Exploration of potential geothermal reservoirs: use of the chemical Na/Li geothermometer and lithium isotopes

One of the major applications of water geochemistry in the exploration of the potential geothermal reservoirs involves estimation of their temperature using chemical and isotopic geothermometers. These tools are based on empirical or semi-empirical laws and commonly use data obtained from chemical and isotopic analyses of surface thermal waters. Unfortunately, the estimations of reservoir temperatures using these tools are not always concordant. The aim of this study is to better understand the use of the Na/Li geothermometer and more especially, the behavior of the lithium and its isotopes, which can result relevant and decisive tools in numerous cases to estimate or validate the temperature of the fluids in the geothermal reservoirs. By integrating new hydrothermal, geothermal and oil-field data, the three existing Na/Li thermometric equations are re-examined and a new equation relative to the seawater-basalt interaction processes is proposed.

Existing data

> Since 1965, several chemical and isotopic geothermometers such as Na-K, Na-K-Ca, Na-K-Ca-Mg, K-Mg, SiO_2, $\delta^{18}O(H_2O)$-$\delta^{18}O(SO_4)$ are commonly used in geothermal exploration but unfortunately, the estimates of reservoir temperatures using these classical tools are not always concordant. The mixing of the deep geothermal fluids with surface waters or their cooling and the associated precipitation/dissolution processes during their rising to the surface can be responsible of these discordances. Other factors such as the presence of seawater, the water salinity or the nature of the rocks surrounding the reservoirs can also influence the estimated temperatures. For instance, the SiO_2 geothermometer underestimates the reservoir temperature when applied to deep geothermal fluids diluted by surface waters or after silica precipitation due to a fluid cooling. Conversely, for dilute thermal waters collected from volcanic or granite areas, the Na/K geothermometer often yields overestimated reservoir temperatures. The Na/K and Na/K/Ca geothermometers cannot be used with seawater.

> In 1981, from numerous data obtained in several world geothermal fields, Fouillac and Michard proposed a new geothermometer for thermal and geothermal waters based on two empirical and statistical thermometric Na/Li relationships (Na/Li is a molar ratio):

log (Na/Li) = 1000/T(°K) - 0.38 for Cl concentrations < 0.3 M (black dashed line in Figure 1)

log (Na/Li) = 1195/T(°K) + 0.13 for Cl concentrations > 0.3 M (red dashed line in Figure 1)

Due to a rather low reactivity of the lithium during the ascent of the geothermal waters up to the surface, the use of this geothermometer often gives more reliable deep temperature estimates than that of the classical geothermometers.

From many data obtained in world geothermal and US oil fields, Kharaka and Mariner (1989) proposed a third empirical and statistical thermometric Na/Li relationship for hot saline fluids discharged from sedimentary basins (Na/Li is a molar ratio):

log (Na/Li) = 1590/T(°K) - 1.299 (green dashed line in Figure 1)

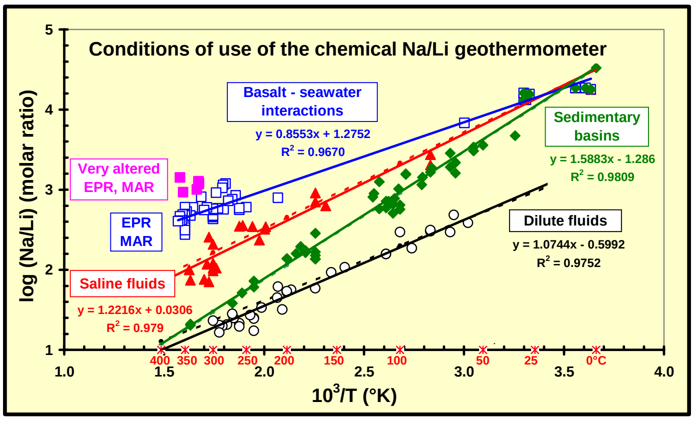

Fig. 1 - Molar sodium/lithium ratios as a function of deep temperature for seawater and fluids collected from hydrothermal systems, geothermal and oil fields and sedimentary basins

