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Keywords: geothermometer, Sodium, Lithium, geothermal waters, well, temperature, analyses, Krafla field, Iceland

ABSTRACT

This paper presents the study which has allowed determining the best adapted Na/Li thermometric relationship for the High-Temperature (HT) dilute waters collected from wells located in the Krafla geothermal area, North-east Iceland. This work was carried out in the framework of the European HITI project (High Temperature Temperatures for supercritical geothermal reservoir characterization and exploitation). This relationship, which can give estimations of temperature ranging from 200 to 325°C with an uncertainty of ± 20°C, was also successfully used on HT dilute fluids collected from wells located in other Icelandic geothermal areas (Namafjall, Nesjavellir and Hveragerði). So, a more general Na/Li geothermometric relationship including these other geothermal areas was obtained. These new relationships determined for Icelandic HT dilute geothermal fluids, which are very different from that commonly used for the dilute world geothermal waters, will be tested on the fluids collected during the international Iceland Deep Drilling Project (IDDP) for which the main objective is to drill deep wells (> 5 km) in supercritical reservoirs located in the Krafla and Reykjanes geothermal areas. Another Na/Li relationship determined for HT saline geothermal fluids derived from sea water and basalt interaction processes will be tested on the Reykjanes supercritical reservoirs. The existence of several different Na/Li geothermometric relationships seems to show that the Na/Li ratios not only depend on the temperature but also on other parameters such as the fluid salinity and origin, or the nature of the geothermal reservoir rocks in contact with the deep hot fluids. Thermodynamic considerations and some case studies in the literature suggest that the Na/Li and Na/K ratios for the HT dilute geothermal waters from Iceland could be controlled by a full equilibrium reaction involving a mineral association constituted, at least, of Albite, K-Feldspar, Quartz and Clay minerals such as Kaolinite, Illite and Na-, Li-Micas.

1. INTRODUCTION

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. Since 1965, several chemical and isotopic geothermometers such as Silica, Na/K, Na/K/Ca, K/Mg, Na/K/Ca/Mg or $\delta^{18}$O(H$_2$O-SO$_4$) are applied on fluid samples collected either from geothermal wells or thermal springs. Most of these geothermometers are based on empirical or semi-empirical laws derived from known or unknown chemical equilibrium reactions between water and minerals occurring in the geothermal reservoirs (White, 1970; Fournier, 1979; Michard, 1979; Giggenbach, 1988; Nicholson, 1993; Serra and Sanjuan, 2004). Unfortunately, the estimations of temperatures given for the deep geothermal reservoirs 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. For instance, 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 sea water.

Given this discordance and from numerous data obtained in several world geothermal and US oil fields, a new geothermometer was proposed for thermal and geothermal waters, based on three empirical and statistical Na/Li thermometric relationships (Fouillac and Michard, 1981; Kharaka and Mariner, 1989). These relationships seem to be essentially dependant on the fluid salinity and on the reservoir type (crystalline or sedimentary rocks). 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 those of classical geothermometers. Unfortunately, the running of the Na/Li geothermometer is poorly known and for the moment, none of these thermometric Na/Li relationships has been tested for very high temperatures (> 350°C).

Figure 1: Location of the geothermal fields selected for this study on the Iceland map

The use, calibration and validation of the Na-Li chemical geothermometer on dilute and saline Icelandic geothermal fluids (Fig. 1) at temperatures up to 500°C is one of the tasks envisaged by BRGM in the European HITI project in order to develop relevant and decisive tools able to estimate the temperatures in supercritical reservoirs located in the Krafla.
and Reykjanes geothermal areas where deep wells must be drilled in the IDDP framework.

The large variety of Icelandic geothermal waters ranging from low to very high temperatures (supercritical conditions) and from low (Krafla geothermal field) to high salinities (Reykjanes area) is an excellent opportunity to develop this geothermometer and to better understand its behavior.

