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Use of a New Sodium/Lithium (Na/Li) Geothermometric Relationship for High-Temperature Dilute Geothermal Fluids from Iceland

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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 Instruments 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 Hveragerdi). 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 reservoir conditions (T > 375°C), 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 $\delta^{18}O(H_2O\text{-}SO_4)$ 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 three thermometric Na/Li relationships has been tested for very high temperatures (> 350°C).

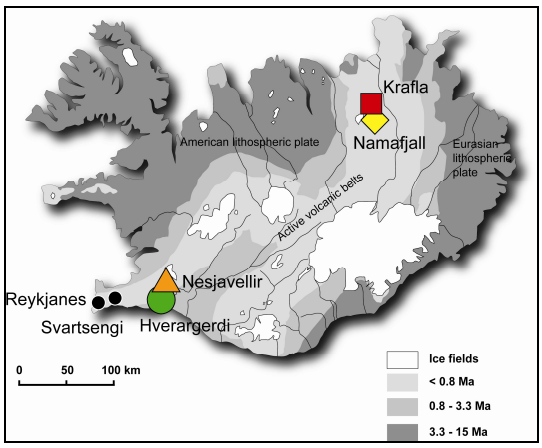

Figure 1: Location of the geothermal fields selected for this study on the Iceland map

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 Hveragerdi, 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 δ^2H and $\delta^{18}O$ isotopic data (Darling and Armannssonn, 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 SO_4, 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 (Einarsson, 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 km^2 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 aquifer rock at Namafjall is the same as at Krafla except that silicic rocks are absent. Intrusive formations dominate below about 1500 m depth.

The depth of the 12 drilled wells varies between 350 and 2100 m (Gudmundsson and Arnorsson, 2002). In the wells drilled prior to the 1975-1984 volcanic episode (n° 1 to 9), the temperatures follow the boiling point curve with depth. In the wells drilled after this episode and in another part of the field, the temperatures at the top of the reservoir are sub-boiling (Giroud, 2008). These low temperatures are considered to be the consequence of cold shallow groundwater incursion along fractures that were activated during the volcanic episode. Maximum recorded temperature in the wells is 320°C (Gudmundsson and Arnorsson, 2002). As at Krafla, the chemical geothermometers indicate that the aquifers producing into wells have considerably lower temperatures than this maximum (Gudmundsson and Arnorsson, 2002).

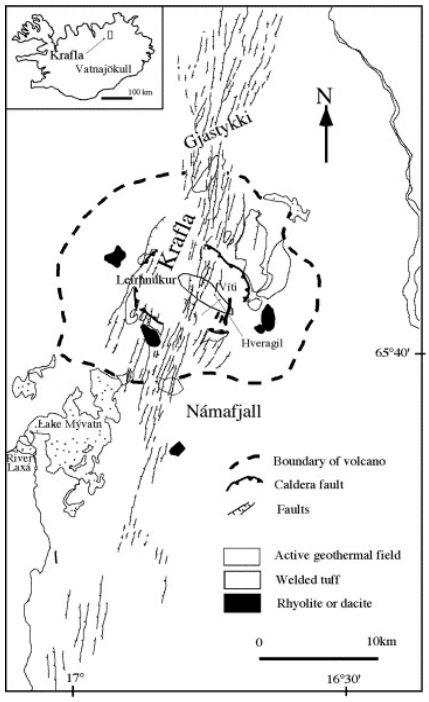

Figure 2: The Krafla and Namafjall geothermal areas and associated central volcano and fissure swarm. From Arnorsson (1995) and Armannsson *et al.* (1987)