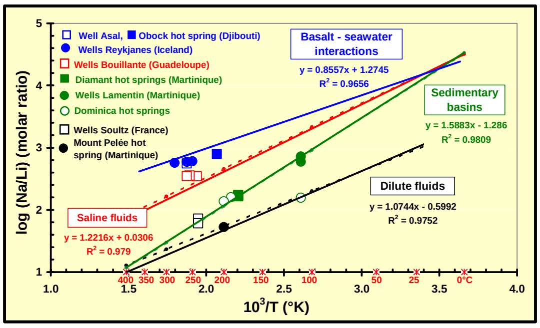

Fig. 2 - Some examples of application of the Na/Li thermometric relationships

> The only hydrothermal fluids discharged from emerged rifts (Djibouti and Iceland) follow the same thermometric relationship.

> The geothermal fluids discharged from the wells of Soultz-sous-Forêts (France) agree with the relationship relative to the oil-fields and sedimentary basin.

> The geothermal fluids produced near the Caribbean island arc (Bouillante in Guadeloupe - Lamentin, Mount Pelée and Diamant in Martinique - Dominica) agree with three of the relationships, following their salinity and the nature of the rocks with which they interact (andesites, volcano-sedimentary rocks…).

Results obtained during this study

> Relative to the previous studies, more than 120 additional data from world geothermal fields (New Zealand, USA, Japan, Mexico, Chile, Honduras, Philippines, Indonesia, Kenya, Ethiopia, Italy, France, Azores, Dominica, Guadeloupe, Martinique…), from oil-fields and sedimentary basins (USA, Israel, France, North Sea…), from oceanic ridges (Mid Atlantic Ridge, East Pacific Rise), emerged rifts (Djibouti, Iceland), and island arcs were examined. The three previously determined thermometric Na/Li relationships were validated by most of the new data (Fig. 1), except for the data relative to the oceanic ridges (MAR, EPR) and emerged rifts, which indicate lower Li concentrations and higher Na/Li ratios at a given temperature. For the fluids discharged from these two particular systems (except for some data relative to old and very altered EPR and MAR, which are depleted in lithium), a new and relatively good thermometric relationship was obtained ($r^2 = 0.97$; Figs. 1 and 2):

log (Na/Li) = 855/T(°K) + 1.275

The mean relative uncertainty for the temperature values estimated using these thermometric relationships is close to ± 6%. The similarity of the slopes for three of the straight lines (0.855, 1.222 and 1.074; Fig. 1) indicates similar values of reaction enthalpy and consequently, suggests the existence of similar chemical reactions.

> Contrary to the dissolved Li concentrations, the data relative to Li isotopes (δ^7Li) in geothermal or oil-field fluids are rather poor and one of our major future objectives will be to obtain additional data on the largest number of world geothermal fields. For the moment, the presently available data of δ^7Li in the geothermal or oil-field fluids indicate values ranging from -1 to 31‰ (Fig. 3). Seawater is characterized by a value of 30-31‰. Generally, fluids from marine sedimentary basins have signatures rather close to seawater (Fig. 3). Since most of the marine hydrothermal solutions are enriched in Li by a factor of 20 to 50 over seawater, dissolved Li is dominated by basaltic Li. One of the more studied systems (oceanic ridges) shows δ^7Li values generally varying from 2.6 to 11.5‰ in the hydrothermal fluids (Fig. 3), which indicate that most of these fluids are enriched in ^7Li relative to the fresh basalts (2-6‰) and are isotopically closer to altered basalts. In these systems, Li appears to be controlled by a path-dependant dissolution/precipitation process, where this element is not quantitatively removed from the rock but is partially retained in the alteration secondary minerals, which preferentially take up the lighter isotope.