2. STUDIED GEOTHERMAL AREAS

This study focuses on the HT Krafla geothermal area, North-East Iceland (Fig. 1), where the first supercritical well must be drilled in 2009 in the IDDP framework. However, other HT geothermal fields such as Namafjall, Nesjavellir and Hveragerði, were also integrated in this study (Fig. 1). In all these areas which are located within or close to the active volcanic belts representing the diverging boundary between the North-American and Eurasian plates, the dilute waters discharged from the geothermal wells indicate temperatures ranging from 180 to 350°C. All these systems are located in basaltic environments and have similar mineralogy. The source water to the geothermal fluids is local or near local meteoric water according to the δ2H and δ18O isotopic data (Darling and Armannsson, 1989; Arnorsson, 1995). The Total Dissolved Solids (TDS) content of the aquifer water in these fields is very low (1-2 g/l) compared to most other geothermal systems in the world. The low salt content is considered to be the consequence of the low Cl content of the host basalt with which the water has reacted (Arnorsson, 1995). The most important anions are Cl and SO₄, the most abundant cation is Na. Silica is the most abundant dissolved solid (Giroud, 2008).

2.1 Krafla

The Krafla field (Fig. 1) lies within the caldera of the Krafla central volcano which has erupted both basaltic and silicic magma (Jonasson, 1994). This caldera is intersected by an about 5-8 km wide and 100 km long NNE-trending fissure swarm (Fig. 2) thought to have formed about 100 ka ago (Saemundsson, 1991). The aquifer rock is, however, largely basaltic, sub-aerially erupted lavas, sub-glacially erupted hyaloclastites as well as small intrusive bodies of basalt, dolerite and gabbro. Intrusions of granophyre also occur (Giroud, 2008). A volcanic episode occurred in the area between 1975 and 1984 and fresh magma was intruded into the roots of the Krafla geothermal system at 4-7 km depth (Einarssson, 1978).

The drilled geothermal reservoir at Krafla has been divided into two main depth zones, an upper sub-boiling zone at 190-200°C, and a lower two-phase zone with temperatures up to 350°C (Armannsson et al., 1987; Arnorsson, 1995). The depth of the 39 drilled wells ranges between 1000 and 2400 m. The temperatures estimated using the Na-K and quartz geothermometers indicate that most of the aquifers producing into the geothermal wells are below 300°C (Gudmundsson and Arnorsson, 2002).

2.2 Namafjall

The Namafjall geothermal field, which lies 8 km south of Krafla (Fig. 1) and is about 3-4 km² in size, may be considered as a parasite to the Krafla volcano (Giroud, 2008). Steaming ground, mud pools and fumaroles are widely spread over the area. It was also affected by the 1975-1984 volcanic episode, which suggests that the heat source to the Namafjall geothermal system is represented by the dykes formed by magma intrusion into tensional fissures from the magma body in the roots of the Krafla system. The

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Figure 2: The Krafla and Namafjall geothermal areas and associated central volcano and fissure swarm. From Arnorsson (1995) and Armannsson et al. (1987)

2.3 Nesjavellir

This field, located in Southwest Iceland (Fig. 1), lies in a tectonically active graben to the northeast of the Hengill central volcano. The drilled formations at depth are largely basalt lavas and basaltic hyaloclastites as well as small intrusions of basalt and dolerite. Granophyre is sporadic (Franzon, 1998). Intrusions are dominant below some 1500 m depth. A volcanic fissure, which lies immediately to the north of the well-field, erupted about 2000 years ago (Saemundsson, 1963, 1992; Bull et al., 2005). The permeability is mostly fracturing controlled (Bödvarsson et al., 1990).

The drilled geothermal system at Nesjavellir is two-phase, at least to the depth penetrated by the deepest wells (about 2200 m). The maximum recorded temperature is higher than 380°C (Giroud, 2008). The well in which this temperature was measured was drilled close to the volcanic fissure.
2.4 Hveragerdi
This field is located at the southwestern boundary of the Hengill area. Well data indicate a temperature of 180-230°C (Arnorsson and Gunnlaugsson, 1985). Hot springs are abundant in the area as well as fumaroles and hot altered ground. Silica sinter deposits are limited. The area is tectonically active although the Hveragerdi field lies outside the main zone of rifting.

Alteration in rocks at depth penetrated by wells in Hveragerdi is intense with minerals indicating temperatures higher than those measured today (Sigvaldason, 1963). Either the system has cooled down or erosion has brought high-temperature hydrothermal minerals closer to the surface (Giroud, 2008). Both explanations are consistent with the geological location of the field that indicates that it is mature and is in the process of drifting out of the active volcanic belt. Possibly the Hveragerdi system has drifted aside from its original magmatic heat source.