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 (Franzson, 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 well-head using a stainless steel (N316) Webre separator to separate water (Arnorsson *et al.*, 2006). The samples were conditioned on site according to the required specifications for analyses. Water samples were filtered though 0.45 µm cellulose acetate membranes, acidified using Suprapur HNO_3 and stored in 100 ml polyethylene bottles in order to analyze the major cations (Na, K, Ca, Mg) and dissolved Li. For the analyses of major anions (Cl, SO_4, HCO_3, NO_3), water samples were filtered though 0.45 µm cellulose acetate membrane and stored in 250 ml polyethylene bottles. Alkalinity was measured on site by HCl titration on a small part of these filtered samples. Untreated water was collected and stored in 1 l polyethylene bottles for isotopic $\delta^{18}O$ analyses in water and in dissolved sulfates. Other water samples were collected for additional analyses such as chemical trace and infra-trace species, isotopic $\delta^{2}H$, $\delta^{34}S$, $\delta^{13}C$, $\delta^{11}B$ and $\delta^{7}Li$ values, $^{87}Sr/^{86}Sr$ 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_{nc}) 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, SiO_2, Li) were performed using standard water analytical techniques such as Ion Chromatography, Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Flame Emission Spectrometry, TIC analysis, Colorimetry. Dissolved Lithium was analyzed using Flame Emission Spectrophotometry or/and ICP-MS. Dissolved Silica was determined using Colorimetry and/or ICP-AES. The precision of the major species and Lithium is better than ± 5 and 10%, respectively. The isotopic analyses were done using Mass Spectrometry. The precision of $\delta^{18}O$ values 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 $\delta^{18}O(H_2O\text{-}SO_4)$ geothermometer (Mizutani and Rafter, 1969) are rarely in good agreement with the other estimations (Table 2).

On the other hand, this selection of temperatures is supported by the relatively good linear correlations obtained between the Na/K and Na/Li ratios determined for the geothermal waters collected from the Krafla area and from the other areas, except Hveragerdi (Fig. 3).

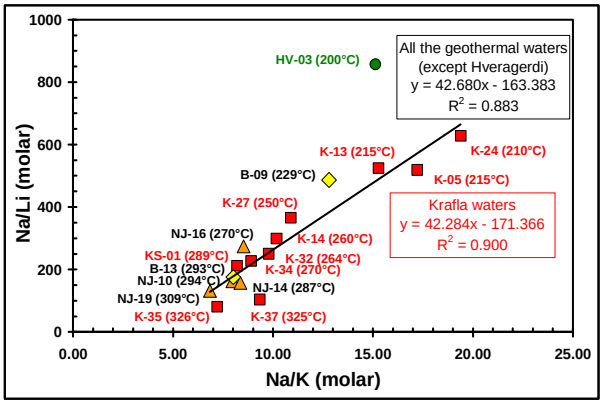

Figure 3: Na/Li and Na/K ratios determined for waters collected from wells located in the Krafla, Namafjall, Nesjavellir and Hveragerdi studied geothermal areas

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.

Geothermal field	Well	Fluid sampling date	T°C Bottom hole	Cond. 25°C mS/cm	TDS g/l	pH	Eh_{nc} mV	$\delta^{18}O_{(H2O)}$ ‰	$\delta^{18}O_{(SO4)}$ ‰
Krafla	**K-32**	10/10/2007	315	1.561	2.0	8.61	-341	-10.4	
	K-34 (1999)	10/10/2007	308	0.974	1.2	7.49	-282	-8.8	
	K-35 (2006)	10/10/2007	326	1.057	1.8	7.43	-242	-9.7	
	K-13 (1980)	11/10/2007	327	1.335	1.4	8.70	-311	-9.8	
	K-14	11/10/2007	324	0.150	0.2	4.97	-183	-11.0	
	KS-01	13/06/2008	300	0.930	0.7	9.36	-305	-6.3	
	K-05	13/06/2008	300	0.820	0.7	9.21	-239		
	K-24	13/06/2008	225	0.950	1.1	9.50	-290	-10.9	-4.2
	K-27	13/06/2008	300	1.087	0.8	8.72	-284	-10.5	-6.2
	K-37	12/06/2008	325		0.5			-7.3	-5.9
	K-39	01/2009	> 350		0.6	8.43		-10.4	
Namafjall	**B-09 (Sept. 1970)**	11/10/2007	262	0.666	1.0	7.25	-318	-12.0	
	B-13	11/10/2007	334	0.613	1.3	8.51	-300	-8.9	
Nesjavellir	**NJ-10**	11/06/2008	290	0.872	0.7	9.03	-31	-5.7	3.6
	NJ-14	11/06/2008	278	0.965	0.6	8.79	-341	-5.8	
	NJ-16	11/06/2008	306	0.860	0.6	8.42	-103	-5.4	-0.1
	NJ-19	11/06/2008	289	0.783	0.5	8.11	-44	-3.9	
Hveragerdi	**HV-03**	12/10/2007	182 ?	7.80	1.0	8.71	-324	-8.1	

