USE OF A NEW SODIUM/LITHIUM (NA/LI) GEOTHERMOMETRIC RELATIONSHIP FOR HIGH-TEMPERATURE (HT) GEOTHERMAL FLUIDS DERIVED FROM SEAWATER/BASALT INTERACTION PROCESSES: APPLICATION TO THE DJIBOUTI CASE

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ABSTRACT
This study has allowed improving the Na/Li geothermometric relationship for High-Temperature (HT) fluids derived from seawater and basalt interaction processes existing in emerged Rifts such as those of Djibouti (Asal-Ghoubbet and Obock geothermal areas) and of Iceland (Reykjanes, Svartsengi and Seltjarnarnes geothermal fields), or in numerous Oceanic Ridges and Rises (Middle-Atlantic Ridge, East Pacific Rise, etc.). The best adapted Na/Li relationship for this type of fluids seems to be:

\[ T (°K) = 920 / [\log (Na/Li) - 1.105] \quad (r^2 = 0.994) \]

where Na and Li are the aqueous concentrations of these elements given in mol/l.

This relationship which can give estimations of temperature for a value range from 0 to 365°C, with an uncertainty of ± 25°C, is very different from the three main relationships known in the literature (Fouillac and Michard, 1981; Kharaka and Mariner, 1989) and from that recently found for the HT dilute geothermal fluids from Iceland (Krafla, Namafjall, Nesjavellir and Hveragerdi geothermal areas; Sanjuan et al., 2010) in the framework of the European HITI project (High Temperature Instruments for supercritical geothermal reservoir characterization and exploitation). The existence of different Na/Li geothermometric relationships seems to indicate that the Na/Li ratios not only depend on the temperature but also on other parameters such as the fluid salinity and origin, the nature of the geothermal reservoir rocks in contact with the deep hot fluids or the equilibrium reactions between these fluids and the reservoir mineral assemblages. Some case studies in the literature and thermodynamic considerations suggest that the Na/Li ratios for the HT geothermal fluids derived from seawater and basalt interaction processes could be controlled by a full equilibrium reaction involving a mineral assemblage constituted, at least, of albite, K-feldspar, quartz and clay minerals such as kaolinite, illite (or muscovite) and Li-micas.

Moreover, this study confirms the presence of a deep seawater-derived geothermal fluid indicating a temperature close to 210°C and salinity of about 35 g/l, which would supply the littoral hot springs located in the Obock area (Houssein et al., 1993). It also suggests that the fluid collected from the thermal spring located near the Ghoubbet Channel (“Passe du Ghoubbet”; Sanjuan et al., 1990) results from a mixing between a marine origin fluid which would interact with basalt rocks at a temperature value close to 160°C and cold seawater.

Key words: geothermometer, marine geothermal fluid, basalt, Asal-Ghoubbet, Obock

INTRODUCTION
Since 1965, several chemical and isotopic geothermometers such as dissolved silica, Na/K, Na/K/Ca, Na/K/Ca/Mg, K/Mg or δ18O (H2O-SO4) are used as geochemical tools in geothermal exploration to estimate the fluid temperature in the deep reservoirs (White, 1970; Fournier, 1979; Michard, 1979; Giggenbach, 1988; Nicholson, 1993; Serra and Sanjuan, 2004). Unfortunately, these classical geothermometers, based on empirical or semi-empirical laws derived from known or unknown equilibrium reactions between water and reservoir minerals, do not always give concordant temperature estimations for the deep geothermal fluid. Different surface processes such as a mixing of this fluid with shallow waters, or the occurrence of mineral precipitation/dissolution reactions during its rising to the surface and its cooling, can be responsible of these discordances. For example, the Na/K geothermometer can give overestimated reservoir temperatures for dilute thermal waters from volcanic and granite areas. On the other hand, erroneous temperatures can be estimated using Na/K and Na/K/Ca for seawater-derived fluids not equilibrated with the reservoir rocks.

In order to obtain auxiliary geothermometers, several relationships combining major and trace elements were investigated. The most known and efficient geothermometric relationships are those associating Na and Li (Fouillac and Michard, 1981; Kharaka and Mariner, 1989). The two empirical and statistical relationships determined by
Fouillac and Michard (1981), dependant on the fluid salinity, were obtained from numerous data relative to several world geothermal fields mainly located in volcanic and granitic areas. The relationship given by Kharaka and Mariner (1989) was determined for hot saline fluids discharged from sedimentary basins, using many data collected from world geothermal and US oil-fields. Given the low Li reactivity during the ascent of the geothermal fluid up to the surface, this auxiliary geothermometer can be considered as a very useful tool to help to select the best estimation of the reservoir temperature, even if the running of this geothermometer is still poorly known.

Unfortunately, this geothermometer seems to be dependant not only on temperature but also on other parameters such as the fluid salinity or the nature of the reservoir rocks. Recent studies carried out in the framework of the European HITI project (High Temperature Instruments for supercritical geothermal reservoir characterization and exploitation) show that two new Na/Li relationships were determined for HT geothermal fluids from Iceland (Sanjuan and Millot, 2009; Sanjuan et al., 2010). One of these relationships was obtained using HT dilute fluids collected from wells located in four Icelandic geothermal fields (Krafla, Namafjall, Nesjavellir and Hverargerdi). The other Na/Li relationship was determined from literature data about HT fluids circulating in several oceanic Ridges and Rises (Middle-Atlantic Ridge, East Pacific Rise, etc.) and using HT saline geothermal fluids sampled in emerged Rifts such as those of Djibouti (Asal-Ghoubbet and Obock geothermal areas) and Iceland (Reykjanes geothermal field). All these fluids are derived from seawater and basalt interaction processes.