3. WATER SAMPLING AND ANALYTICAL METHODS
3.1 Water Sampling
In this study, BRGM benefited from the collaboration and help of ISOR for all the water samples collected from wells located in the selected geothermal areas, during the two field campaigns carried out in October 2007 and June 2008.

10 productive wells (KS-01, K-05, K-13, K-14, K-24, K-27, K-32, K-34, K-35 and K-37) were sampled in the Krafla geothermal field whereas only 2 (B-09 and B-13), 4 (NJ-10, NJ-14, NJ-16 and NJ-19) and 1 well (HV-03) were sampled in the Namafjall, Nesjavellir and Hveragerdi geothermal areas, respectively.

Water samples were collected from two phase pipeline at the water outlet of the system. The samples were collected in 1 l polyethylene bottles for isotopic analyses in water and in dissolved sulfates is ±0.1‰ and ±0.5‰, respectively. Results are reported in Table 1.

4. Na/Li RELATIONSHIPS FOR HT DILUTE GEOTHERMAL WATERS FROM ICELAND
4.1 Temperature Estimated for the Geothermal Waters Discharged from the Deep Aquifers
As suggested by Gudmundsson and Arnorsson (2002), the down-hole temperatures measured after thermal recovery of the wells are not always representative of the temperature of the geothermal fluid discharged from the deep reservoir. Only, the temperatures estimated using chemical and gas geothermometers, if they are concordant, can give an average value close to the temperature of the geothermal fluid discharged from the wells.

The relatively good agreement between the temperature estimations using the Na/K, Na/K/Ca and Silica-quartz geothermometers (Fournier, 1979; Michard, 1979; Fournier and Truesdell, 1973; Fournier and Rowe, 1966) compared with the down-hole measured temperatures has permitted to select an average temperature value (Table 2), considered as the most representative value of the geothermal fluids discharged from the wells. As the chemical compositions were determined on water samples separated from vapor, the estimations of temperature given by the Silica-quartz vapor are recommended in Table 2 (rather than those estimated using Silica-quartz without corrections). As the other geothermometers are constituted of elemental ratios, their use is independent on the absolute concentration values. We can notice that the temperatures estimated using the isotopic δ¹⁸O values in H₂O, δ¹³C, δ¹⁵N and ⁷Li values, ⁸⁷Sr/⁸⁶Sr ratios, for which the results will be presented and interpreted in other studies.

3.2 Analytical Methods
The results of physico-chemical parameters measured on site and on untreated samples such as conductivity at 25°C, pH and non corrected Redox potential (Eh) are reported in Table 1. Absolute uncertainty on the measurements of pH is 0.05 pH unit. For the other parameters, relative uncertainty is about 5%.

All the chemical and isotopic analyses were carried out in the BRGM laboratories, at Orleans. The chemical analyses (major cations and anions, Total Inorganic Carbon, SiO₂, Li) were performed using standard water analytical techniques such as Ion Chromatography, Inductively Coupled Plasma-
Table 1. Chemical and isotopic compositions determined on water samples separated from steam and collected from wells located in the Krafla, Namafjall, Nesjavellir and Hveragerdi studied geothermal areas.

<table>
<thead>
<tr>
<th>Geothermal field</th>
<th>Well</th>
<th>Fluid sampling date</th>
<th>T°C</th>
<th>Cond. 25°C</th>
<th>TDS</th>
<th>pH</th>
<th>Eh</th>
<th>δD</th>
<th>δ18Owater</th>
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Table 2. Down-hole measured temperatures and temperatures estimated using the chemical and isotopic geothermometers Na/K, Na/K/Ca, Silica-quartz and δ18O(H2O-SO4).

<table>
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<tr>
<th>Geothermal field</th>
<th>Well</th>
<th>Fluid sampling date</th>
<th>Tbottom-hd °C</th>
<th>TNa/K °C</th>
<th>TaNa/KF °C</th>
<th>TaNa/Ca °C</th>
<th>TaSO4 °C</th>
<th>TNa/KF/SO4 °C</th>
<th>T1000 °C</th>
<th>log(Na/Li)</th>
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<td>187</td>
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<td>268</td>
<td>215</td>
<td>260</td>
<td>2.11</td>
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</tbody>
</table>
All these results are in good agreement with the conclusions drawn by Arnórsson et al. (1983) who have demonstrated that numerous Icelandic geothermal waters are in full chemical equilibrium with the reservoir rocks.

