenges, E.; Zimmermann, G. (2005): Hydraulic fracturing in a sedimentary geothermal reservoir: Results and implications. In *International Journal of Rock Mechanics and Mining Sciences* 42 (7-8), pp. 1028–1041. DOI: 10.1016/j.ijrmms.2005.05.014.
- Linnen, R. L.; van Lichtervelde, M.; Cerny, P. (2012): Granitic Pegmatites as Sources of Strategic Metals. In *Elements* 8 (4), pp. 275–280. DOI: 10.2113/gselements.8.4.275.
- Lithium Australia NL (Ed.) (2022): About lithium. Available online at <https://lithium-au.com/about-lithium/>, checked on 5/20/2022.
- Neveu, M.; Desch, S. J.; Castillo-Rogez, J. C. (2017): Aqueous geochemistry in icy world interiors: Equilibrium fluid, rock, and gas compositions, and fate of antifreezes and radionuclides. In *Geochimica et Cosmochimica Acta* 212, pp. 324–371. DOI: 10.1016/j.gca.2017.06.023.
- Norton, J. J.; Schlegel, D. M. (1955): Lithium resources of North America. A CONTRIBUTION TO ECONOMIC GEOLOGY. WASHINGTON (GEOLOGICAL SURVEY BULLETIN, 1027-G). Available online at <https://doi.org/10.3133/b1027G>.
- Palandri, J. L.; Kharaka, Y. K. (2004): A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling. Edited by U.S. GEOLOGICAL SURVEY. National Energy Technology Laboratory – United States Department of Energy. Menlo Park, California (Open-File Report, 2004-1068). Available online at <https://doi.org/10.3133/ofr20041068>.
- Parkhurst, D. L.; Appelo, C. (2013): Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Edited by U.S. GEOLOGICAL SURVEY (Techniques and Methods, book 6, chap. A43). Available online at <https://pubs.usgs.gov/tm/06/a43/pdf/tm6-A43.pdf>.
- Schmidt, M. (2017): Rohstoffrisikobewertung – Lithium. Edited by Deutsche Rohstoffagentur (DERA). Bundesanstalt für Geowissenschaften und Rohstoffe (BGR). Berlin (DERA Rohstoffinformationen, 33). Available online at https://www.deutsche-rohstoffagentur.de/DERA/DE/Downloads/Studie_lithium_2017.html, checked on 5/20/2022.
- Starkey, H. C. (1982): The role of clays in fixing lithium. A study of some methods by which lithium is retained in clay minerals. WASHINGTON (GEOLOGICAL SURVEY BULLETIN, 1278-F). Available online at <https://doi.org/10.3133/b1278F>.
- Voigt, M.; Marieni, C.; Clark, D. E.; Gíslason, S. R.; Oelkers, E. H. (2018): Evaluation and refinement of thermodynamic databases for mineral carbonation. In *Energy Procedia* 146, pp. 81–91. DOI: 10.1016/j.egypro.2018.07.012.
- Warren, John K. (2016): Evaporites. Cham: Springer International Publishing.
- Zhang, Y.; Hu, B.; Teng, Y.; Tu, K.; Zhu, C. (2019): A library of BASIC scripts of reaction rates for geochemical modeling using phreeqc. In *Computers & Geosciences* 133, p. 104316. DOI: 10.1016/j.cageo.2019.104316.

Acknowledgements

This work is funded by the German Federal Ministry for Economic Affairs and Climate Action with the Grant number: FKZ: 03EE4034B.