The main objectives of this study are:
- to improve the Na/Li relationship relative to this last type of fluids, and investigate the mechanisms involved in this relationship;
- to confirm or invalidate the temperatures estimated for this type of fluids discharged from littoral hot springs located in the Obock and North-Ghoubbet areas of Djibouti (Sanjuan et al., 1990; Houssein et al., 1993).

**STUDIED AREAS**

**Republic of Djibouti**

In order to obtain data from geothermal fluids derived from seawater-basalt interaction processes, two geothermal areas of this country located in the horn of Africa, at the Afar triple junction between the Red Sea, Gulf of Aden-Tadjourah and East African Rift systems, were studied.

**Asal-Ghoubbet area**

The distension system which separates the two plates from North to South of Tadjourah Gulf (Arabian and Somalia plates) belongs to the largest and most complex Rift system of the East part of Africa (Fig. 1). The separation of these plates induces a relative decrease of the crust thickness in the central area of the Gulf and a submarine volcanism, which produces a new oceanic crust. As a consequence, an anomalous heat flow which can be 4 to 6 times higher than the mean terrestrial flow occurs. The spreading area (with active volcanism) is segmented and dislocated by a system constituted of relatively long transform faults (Fig. 1). More recent studies indicate the importance of active structures with 130-140°N directions (Chouckroune et al., 1988; Lépine and Hirn, 1992; Dauteuil et al., 2001).
The Asal-Ghoubbet Rift seems to be largely underlain by pre-Asal crust not replaced by newly formed one, and to be still in a pre-oceanic stage. However, it presents remarkable analogies (morphology, volcanism, tectonic) with the axial valley of the oceanic ridges (Stieljes, 1973). At surface, it is exclusively constituted of volcanic rocks with a Quaternary age lower than 1 My. Its opening is recent and has not more than 1 My (Barberi et al., 1975). Most of the faults are normal and symmetrical on both side of the Rift and indicate a general NW-SE direction. However, some reverse faults are also present. Out of the axial Rift area, the normal faults intersect some previous normal N350 and N280 direction faults. Open fissures with or without vertical offset are largely responsible for the horizontal extension.

The Asal Rift is markedly asymmetrical with respect of its median axis. The most active and recent part of the Afar depression is the so-called Inner Rift where the volcano axial chain is observed and the last eruption (Ardoukoba volcano) occurred in 1978. It is about 3 km wide and is shifted to the NE part of the main Rift. This Inner Rift is characterized by intense fracturing and recent lava flows. The axis of crustal divergence of the Rift seems to migrate from SW to NE. The rise of hot material beneath the Rift is thus considered to proceed from SW to NE by successive pulses. The existence of an area of crust fusion at low depth, the important seismic activity, the presence of fumaroles and hot springs suggest that this region has a high geothermal potential.

The southern flank of the Asal-Ghoubbet Rift has been explored by six geothermal wells drilled at depths ranging from 1150 m to 2000 m. Beneath the Asal series formed during rifting (basalts and hyaloclastites less than 1 My old), all the wells encountered basalts with some rhyolithes 1-4 My old attributed to the Afar Stratoid series and basaltic lava flows with some intercalations of rhyolites and trachytes 4-9 My old corresponding to the Dalha basalt series. The maximum temperatures were measured around 340-350°C in the bottom-hole of Asal 4 and 5 but these wells were considered as unproductive (Houssein and Axelsson, 2010). These temperatures indicate strong geothermal gradients which may be related to the presence of magma chambers below about 4000 m in the central part of the Rift. Geothermal brine (TDS about 120 g/l) with a temperature close to 255-265°C was encountered in the wells Asal 1, 3 and 6, at depths ranging from 1050 to 1350 m. This saline geothermal reservoir is located in the fractured Dahlia basalt series.
Numerous thermal springs (Fig. 2) and fumaroles are present in the Asal-Ghoubbet Rift. These surface manifestations and the fluids collected from the geothermal wells were studied by several teams of researchers since 1973 (Bosch et al., 1977; Fontes et al., 1979; Fouillac et al., 1983; Marini, 1987; Sanjuan et al., 1990; D’Amore et al., 1998). From a chemical and Strontium isotopic study, Sanjuan et al. (1990) conclude that the hot waters collected from this area result from basalt-seawater interaction, associated with variable evaporation rates due to the aridity of this region. Some thermal waters result from a mixing between deep geothermal water and seawater or Asal lake water. Dissolution from evaporitic rocks appears unimportant.

For this study, only the waters for which the deep temperature was well known were selected. So, according to Sanjuan et al. (1990), the brines collected from the geothermal wells Asal 1, Asal 3 and Asal 6 are in equilibrium with a mineralogical assemblage at a temperature close to 255-265°C, temperature which was also measured into the wells. For the three wells, the selected water samples were collected after the phase separator. Only one water sample was directly sampled at the Asal 3 bottom-hole (BH in table 1).

The results of the chemical analyses of these waters which were corrected taking into account the concentration factor due to the phase separation were extracted from Sanjuan et al. (1990) and are reported in table 1. The results obtained using different classical chemical geothermometers such as Na/K, Na/K/Ca, K/Mg or Silica (quartz) are presented in table 2 and are close to the measured temperatures. The chemical composition given by these authors for three water samples collected from Asal Lake (Fig. 2) is also reported in table 1.