4.2 Na/Li Relationship for HT Dilute Waters Discharged from the Krafla Geothermal Area

As shown in Figure 4, a Na/Li thermometric relationship can be statistically defined for the HT dilute waters discharged from the Krafla geothermal area. For the moment, this relationship:

\[
\log (\text{Na/Li}) = 1967/T(°\text{K}) - 1.267 \quad (r^2 = 0.958)
\]

can be considered as reliable for temperature values ranging from 200 to 325°C. Absolute uncertainty on the estimated temperatures is close to ±20°C.

![Figure 4: Sodium/Lithium thermometric relationships existing in the literature and new Na/Li relationships determined for Icelandic HT geothermal waters, during this study](image)

This thermometric relationship is very different from that determined by Fouillac and Michard (1981) for the dilute geothermal waters in volcanic and granite environments (Chloride concentrations < 0.3 M):

\[
\log (\text{Na/Li}) = 1000/T(°\text{K}) - 0.38 \quad \text{(red line in Figure 4)}.
\]

Surprisingly, it is closer to the equation used by these same authors for saline geothermal waters in volcanic and granite environments (Chloride concentrations ≥ 0.3 M):

\[
\log (\text{Na/Li}) = 1195/T(°\text{K}) + 0.13 \quad \text{(brown line in Figure 4)}.
\]

Fouillac and Michard (1981) had already observed that two Icelandic dilute geothermal waters (Hveragerdi well G3 and Geyser) fell far outside their thermometric relationship determined for the dilute geothermal waters in volcanic and granite environments and were close to their relationship defined for the saline waters. They attributed this shift to the rainwater contribution in the chemistry of these two waters, which cannot be neglected in Iceland. However, we will see later that another explanation is much more probable.

Logically, the Na/Li thermometric relationship found in this study is very different from that determined by Kharakha and Mariner (1989) for hot saline fluids discharged from sedimentary basins located in world geothermal and US oil fields:

\[
\log (\text{Na/Li}) = 1590/T(°\text{K}) - 1.299 \quad \text{(green line in Figure 4)}.
\]

It is also different from that determined by Sanjuan and Millot (2009) for the marine origin fluids which interact with basalt rocks between 60 and 350°C and are discharged from the oceanic ridges (Middle Atlantic Ridge: MAR, East Pacific Ridge: EPR) or from emerged rifts (Djibouti, Iceland). The equation of this relationship is:

\[
\log (\text{Na/Li}) = 855/T(°\text{K}) + 1.275 \quad \text{(blue line in Figure 4)}
\]

As shown in Figure 4, the data collected for the marine origin waters discharged from the Reykjanes and Svartsengi geothermal fields are in very close agreement with this last relationship (Sanjuan et al., in preparation).

The Na/Li relationship obtained for HT dilute waters discharged from the Krafla geothermal was applied on a water sample collected by ISOR from the well K-39 and analyzed by BRGM. This new well located in the Krafla area was unexpectedly drilled into a supercritical regime at a depth close to 2700 m and the bottom section was cemented at the end of drilling because this well was considered to be too powerful. It turned out to be blocked for measurements at a depth of about 1600 m. The objective of the temperature estimation was to determine from which aquifer this water could come and know if it had reached supercritical conditions of temperature (>375°C).

The temperature estimated using the new Na/Li geothermometer gave a value close to 257°C, a value far from the supercritical conditions. However, this value was in good agreement with those estimated using the classical Silica-quartz and Na/K/Ca geothermometers (254 and 264°C, respectively). It was also very close to the maximum temperature value (265°C) measured into the well at a depth of about 1000-1100 m in December 2008, after thermal recovery of the well.

4.3 Na/Li Relationship for HT Dilute Geothermal Waters from Iceland

As illustrated in Figure 4, the data collected from the HT dilute waters discharged from the Namafjall, Nesjavellir and Hveragerdi geothermal areas (Tables 1 and 2) are in good agreement with the Na/Li relationship determined for the Krafla geothermal area. When integrated in the statistical determination of the Na/Li thermometric relationship, the corresponding equation becomes (Fig. 4):

\[
\log (\text{Na/Li}) = 2002/T(°\text{K}) - 1.322 \quad (r^2 = 0.967)
\]

Absolute uncertainty on the estimated temperatures is close to ±20°C. It is highly probable that this more general equation can be applied to many HT dilute geothermal waters from Iceland. Additional chemical analyses must be performed on dilute waters discharged from wells in Iceland at temperatures lower than 200°C and higher than 325°C in order to test and validate, or re-calibrate this Na/Li thermometric relationship at these temperatures.