> Most of the present available δ^7Li data and the Na/Li thermometric relationships suggest that the lithium dissolved in the geothermal and oil-field fluids is not only controlled by temperature but by other influent factors such as the nature of the rock, its degree of alteration, the water-rock ratio or the fluid composition and salinity.

> In some cases as those presented in figure 4 (Bouillante geothermal field in Guadeloupe and Lamentin plain in Martinique, French West Indies), the determination of both Li concentrations and δ^7Li values can be also useful to show or confirm the presence of mixing processes between seawater and a hot fluid end-member in fluids collected from thermal springs.

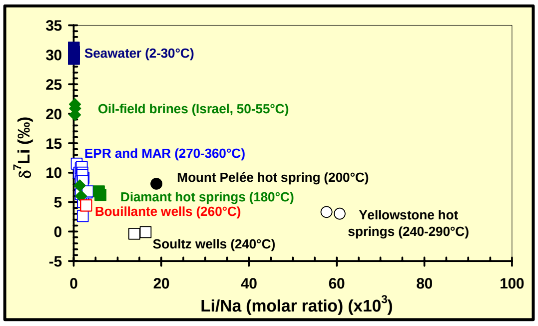

Fig. 3 - δ^7Li values versus molar lithium/sodium ratios for seawater and fluids collected from hydrothermal systems, geothermal and oil fields and sedimentary basins. Note the scarcity of the δ^7Li analyses relative to the chemical and temperature data collected during this study

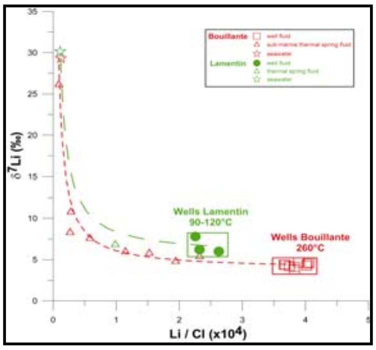

Fig. 4 - δ^7Li values versus mass lithium/chloride ratios for seawater and fluids collected from thermal springs located in the Bouillante geothermal field (Guadeloupe) and in the Lamentin plain (Martinique, French West Indies). Note the existence of hyperbolic functions which traduces mixing processes between seawater and a hot fluid end-member (reservoir fluid)

Main Conclusions

> In this study, the integration of more than 120 additional temperature and chemical data collected from world geothermal and oil fields, sedimentary basins, oceanic ridges, emerged rifts and island arcs, has allowed to confirm and refine the three existing Na/Li thermometric relationships. A new Na/Li thermometric relationship relative to the processes of seawater-basalt interaction occurring in the oceanic ridges and emerged rifts is proposed. For geothermal exploration, the deep temperatures estimated using these thermometric relationships will have to be compared, discussed and validated with those given by the other chemical and isotopic geothermometers.

> The scarcity of the δ^7Li values analyzed in the geothermal and oil-field fluids and the presently available data indicate that it is necessary to acquire additional data in both fluids and rocks to better understand the Li behavior in the processes of water-rock interaction. However, as the dissolved Li during these processes seems to be controlled by several influent factors such as temperature, water/rock ratio, rock mineralogy, degree of rock alteration, fluid composition and salinity, it is recommended to study the Li behavior at different temperatures for a same type of process of water-rock interactions in order to obtain a thermometric relationship involving the δ^7Li values.

Authors

SANJUAN Bernard, MILLOT Romain, BRACH Michel
Division Metrology, Monitoring, Analysis (MMA)

ENGINE Workshop, Postdam (Germany), 6-8 November 2006

References

Fouillac Ch. and Michard G. (1981) - Sodium/lithium ratio in water applied to geothermometry of geothermal reservoirs. *Geothermics*, vol. 10, n°1, 55-70.

Kharaka Y.K. and Mariner R.H. (1989) - Chemical geothermometers and their application to formation waters from sedimentary basins. *In Thermal History of Sedimentary Basins (Ed. N.D. Naeser and T. McCulloch, Springer Verlag)*, 99-117.

www.brgm.fr