![Figure 2: Location map of the geothermal wells studied in this study and of main thermal springs (Eounda Aliftita, Eadkorar, Manda, Korili, Oued Kalou, Ghoubbet Channel) in the Asal Rift and the North-Ghoubbet. Three water samples collected from Asal Lake and a sample of seawater (SW) were also integrated in this study.](image)

During the collection of the water sample from the littoral thermal spring located near the Ghoubbet Channel (Figs. 1 and 2), tide was high and this spring was recovered by seawater. Consequently, the collected water sample (G2) is a mixing with a high proportion of cold seawater. As the Chloride concentration of this mixing is slightly lower than for seawater (see table 1), it can be concluded that a small proportion of shallow freshwater, estimated to be close to 1%, is also present. As noticed by Sanjuan et al. (1990) and Houssein et al. (1993), the hot seawater-derived solutions reacting with basalt in submarine hydrothermal springs, in geothermal wells or in laboratory are characterized by a strong depletion in Magnesium and Sulfates, and enrichment in Calcium, Potassium, Silica and Lithium. In the figure 3, the Mg/Cl and SO$_4$/Cl ratios extrapolated to zero, using the best linear regression coefficients, lead to the same Li/Cl value. This result suggests that the collected sample of
thermal water would be also constituted of a hot end-member without Mg and SO₄, reacting with basalt (probably Gulf basaltic series 1 to 3 My old).

The graphical determination of the Na/Cl, Ca/Cl and SiO₂/Cl ratios for the hot end-member can be obtained using the previously determined Li/Cl value (Fig. 4). The chemical composition of the hot end-member was reconstructed using the Chloride concentration of seawater (Tab. 1). Contrary to the literature observations, the K/Cl ratio determined in the G2 thermal water sample is lower than for seawater. In order to discard this anomalous result (probably due to an uptake of K by mineral precipitation/adsorption reaction during the rising and cooling of the hot end-member or eventually, to an analytical error because the difference relative to seawater is low), we have preferred to select a K/Cl ratio close to that of seawater (Fig. 4). Moreover, this ratio allows estimating a temperature for the hot end-member using the Na/K and Na/K/Ca geothermometers similar to that given by the Silica (quartz) geothermometer (Tab. 2). The temperature selected for the hot end-member was 160°C. This value is close to those (160-180°C) estimated by Marini (1987) using chemical geothermometers applied to non condensable gases collected from several fumaroles located in the vicinity of this thermal spring, in the North-Ghoubbet. The temperature and the chemical composition of a Ghoubbet seawater sample, collected near the thermal spring (SW in figure 2) by Sanjuan et al. (1990), are also reported in table 1.

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![Figure 3: Determination of the Li/Cl ratio for the Hot End-Member (HEM) of the thermal spring Ghoubbet Channel (G2) using the Mg/Cl and SO₄/Cl variations.](image)

![Figure 4: Determination of the Na/Cl and SiO₂/Cl ratios for the Hot End-Member (HEM) of the thermal spring Ghoubbet Channel (G2) using the Mg/Cl and SO₄/Cl variations.](image)
Figure 4: Determination of the Na/Cl, SiO2/Cl, Ca/Cl and K/Cl ratios for the hot end-member of the thermal spring G2 using the Li/Cl determined in figure 3.

Table 1: Chemical and isotopic compositions of geothermal seawater-derived fluid samples collected from Djibouti and Iceland selected for this study. These data were extracted from Sanjuan et al. (1990), Houssein et al. (1993), Bjornsson et al. (1972), Olafsson and Riley (1978), Truesdell et al. (1981), Sanjuan et al. (2010; in prep.).
Table 2: Measured temperatures, temperatures of deep geothermal fluid estimated using chemical geothermometers and values of temperature selected for this study.

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<th>$T_{\text{Na/K/Ca}}$</th>
<th>$T_{\text{K/Mg}}$</th>
<th>$T_{\text{Qz}}$</th>
<th>$T_{\text{Qz vapor}}$</th>
<th>$T_{\text{Chalc.}}$</th>
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$T_{\text{Na/KM}}$: Na/K geothermometer (Michard, 1979)
$T_{\text{Na/KF}}$: Na/K geothermometer (Fournier, 1979)
$T_{\text{Na/K/Ca}}$: Na/K/Ca geothermometer (Fournier and Truesdell, 1973)
$T_{\text{K/Mg}}$: K/Mg geothermometer (Giggenbach, 1988)
$T_{\text{Qz}}$: Silica-quartz geothermometer taking into account the water vapourisation before water sampling (Fournier and Rowe, 1966)
$T_{\text{Qz vapor}}$: Silica-Chalcedony geothermometer (Arnorsson, 1983)
$T_{\text{Na/Li}}$: Na/Li geothermometer (this study)
**Obock area**

The Obock area, located in the northern part of the Republic of Djibouti, is practically constituted of a quaternary formation of coralline limestone, 120-130 Ky old (Faure *et al.*, 1980) with a thickness probably lower than 50 m. Other present calcareous formations and detrital materials are also observed. All these formations are above basalt formations of the Tadjourah Gulf, 2 My old (Varet, 1975). During the 1980 years, the regional tectonic was considered to be as dominated by the famous normal-transform system of the Tadjourah Gulf in which the normal faults were E-W direction and the transform faults were NE-SO direction (Richard and Varet, 1979). However, more recent studies indicate a different configuration (Fig. 5) and the importance of active structures with 130-140°N directions (Chouckroune *et al.*, 1988; Lépine and Hirn, 1992; Dauteuil *et al.*, 2001).

The four littoral thermal springs, which were studied by Houssein *et al.* (1993), are located in an intensively fractured area (Fig. 1). They were sampled during low tide. The temperatures of emergence range from 50 to 80°C. The results of the chemical and isotopic analyses presented by Houssein *et al.* (1993) are reported in table 1. Using these data and chemical geothermometers, these authors showed that the origin and the evolution of these thermal waters seem to be:

- seawater which reacts with basalt at 210°C for enough time to reach equilibrium;
- a mixture of this hot fluid with cold seawater while it emerges through the fractures;
- dilution with small quantities of freshwater which may explain the lower Chloride concentration of these springs.