5. THERMODYNAMIC CONSIDERATIONS

For the dilute geothermal waters at high temperature, Fouillac and Michard (1981) noticed an increase of the concentrations of dissolved Sodium with temperature that they attributed to the increase of Albite solubility. This 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 Arnórsson, 2000).

Fouillac and Michard (1981) also observed an increase of the concentrations of dissolved Lithium with increasing...
temperature that they interpreted as mainly caused by rock
dissolution, probably enhanced by the uptake of Li in some
weathering products (clays) at low temperature. Contrary to
the Na/K ratios, these authors emphasized that studies by
Volfinger (1976) on the partition coefficients of the alkali
ions between feldspars and aqueous solutions at high
temperature (T > 400°C) did not give reliable results for Li.
They considered that Lithium behaves in hot waters as a
“soluble” element, i.e. it is not co-precipitated with any
secondary mineral, except perhaps near-surface clays.
However, they noticed that it was surprising to not observe
an influence of the water-rock ratio or of the rock type on
the Li concentrations.

According to the literature data, sites exist within clay
minerals which are highly specific for Li. McDowell and
Marshall (1962) noted a high affinity of Micas for small
amounts of Li and concluded that it may be the result of an
dedge effect, because Li can be accommodated in the
octahedral layer. Maurel and Volfinger (1977) observed that
most of Li was incorporated in the octahedral sites (as Mg)
of the Phengite that they synthesized from a gel constituted
of 90% Muscovite and 10% Celadonite in presence of
Lithium Chloride at 500°C. About 33% of Li were adsorbed
on this Mica. Calvet and Prost (1971) noted the strong
temperature-dependence on the amount of Li that enters the
lattice of Montmorillonite, ranging from 9% at 90°C to 68%
at 220°C.

Shaw and Sturchio (1992) showed that thermal waters
collected from the Biscuit Basin Flow, Yellowstone
National Park (USA), reflected leaching from the fresh
rocks, but contained much less Li than B (B/Li ≈ 3
compared with 0.8 in fresh Obsidian). They clearly
demonstrated that Lithium was 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 and mixed layer
Clays. Similar observations were made by these authors on
weathering products (clays) at low temperature. Contrary to
these results, the equilibrium constant K_T can be then
expressed as:

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

where [Na^+] and [Li^+] are the concentrations of the dissolved
Sodium and Lithium ions.

If we consider that for dilute waters, the activity coefficients
are very close to 1 and Na and Li are essentially in form of
Na^+ and Li^+, the equilibrium constant K_T can be then
expressed as:

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

where [Na^+] and [Li^+] are the concentrations of the dissolved
Sodium and Lithium ions and Na and Li are the concentrations
total dissolved Sodium and Lithium.

For this reaction, the integration of the van’t Hoff equation:

\[ \log K_T/T = \Delta H^o/RT^2 \]

allows to express the equilibrium constant K_T as a function of temperature following the relationship:

\[ \log K_T = \log K_{298} - \Delta H^o/2.303 \times R \times (1/T - 1/298.15) \]

where K_{298} is the equilibrium constant at 298.15°C (25°C),
\(\Delta H^o\) (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 (≈ 8.314 J.K\(^{-1}\).mol\(^{-1}\)). Temperature
T is given in °K.

We can then write:

\[ \log (Na/Li) = \log K_{298} + \Delta H^o/5709 - \Delta H^o/19.1478 x T \]

If we compare the Na/Li thermometric relationship obtained
in paragraph 4.3 with this last equation, we can estimate the
values of the corresponding reaction enthalpy and
equilibrium constant at 298 K (25°C) as follows:

\[ \Delta H^o/19.1478 = -2002 \text{ (slope of the straight line in Figure 4)} \]

and:

\[ \log K_{298} + \Delta H^o/5709 = 1.322 \text{ (constant of the straight line in Figure 4)} \]

This implies that \(\Delta H^o = -38334 \text{ J.mol}^{-1} = -38.3 \text{ KJ.mol}^{-1}\) and
log K_{298} = 5.393.

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

\[ \Delta G^o = -\log K_{298} \times R \times 298.15 \times 2.303 = -30788 \text{ J.mol}^{-1} \]

\(= -30.8 \text{ KJ.mol}^{-1}\)

Let us consider the equilibrium reaction between the two
hydrated Na- and Li-Micas (reaction 1):

\[ \text{NaAlSi}_3\text{O}_8(\text{OH})_2 + \text{Li}^+ = \text{LiAlSi}_3\text{O}_8(\text{OH})_2 + \text{Na}^+ \]

The corresponding \(\Delta G^o\) can be calculated using the
following fundamental thermodynamic relationship:

\[ \Delta G^o = \Sigma \eta_i \Delta G^o_{i} (\text{right compounds}) - \Sigma \eta_i \Delta G^o_{i} (\text{left compounds}) \]

where \(\eta_i\) is the reaction coefficient of each compound and
\(\Delta G^o_{i}\) 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.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical formula</th>
<th>$\Delta G^\circ_f$ (kJ/mol)</th>
<th>Authors</th>
<th>EQ3/6 data base</th>
<th>$\Delta G^\circ_f$ selected (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water</strong></td>
<td>$H_2O$</td>
<td>-237.17</td>
<td>Johnson et al. (1992)</td>
<td>X</td>
<td>-237.17</td>
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<tr>
<td><strong>Aqueous Lithium ion</strong></td>
<td>$Li^+$</td>
<td>-293.30</td>
<td>Robie et al. (1978), Tardy and Duplay (1992)</td>
<td></td>
<td>-293.30</td>
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<td><strong>Aqueous Sodium ion</strong></td>
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<td>X</td>
<td>-261.88</td>
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<td>Albite</td>
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<td>Helgeson et al. (1978) and Johnson et al. (1992)</td>
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<td>Berman (1988)</td>
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<td><strong>Paragonite (Na-Mica)</strong></td>
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<td>estimated by Tardy and Duplay (1992)</td>
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<td><strong>Quartz</strong></td>
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<td>Helgeson et al. (1978) and Johnson et al. (1992)</td>
<td>X</td>
<td>-856.24</td>
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</table>

Table 3. Values of the standard molar Gibbs free energies of formation $\Delta G^\circ_f$ found in the literature and selected for the compounds used in this study (last column).
Most of these values 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 molar thermodynamic properties of minerals, gases, aqueous species and reactions. However, for Micas, in the absence of data for Li-Mica, all the values (Table 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 $\Delta G_f$ value is identical to that proposed in the EQ3/6 data base. For Paragonite (Na-Mica), this value is more negative but close to that given by Berman (1988) or proposed by Sverjensky et al. (1991).

As indicated in this table, 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. However, as the minerals formed at high temperature are rather well crystallized and then, more stable (contrary to those precipitated at low temperature), the accuracy on these values is better at high temperature, which are closer to the selected values. The influence of the mineral crystallinity state, purity or grain size on these values, important at low temperature, is much lesser at high temperature.

A value of 0.5 KJ.mol$^{-1}$ is found for the $\Delta G_f$ relative to the equilibrium reaction between the two Na- and Li-Micas. This value suggests that the Na/Li ratios are not controlled by this type of reaction because it is very different from that estimated at -30.8 KJ.mol$^{-1}$, using the Na/Li thermometric relationship obtained in paragraph 4.3.

On the other hand, if we consider the following equilibrium reaction (reaction 2):

\[
2 \text{NaAlSi}_3\text{O}_8\text{(Albite)} + \text{KAl}_2\text{Si}_3\text{O}_10\text{(OH)}_2\text{(Muscovite)} + \text{Al}_2\text{Si}_3\text{O}_10\text{(OH)}_4\text{(Kaolinite)} + \text{Li}^+
\]

\[
= \text{KAlSi}_3\text{O}_8\text{(K-Feldspar)} + \text{NaAlSi}_3\text{O}_10\text{(OH)}_2\text{(Na-Mica)} + \text{LiAl}_2\text{Si}_3\text{O}_10\text{(OH)}_2\text{(Li-Mica)} + 2 \text{SiO}_2\text{(Quartz)} + \text{H}_2\text{O} + \text{Na}^+
\]

we find a corresponding $\Delta G_f$ of about -30.4 KJ.mol$^{-1}$ from the $\Delta G_f$ values selected for each compound of this reaction (Table 3). This value can be considered to be very close to that estimated at -30.8 KJ.mol$^{-1}$, especially if we take into account the inaccuracy of the $\Delta G_f$ values for minerals such as clay minerals (Table 3).