The isotopic $\delta^{18}$O and $\delta^{34}$S marine signature of the dissolved Sulfates determined by BRGM for the four water samples (Tab. 1) confirms the mixture of a hot seawater-derived fluid (absence of Sulfates) with cold seawater. Only the hot end-member was used in this study.

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**Figure 5**: Fault pattern of the Gulf of Tadjourah deduced from detailed analysis of shaded relief, stereoscopic and acoustic reflectivity images. Four kinds of structures are identified (main active faults, minor active or inactive faults, inactive faults, and canyons) (figure extracted from Dauteuil *et al.*, 2001).
Iceland

This study focuses on two high-temperature areas that have been extensively drilled for electrical power generation and are being exploited today. These are Reykjanes and Svartsengi, southwest Iceland (Fig. 6). These areas are located within the active volcanic belts, the axes of which represent the plate boundary between the Eurasian and North-American lithospheric plates. Another studied area is the medium-temperature Seltjarnarnes geothermal field, which is sited outside the active volcanic zone, in Quaternary flood basalts (Fig. 6).

The three geothermal fields are both located on the Reykjanes peninsula in southwestern Iceland which represents the landward continuation of the Reykjanes Ridge (Fig. 6). This Ridge is itself a projection of the Mid-Atlantic Ridge (Olafsson and Riley, 1978). The peninsula consists mostly of Holocene lavas protruded by hyaloclastite hills formed by sub-glacial eruptions during the last glaciation (Clifton and Kattenhorn, 2006). They lie astride setting, the heat source to these systems are considered to be shallow (1-3 km) sheeted dyke complexes and the permeability is fracture controlled. The two high-temperature geothermal systems are hosted by basaltic rocks, subglacial hyaloclastites, breccias, and pillow lavas as well as tuffaceous sediments (Giroud, 2008). Abundance of intrusions increases with depth and dominate the succession at the greatest depth reached by the wells.

At Reykjanes, the measured temperatures at the bottom-hole can vary from 225 to 320°C. The highest temperature recorded in the geothermal wells is close to 320°C, at a depth of 2000 m. The aquifer is two-phase above 1000 m but sub-boiling at greater depths. The Svartsengi geothermal field is classified as high-temperature and liquid-dominated (Gudmundsson and Thorhallsson, 1986). The temperature in Svartsengi is very homogeneous. Between 500 and 2000 m depth, it is close to 240°C, reflecting good vertical permeability in the system which presents abundant vertical fractures. At Seltjarnarnes, the maximum measured temperature was 114°C (Arnorsson and Andresdottir, 1995).

The geothermal fluids selected for this study are those found in the literature for the Reykjanes field (Bjornsson et al., 1972; Olafsson and Riley, 1978; Truesdell et al., 1981) and those sampled by Sanjuan et al. (2010, in preparation) with the collaboration and help of ISOR on October 2007, June 2008 and June 2009, in the framework of the European HITI project (HIgh Temperature Instruments for supercritical geothermal reservoir characterization and exploitation). These fluid samples were collected at the well-head using a stainless steel (N316) Webre separator to separate water (Sanjuan et al., 2010, in prep.) from the wells:
A sample of seawater was also selected. The results of the corresponding chemical analyses are reported in table 1. The chemical composition of the geothermal fluids sampled by Sanjuan et al. (2010, in prep.) was not corrected taking into account the concentration factor due to the phase separation because most of the chemical geothermometers are based on element concentrations ratios. However, for the temperatures estimated using the Silica (quartz) geothermometer, the relationship considering the water vaporization was selected (Tab. 2). Contrary to the Svartsengi and Seltjarnarnes geothermal fields where the temperatures measured at the bottom-hole are close to those estimated using the chemical geothermometers, the bottom-hole temperatures in the Reykjanes geothermal field are often different from the estimations (Tab. 2). For the geothermal waters of this field, we have considered that they were not always in equilibrium with surrounding rocks at the temperature measured in the bottom-hole and have preferred to select the average temperature estimated using the chemical geothermometers as the most representative of these waters (Tab. 2).

The geothermal fluids at Reykjanes represent seawater which has reacted with basalt (Arnorsson, 1995) and experienced stable isotope exchange with alteration minerals (Pope et al., 2009; 2010). The Cl concentration of the unboiled aquifer water is thus close to that of seawater. The Svartsengi geothermal system has a mixed meteoric-seawater fluid origin with Cl content corresponding to about 2/3 that of seawater and the deuterium content of this water is consistent with such an origin (Giroud, 2008). This mixture has reacted with basalt at 240°C for enough time to reach chemical equilibrium. The geothermal fluids at Seltjarnarnes represent seawater highly diluted by freshwater (about ten times), which has interacted and would be in equilibrium with basalt at relatively low temperature (114°C).

**Mid-Ocean Ridges and Rises**

Numerous chemical and Li isotopic data from literature were obtained for the very hot fluids circulating in Mid-Ocean Ridges (Mid-Atlantic Ridge, Middle Valley Ridge, etc.) and Rises (East Pacific Rise...), in the bibliographical review done by Sanjuan and Millot (2009) in the framework of the European project HITI. The data selected for this study were extracted from the bibliographical review and are reported in Appendix 1. The temperatures given in the literature are often close to those estimated using the silica geothermometer (quartz). Depletion in Lithium can be observed for the fluids circulating in old and much altered MAR and EPR, such as vent fluids from the Lucky Strike field or vent fluids at 13°N...

**Na/Li Relationship for Geothermal Fluids Derived from Seawater-Basalt Interaction Processes**

As shown in figure 7, a Na/Li thermometric relationship can be statistically defined for seawater and geothermal waters derived from seawater-basalt interaction processes such as those discharged from the emerged Riffs of Djibouti and Iceland. This relationship:

$$T (°K) = 920 / [\log (Na/Li) - 1.105] \quad (r^2 = 0.994)$$

can be considered as the most reliable and accurate for temperature values ranging from 0 to 365°C. Absolute uncertainty on the estimated temperatures is close to ± 25°C. This uncertainty is in good agreement with the temperatures estimated using this geothermometric relationship in this study (Tab. 2). For seawater, several examples were selected (see Table 1 and Appendix 1). The data for the hot fluids circulating in the Mid-Ocean Ridges and Rises (Appendix 1) have not been integrated for determining this relationship in order to obtain a more accurate relationship for the fluids discharged from emerged Riffs. However, except the fluids from old and much altered MAR and EPR, depleted in Li, most of them fit this relationship very well (Fig. 7).
The excellent regression coefficient obtained for this relationship confirms the temperatures estimated for the hot marine end-member of the thermal waters collected from the Ghoubbet Channel (160°C) and Obock (210°C), using the other chemical geothermometers (Tab. 2).

This thermometric relationship is slightly different from that determined by Sanjuan and Millot (2009):

$$T \, (^{\circ}K) = 855 / [\log (Na/Li) - 1.275] \quad (r^2 = 0.967)$$

which integrated most of the literature data about HT fluids circulating in Oceanic Ridges and Rises as well as data from Djibouti, but used limited data from Iceland.

This thermometric relationship is very different from that determined by Fouillac and Michard (1981) for saline geothermal waters in volcanic and granite environments (Cl concentrations ≥ 0.3 M):

$$T \, (^{\circ}K) = 1195 / [\log (Na/Li) - 0.13] \quad \text{(brown line in figure 7).}$$

and from that described by Kharaka and Mariner (1989) for hot saline fluids discharged from sedimentary basins located in world geothermal and US oil fields:

$$T \, (^{\circ}K) = 1590 / [\log (Na/Li) + 1.299] \quad \text{(green line in figure 7).}$$

However, we can note that the data relative to the brines collected from the Asal Lake, reported in table 1, fit this last relationship very well (Fig. 7).

Finally, the Na/Li relationship determined for geothermal fluids derived from seawater-basalt interaction processes is also very different from those determined for:

- the HT dilute geothermal waters (Cl concentrations < 0.3 M) in volcanic and granite environments by Fouillac and Michard (1981; Fig. 7);

- the HT dilute geothermal waters from Iceland by Sanjuan et al. (2010; Fig. 7).

**THERMODYNAMIC CONSIDERATIONS**

The sodic feldspar is commonly observed in the rocks of the volcanic and granitic geothermal reservoirs and is often involved with K-feldspar in the control of the aqueous Na/K ratios (see Na/K thermometric relationships). However,
in other environments such as sedimentary rocks, clay minerals can be also involved (D’Amore and Arnorsson, 2000).

As discussed in Sanjuan et al. (2010), dissolved Li generally increases with increasing temperature which can be interpreted as mainly caused by rock leaching or dissolution. However, Shaw and Sturchio (1992) noted that Li was also preferentially trapped in illitic alteration products when temperature increased and that, consequently, the retention of this element was favoured by abundant illitic alteration. Li can be also scavenged by other clays such as smectites, mixed layer clays or micas.

In order to understand the mechanisms involved in the thermometric Na/Li relationship determined for geothermal waters derived from seawater-basalt interaction processes in this study, a thermodynamic approach was carried out. As muscovite (KAl$_3$Si$_4$O$_{10}$(OH)$_2$) is relatively easily available as mineralogically pure phase, and consequently is chemically and thermodynamically better defined, it is widely used as a proxy for illites in the system K$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O (Manning, 2003; Sanjuan et al., 2003). Consequently, muscovite replaced illite in the thermodynamic calculations of this study.

If we consider the following equilibrium reaction:

$$\text{NaAlSi}_3\text{O}_8 \text{(albite)} + \text{KAlSi}_3\text{O}_8 \text{(K-feldspar)} + 2 \text{Al}_2\text{Si}_2\text{O}_5\text{(OH)}_4 \text{(Kaolinite)} + \text{Li}^+ = \text{KAl}_3\text{Si}_3\text{O}_{10} \text{(OH)}_2 \text{(Muscovite)} + \text{LiAl}_3\text{Si}_3\text{O}_{10} \text{(OH)}_2 \text{(Li-Mica)} + 4 \text{SiO}_2 \text{(Quartz)} + 2 \text{H}_2\text{O} + \text{Na}^+,$$

the equilibrium constant for this reaction at temperature \(T\) (K) is given by:

$$K_T = \frac{[\text{Na}^+]}{[\text{Li}^+]}$$

where \([\text{Na}^+]\) and \([\text{Li}^+]\) are the activities of the dissolved Sodium and Lithium ions.

If we consider that Na and Li are essentially in form of \(\text{Na}^+\) and \(\text{Li}^+\) and the activity coefficients for these ions are very close, \(K_T\) can be then expressed as:

$$K_T = \frac{[\text{Na}^+]}{[\text{Li}^+]} = \frac{[\text{Na}]}{[\text{Li}]}$$

where \([\text{Na}]\) and \([\text{Li}]\) are the concentrations of the dissolved Sodium and Lithium ions and Na and Li are the concentrations of total dissolved Sodium and Lithium.