These similar values for $\Delta G_f$ suggest that the Na/Li ratios of the relationship obtained in paragraph 4.3 are most probably controlled by this type of equilibrium reaction, where the formulae of the clay minerals (Na-, 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 illicic and Mica minerals, at high temperature. This equilibrium reaction is also in good agreement with the linear correlation found between the Na/Li and NaK ratios in Figure 3 and the control of the Na/K ratios by Albite and K-Feldspar.

If we consider the Na/Li relationship obtained by Fouillac and Michard (1981) for the dilute geothermal waters in volcanic and granite environments (Chloride concentrations < 0.3 M), we can estimate the values of $\Delta H_f$ and log $K_{298}$ as previously:

\[
\Delta H_f/19.1478 = -1000 \text{ (slope of the straight line in Figure 4)}
\]

and:

\[
\log K_{298} + \Delta H_f/5709 = -0.38 \text{ (constant of the straight line in Figure 4)}
\]

This implies that $\Delta H_f = -19148 \text{ J.mol}^{-1} = -19.2 \text{ KJ.mol}^{-1}$ and $\log K_{298} = 2.974$. We can also determine the value for the corresponding $\Delta G_f$ following the thermodynamic relation:

\[
\Delta G_f = -\log K_{298} \times R \times 298.15 \times 2.303 = -16978 \text{ J.mol}^{-1} = -17.0 \text{ KJ.mol}^{-1}
\]

These values are very different from those found for the HT dilute geothermal waters from Iceland in this study.

The equilibrium reaction which could control the Na/Li ratios and is in better agreement with the $\Delta G_f$ value is the following one (reaction 3):

\[
\text{NaAlSi}_3\text{O}_8\text{(Albite)} + \text{Al}_2\text{Si}_3\text{O}_10\text{(OH)}_2\text{(Kaolinite)} + \text{Li}^+
\]

\[
= \text{LiAl}_2\text{Si}_3\text{O}_10\text{(OH)}_2\text{(Li-Mica)} + 2 \text{SiO}_2\text{(Quartz)} + \text{H}_2\text{O} + \text{Na}^+
\]

Indeed, a $\Delta G_f$ value of about -17.6 KJ.mol$^{-1}$ is found, using the $\Delta G_f$ values determined for each compound of this reaction (Table 3). This value is very close to that estimated using the Na/Li relationship obtained from Fouillac and Michard (1981). This result suggests that for this last relationship, fewer clay minerals are involved in equilibrium reactions (Muscovite and Na-Mica are absent) than for the Na/Li relationship found for the HT Icelandic dilute geothermal waters in this study and that the control of the potassium by K-Feldspar is not necessary. The Li concentrations are controlled by a less abundant illicic and Mica alteration.

The $\Delta H_f$ value relative to a reaction can be calculated using the values of standard molar enthalpy of formation ($\Delta H_f$) for each compound following the fundamental thermodynamic relationship:

\[
\Delta H_f = \Sigma n_i \Delta H_f^{\text{left compounds}} - \Sigma n_i \Delta H_f^{\text{right compounds}}
\]

where $n_i$ is the reaction coefficient of each compound.

Normally, the $\Delta H_f$ values for the reactions 2 and 3 cannot be calculated using this relationship because of the absence of data available for Li-Mica in the literature (Table 4). However, a value of -5992.00 KJ.mol$^{-1}$ used for this mineral and the values selected by Vieillard (1994) for K- and Na-Micas (Muscovite and Paragonite; Table 4) allows finding $\Delta H_f$ values of -37.0 and -19.8 KJ.mol$^{-1}$ for the reactions 2 and 3, respectively. If we consider the inaccuracy of the $\Delta H_f$ values (Table 4), these values are very close to those estimated using the Na/Li relationships obtained in paragraph 4.3 and proposed by Fouillac and Michard (1981): -38.3 and -19.2 KJ.mol$^{-1}$, respectively.