For this reaction, the integration of the Van’t Hoff equation: \(\partial \ln K_T/\partial T = \Delta H°_R/RT^2\) allows expressing the equilibrium constant \(K_T\) as a function of temperature following the relationship:

$$\log K_T = \log K_{298} + \Delta H°_R/(2.303 \times R) \times (1/T - 1/298.15)$$

where \(K_{298}\) is the equilibrium constant at 298.15°K (25°C), \(\Delta H°_R\) (J.mol$^{-1}$) is the standard molar enthalpy of reaction assumed to be constant in function of temperature, and \(R\) is the perfect gas constant (≈ 8.3143 J.K$^{-1}$.mol$^{-1}$).

Temperature \(T\) is given in °K.

We can then write:

$$\log (\text{Na}/\text{Li}) = \log K_{298} + \Delta H°_R/5709 - \Delta H°_R/(19.1478 x T)$$

If we compare the Na/Li thermometric relationship obtained in paragraph 3 with this last equation, we can estimate the values of the corresponding reaction enthalpy and equilibrium constant at 298°K (25°C) as follows:

$$\Delta H°_R/19.1478 \approx -920 \text{ (slope of the straight line in figure 7)}$$

$$\log K_{298} + \Delta H°_R/5709 \approx 1.105 \text{ (constant of the straight line in figure 7)}$$

This implies that \(\Delta H°_R = -17616 \text{ J.mol}^{-1} = -17.6 \text{ KJ.mol}^{-1}\) and \(\log K_{298} = 4.191\).

Knowing this last parameter, we can determine the value for the corresponding standard Gibbs free energy of reaction \(\Delta G°_R\) following the fundamental thermodynamic relation:

$$\Delta G°_R = - \log K_{298} \times R \times 298.15 \times 2.303 = -23924 \text{ J.mol}^{-1} = -23.9 \text{ KJ.mol}^{-1}.$$
where \( n_i \) is the reaction coefficient of each compound and \( \Delta G^\circ_i \) refers to the standard Gibbs free energy of formation of each compound of the reaction and for which the values are reported in table 3.

We can then write:

\[
\Delta G^\circ_R = \Delta G^\circ_f (\text{muscovite}) + \Delta G^\circ_f (\text{Li-mica}) + 4 \Delta G^\circ_f (\text{quartz}) + 2 \Delta G^\circ_f (\text{H}_2\text{O}) + \Delta G^\circ_f (\text{Na}^+) - \Delta G^\circ_f (\text{albite}) - \Delta G^\circ_f (\text{K-feldspar}) - 2 \Delta G^\circ_f (\text{kaolinite}) - \Delta G^\circ_f (\text{Li}^+)
\]

\[= -23.1 \text{ KJ.mol}^{-1}.\]

Most of the \( \Delta G^\circ_i \) values (Tab. 3) were selected from the thermodynamic data base data0.com.R2 of the EQ3/6 code (Wolery, 1995) which relies heavily on the SUPCRT92 consistent data base (Johnson et al., 1992), a reference software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species and reactions.

However, for micas, in the absence of data for Li-Mica, all the values (Tab. 3) were extracted from the paper written by Tardy and Duplay (1992), who use a method of estimating the standard Gibbs free of formation of clays minerals and thermodynamic values similar to those found in the EQ3/6 data base. Note that for muscovite (K-mica), the \( \Delta G^\circ_i \) value is identical to that proposed in the EQ3/6 data base. As shown in Sanjuan et al. (2010), the values of standard Gibbs free energy of formation found in the literature for the aluminosilicate minerals, especially for clay minerals, can have large variations. It is why the most important requirement is the consistence and the coherence of the selected data base.

The value found for \( \Delta G^\circ_R \) close to that determined from the relationship obtained in paragraph 3 (-23.9 KJ.mol\(^{-1}\)) suggests that the Na/Li ratios are most probably controlled by this type of equilibrium reaction, where the formulae of the clay minerals (K- and Li-micas) are certainly simplified but represent relatively well the interacting phases. Consequently, the Li concentrations could be well controlled by clay alteration products, partially constituted of illitic and mica minerals, at high temperature. As shown by Sanjuan et al. (2010), other equilibrium reactions involving slightly different mineral assemblages could explain the other existing Na/Li relationships.

The \( \Delta H^\circ_R \) value relative to the considered equilibrium reaction can be calculated using the values of standard molar enthalpy of formation (\( \Delta H^\circ_i \)) for each compound following the fundamental thermodynamic relationship:

\[
\Delta H^\circ_R = \sum n_i \Delta H^\circ_f (\text{right compounds}) - \sum n_i \Delta H^\circ_f (\text{left compounds})
\]

where \( n_i \) is the reaction coefficient of each compound.

We can then write:

\[
\Delta H^\circ_R = \Delta H^\circ_f (\text{muscovite}) + \Delta H^\circ_f (\text{Li-mica}) + 4 \Delta H^\circ_f (\text{quartz}) + 2 \Delta H^\circ_f (\text{H}_2\text{O}) + \Delta H^\circ_f (\text{Na}^+) - \Delta H^\circ_f (\text{albite}) - \Delta H^\circ_f (\text{K-feldspar}) - 2 \Delta H^\circ_f (\text{kaolinite}) - \Delta H^\circ_f (\text{Li}^+)
\]

\[= -17.5 \text{ KJ.mol}^{-1}.\]

As for the \( \Delta G^\circ_R \), the \( \Delta H^\circ_i \) values (Tab. 4) were selected from the thermodynamic data base data0.com.R2 of the EQ3/6 code (Wolery, 1995), except for Li-mica and muscovite, which were those proposed in Sanjuan et al. (2010). The \( \Delta H^\circ_f \) value selected for muscovite was determined by Vieillard (1994) and is very close to that of the EQ3/6 data base (Tab. 4). The \( \Delta H^\circ_f \) value selected for Li-mica was estimated by Sanjuan et al. (2010) because it was not available in the literature.

In spite of the inaccuracy related to the \( \Delta H^\circ_i \) values (Sanjuan et al., 2010), the value determined for \( \Delta H^\circ_R \) is very close to that estimated using the Na/Li relationship determined in paragraph 3: -17.6 KJ.mol\(^{-1}\). This result is in good agreement with that obtained from the \( \Delta G^\circ_R \) values and strengthen the conclusions drawn up from these last. It is concordant with the \( \Delta H^\circ_f \) value estimated for Li-mica by Sanjuan et al. (2010).
Table 3: Values of the standard molar Gibbs free energies of formation $\Delta G^\circ_f$ selected for the compounds used in this study.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical formula</th>
<th>Authors</th>
<th>$\Delta G^\circ_f$ selected KJ.mol$^{-1}$</th>
<th>EQ3/6 data base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>$H_2O$</td>
<td>Johnson et al. (1992)</td>
<td>-237.17</td>
<td>X</td>
</tr>
<tr>
<td>Aqueous Lithium ion</td>
<td>$Li^+$</td>
<td>Robie et al. (1978), Tardy and Duplay (1992)</td>
<td>-293.30</td>
<td>X</td>
</tr>
<tr>
<td>Aqueous Sodium ion</td>
<td>$Na^+$</td>
<td>Shock and Helgeson (1988) and Johnson et al. (1992)</td>
<td>-261.88</td>
<td>X</td>
</tr>
<tr>
<td>Albite</td>
<td>$NaAlSi_3O_8$</td>
<td>Helgeson et al. (1978) and Johnson et al. (1992)</td>
<td>-3708.31</td>
<td>X</td>
</tr>
<tr>
<td>K-Feldspar</td>
<td>$KAlSi_3O_8$</td>
<td>Helgeson et al. (1978) and Johnson et al. (1992)</td>
<td>-3746.24</td>
<td>X</td>
</tr>
<tr>
<td>Illite</td>
<td>$K_{0.6}Mg_{0.25}Al_2Si_3O_10(OH)_2$</td>
<td>Wolery (1978)</td>
<td>-5455.81</td>
<td>X</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>$Al_2Si_3O_10(OH)_4$</td>
<td>Helgeson et al. (1978) and Johnson et al. (1992)</td>
<td>-3789.09</td>
<td>X</td>
</tr>
<tr>
<td>Li-Mica</td>
<td>$LiAlSi_3O_10(OH)_2$</td>
<td>estimated by Tardy and Duplay (1992)</td>
<td>-5596.80</td>
<td>X</td>
</tr>
<tr>
<td>Muscovite (K-Mica)</td>
<td>$KAlSi_3O_10(OH)_2$</td>
<td>estimated by Tardy and Duplay (1992)</td>
<td>-5591.10</td>
<td>X</td>
</tr>
<tr>
<td>Quartz</td>
<td>$SiO_2$</td>
<td>Helgeson et al. (1978) and Johnson et al. (1992)</td>
<td>-856.24</td>
<td>X</td>
</tr>
</tbody>
</table>

Table 4: Values of the standard molar enthalpies of formation $\Delta H^\circ_f$ selected for the compounds used in this study.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical formula</th>
<th>Authors</th>
<th>$\Delta H^\circ_f$ selected KJ.mol$^{-1}$</th>
<th>EQ3/6 data base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>$H_2O$</td>
<td>Robie et al. (1978), Johnson et al. (1992)</td>
<td>-285.84</td>
<td>X</td>
</tr>
<tr>
<td>Aqueous Lithium ion</td>
<td>$Li^+$</td>
<td>Shock and Helgeson (1988) and Johnson et al. (1992)</td>
<td>-278.45</td>
<td>X</td>
</tr>
<tr>
<td>Aqueous Sodium ion</td>
<td>$Na^+$</td>
<td>Shock and Helgeson (1988) and Johnson et al. (1992)</td>
<td>-240.30</td>
<td>X</td>
</tr>
<tr>
<td>Albite</td>
<td>$NaAlSi_3O_8$</td>
<td>Helgeson et al. (1978) and Johnson et al. (1992)</td>
<td>-3931.62</td>
<td>X</td>
</tr>
<tr>
<td>K-Feldspar</td>
<td>$KAlSi_3O_8$</td>
<td>Helgeson et al. (1978) and Johnson et al. (1992)</td>
<td>-3971.40</td>
<td>X</td>
</tr>
<tr>
<td>Illite</td>
<td>$K_{0.6}Mg_{0.25}Al_2Si_3O_10(OH)_2$</td>
<td>Wolery (1978)</td>
<td>-5835.29</td>
<td>X</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>$Al_2Si_3O_10(OH)_4$</td>
<td>Helgeson et al. (1978) and Johnson et al. (1992)</td>
<td>-4109.61</td>
<td>X</td>
</tr>
<tr>
<td>Li-Mica</td>
<td>$LiAlSi_3O_10(OH)_2$</td>
<td>no data found in the literature - proposed in this study</td>
<td>-5992.00</td>
<td>X</td>
</tr>
<tr>
<td>Muscovite (K-Mica)</td>
<td>$KAlSi_3O_10(OH)_2$</td>
<td>Krupka et al. (1979), value also selected by Vieillard (1994)</td>
<td>-5971.60</td>
<td>X</td>
</tr>
<tr>
<td>Quartz</td>
<td>$SiO_2$</td>
<td>Helgeson et al. (1978) and Johnson et al. (1992)</td>
<td>-910.65</td>
<td>X</td>
</tr>
</tbody>
</table>