These results are in good agreement with those obtained from the $\Delta G_f$ values and strengthen the conclusions drawn up from these last. As for the $\Delta G_f$, the $\Delta H_f$ values were selected from the thermodynamic data base [data0.com].R2 of the EQ3/6 code (Wolery, 1995), except for Micas (Table 4). Note that for Muscovite, the selected $\Delta H_f$ value is very close to that proposed in the EQ3/6 data base. According to Roux and Hovis (1996), there would be no directly measured values in the literature for the enthalpy of formation of Paragonite. We have selected the value proposed by Robie and Hemingway (1984) and Vieillard (1994) for ordered Paragonite (Table 4), which is close to that given by Berman (1988).
Table 4. Values of the standard molar enthalpies of formation $\Delta H^\circ_f$ found in the literature and selected for the compounds used in this study (last column).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical formula</th>
<th>$\Delta H^\circ_f$ KJ.mol$^{-1}$</th>
<th>Authors</th>
<th>EQ3/6 data base</th>
<th>$\Delta H^\circ_f$ selected KJ.mol$^{-1}$</th>
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<td>Water</td>
<td>H$_2$O</td>
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<td>Kaolinite</td>
<td>Al$_2$Si$_2$O$_5$(OH)$_4$</td>
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<td>-5911.60</td>
<td>Kripka et al. (1979), value also selected by Vieillard (1994)</td>
<td>X</td>
<td>-5971.60</td>
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<td></td>
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<td>-5977.77</td>
<td>Roux and Hovis (1996)</td>
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<td></td>
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<td>-5976.74</td>
<td>Robie et al. (1978), Berman (1988)</td>
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<td>-5972.28</td>
<td>Helgeson et al. (1978) and Johnson et al. (1992)</td>
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<td>-5970.45</td>
<td>Haselton et al. (1995)</td>
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<td>Sverjensky et al. (1991)</td>
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<td>-5967.50</td>
<td>Michard (1983)</td>
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<td>Paragonite (Na-Mica)</td>
<td>NaAl$_2$Si$_2$O$_5$(OH)$_2$</td>
<td>-5949.01</td>
<td>Robie and Hemingway (1984) for ordered Paragonite, value also selected by Vieillard (1994)</td>
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<td>-5949.01</td>
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<td>-5937.52</td>
<td>Roux and Hovis (1996)</td>
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<td>-5933.07</td>
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<td>Quartz</td>
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<td>Robie et al. (1978)</td>
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<td>Michard (1983)</td>
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CONCLUSION

In the framework of this study, a specific Na/Li thermometric relationship was statistically obtained for HT dilute waters collected from wells located in the Krafla geothermal area. This relationship, which can be applied at temperature values ranging from 200 to 325°C, can be described as:

$$\log (\text{Na/Li}) = 1967/T(°\text{K}) - 1.267 \quad (r^2 = 0.958)$$

It was successfully used on a water sample collected from a new well drilled in this geothermal area and is also in good agreement with the data collected for the HT dilute waters discharged from other geothermal areas such as Namafjall, Nesjavellir and Hveragerdi. When these data are incorporated in the statistical determination of the thermometric Na/Li relationship, the more general equation is:

$$\log (\text{Na/Li}) = 2002/T(°\text{K}) - 1.322 \quad (r^2 = 0.967)$$

These thermometric relationships are very different from that previously proposed for the world dilute geothermal waters but, surprisingly, are closer to that determined for the geothermal saline waters in volcanic and granite environments.

They are also very different from that determined for the HT marine origin geothermal waters which interact with basalts such as the waters discharged from the Reykjanes and Svartsengi areas.

Additional chemical analyses must be performed on dilute waters discharged from geothermal wells in Iceland at temperatures lower than 200°C and higher than 325°C in order to test and validate, or re-calibrate the Na/Li thermometric relationships at these temperatures.

Even if the running of Na/Li is still poorly understood, 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, or the nature of the geothermal reservoir rocks in contact with the deep hot fluids.

Thermodynamic calculations and some case studies found in the literature suggest that the Na/Li and Na/K ratios for the HT dilute geothermal waters from Iceland could be controlled by a full equilibrium reaction between, at least, Albite, K-Feldspar, Quartz, Kaolinite and clay alteration products such as Illite, Na- and Li-Micas.

An equilibrium reaction involving fewer minerals than for the Icelandic HT geothermal waters (only Albite, Quartz, Kaolinite and Li-Mica) could thermodynamically explain the thermometric Na/Li relationship found by Fouillac and Michard (1981) for other dilute geothermal waters.

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

REFERENCES