CONCLUSION

In the framework of this study, a specific Na/Li thermometric relationship was statistically obtained for HT fluids derived from seawater and basalt interaction processes existing in emerged Rifts such as those of Djibouti (Asal-Ghoubbet and Obock geothermal areas) and of Iceland (Reykjanes, Svaartsengi and Seltjarnarnes geothermal fields), or in numerous Oceanic Ridges and Rises (Middle-Atlantic Ridge, East Pacific Rise, etc.). This relationship, which can be applied at temperature values ranging from 0 to 365°C, with an uncertainty of ± 25°C, can be described as:

$$T (°K) = 920 / [\log (Na/Li) - 1.105] \quad (r^2 = 0.994)$$

This relationship is slightly different from that determined by Sanjuan and Millot (2009) which integrated numerous literature data about HT fluids circulating in Oceanic Ridges and Rises as well as data from Djibouti, but used limited data from Iceland. The use of the thermometric Na/Li relationship determined in this study is recommended. The excellent regression coefficient obtained for this relationship confirms the temperatures estimated for the hot seawater derived end-member of the thermal waters collected from the Ghoubbet Channel (160°C) and Obock (210°C), using the other chemical geothermometers.
This thermometric Na/Li relationship is very different from the three relationships previously described and known in the literature and that proposed by Sanjuan et al. (2010) for the HT dilute geothermal waters from Iceland.

The existence of new Na/Li thermometric relationships confirms that the Na/Li ratios not only depend on the temperature but also on other parameters such as the fluid salinity and origin, the nature of the geothermal reservoir rocks in contact with the deep hot fluids or the equilibrium reactions between these fluids and the reservoir mineral assemblages.

Some case studies found in the literature and thermodynamic considerations suggest that the Na/Li ratios for the HT geothermal fluids derived from seawater and basalt interaction processes could be controlled by a full equilibrium reaction involving a mineral assemblage constituted, at least, of albite, K-feldspar, quartz and clay minerals such as kaolinite, illite (or muscovite) and Li-micas. Other equilibrium reactions involving slightly different mineral assemblages could explain the other existing Na/Li relationships (Sanjuan et al., 2010).

This study shows that it is essential to well define the environment in which the Na/Li geothermometer is applied before its use. Additional developments relative to this auxiliary geothermometer in different environments and regions are necessary in order to improve its use, which can be more reliable than other classical geothermometers in many cases and consequently, very useful for geothermal exploration. Experimental works in laboratory involving water-rock interaction processes as a function of temperature and integrating chemical, isotopic and mineralogical analyses should allow improving knowledge and understanding of the running of this geothermometer.

Acknowledgments: I would like to thank the International Division of BRGM, especially J.-Ph. Rançon and J.-C. Guillaumeau, who supported financially this study. This study benefited from the results obtained during my stay in Djibouti (1986-1990), at ISERST (presently CERD), and in the framework of the FP6 European project HITI (2007-2010). My colleagues from BRGM (especially R. Millot and M. Brach), CERD (especially A. Abdillahi, A. Abdillahi and I. Houssein), Prof. G. Michard (University of Paris 7) as well as ISOR (especially, R. Asmundsson and N. Giroud) are also thanked.

REFERENCES


Appendix I

Review of Lithium chemical and isotopic data relative to worldwide hydrothermal submarine fluids (extracted from Sanjuan and Millot, 2009). The data in italic do not fit the Na/Li geothermometric relationship determined in this study.

<table>
<thead>
<tr>
<th>Hydrothermal Springs</th>
<th>T (°C)</th>
<th>Liquid H2O (g/l)</th>
<th>Na (ppm)</th>
<th>Li (ppm)</th>
<th>Mg (ppm)</th>
<th>Ca (ppm)</th>
<th>Sr (ppm)</th>
<th>Ba (ppm)</th>
<th>Fe (ppm)</th>
<th>Zr (ppm)</th>
<th>Alk</th>
<th>Na/Li</th>
<th>Li/Na</th>
<th>Li/Cl</th>
<th>Na/Cl</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guaymas Basin hydrothermal fluid 1 (South Field, Gulf of California, USA, 2002)</td>
<td>300</td>
<td>1.74</td>
<td>1.06</td>
<td>1.74</td>
<td>1.06</td>
<td>384</td>
<td>2.56</td>
<td>2.78</td>
<td>1.90</td>
<td>1.90</td>
<td>2.92</td>
<td>0.57</td>
<td>0.78</td>
<td>0.90</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>Guaymas Basin hydrothermal fluid 2 (South Field, Gulf of California, USA, 1982)</td>
<td>300</td>
<td>1.74</td>
<td>1.06</td>
<td>1.74</td>
<td>1.06</td>
<td>384</td>
<td>2.56</td>
<td>2.78</td>
<td>1.90</td>
<td>1.90</td>
<td>2.92</td>
<td>0.57</td>
<td>0.78</td>
<td>0.90</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>Guaymas Basin hydrothermal fluid 3 (South Field, Gulf of California, USA, 1982)</td>
<td>300</td>
<td>1.74</td>
<td>1.06</td>
<td>1.74</td>
<td>1.06</td>
<td>384</td>
<td>2.56</td>
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<td>1.90</td>
<td>1.90</td>
<td>2.92</td>
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<td>0.78</td>
<td>0.90</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>Guaymas Basin hydrothermal fluid 4 (South Field, Gulf of California, USA, 1982)</td>
<td>300</td>
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Fig. 2: Temperature estimated using the Silica-quartz geothermometer (Fourier and Rowe, 1966).