Geothermal field	Well	Fluid sampling date	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Cl mg/l	Alk. meq/l	TIC mg/l	SO_4 mg/l	NO_3 mg/l	SiO_2 (col.) mg/l	SiO_2 (ICP) mg/l	Li µg/l	Na/K molar	Na/Li molar
Krafla	**K-32**	10/10/2007	287	49.9	2.6	< 0.05	49.6	5.59	18.2	407	< 0.25	844	864	346	9.78	250
	K-34 (1999)	10/10/2007	164	31.3	1.17	< 0.05	138	2.95	23.3	47.8	< 0.25	641	611	218	8.91	227
	K-35 (2006)	10/10/2007	168	39.6	1.44	< 0.05	258	0.83	4.43	16.1	< 0.25	1272	1288	628	7.22	81
	K-13 (1980)	11/10/2007	238	26.5	3.5	< 0.05	35.8	3.91	18.8	344	< 0.25	525	500	137	15.28	524
	K-14	11/10/2007	22.8	3.81	0.06	< 0.05	4.10	0.94	10.3	< 20	< 0.25	127	124	23	10.18	299
	KS-01	13/06/2008	175	36.4	0.34	< 0.25	76.1	6.55		40.6	< 0.25		1001	250	8.20	212
	K-05	13/06/2008	180	17.8	8.83	< 0.25	45.0	2.62		248	< 0.25		361	105	17.22	519
	K-24	13/06/2008	193	17.0	3.46	< 0.25	47.8	8.98		254	< 0.25		383	93	19.39	628
	K-27	13/06/2008	206	32.1	3.13	< 0.25	39.2	3.88		296	< 0.25		538	170	10.90	365
	K-37	12/06/2008	268	48.8	1.46	< 0.25	64.7			130	< 0.25		1333	780	9.34	104
	K-39	01/2009	178	47.5	3.20	< 0.25	182	2.38		43.8	< 0.25		728	194	6.37	277
Namafjall	**B-09 (Sept. 1970)**	11/10/2007	137	18.2	2.42	< 0.05	32.7	4.28	13.5	64.1	< 0.25	504	475	85	12.80	486
	B-13	11/10/2007	98.5	20.9	0.19	< 0.05	55.1	3.21	4.97	42.2	< 0.25	897	825	169	8.02	176
Nesjavellir	**NJ-10**	11/06/2008	157	33.4	< 0.5	< 0.25	129	4.22		81.6	< 0.25		752	291	7.97	162
	NJ-14	11/06/2008	161	32.8	< 0.5	< 0.25	193	2.60		44.0	< 0.25		718	310	8.36	157
	NJ-16	11/06/2008	145	29.0	< 0.5	11.7	69.7	4.85		90.5	< 0.25		697	160	8.52	274
	NJ-19	11/06/2008	126	31.4	< 0.5	< 0.25	162	2.10		35.9	< 0.25		797	290	6.84	131
Hveragerdi	**HV-03**	12/10/2007	193	21.7	2.23	< 0.05	181	1.95	11.3	67.8	< 0.25	454	424	68	15.13	857

Table 2. Down-hole measured temperatures and temperatures estimated using the chemical and isotopic geothermometers Na/K, Na/K/Ca, Silica-quartz and $\delta^{18}O(H_2O\text{-}SO_4)$.

Geothermal field	Well	Fluid sampling date	$T_{bottom\text{-}hole}$ °C	$T_{Na/KM}$ °C	$T_{Na/KF}$ °C	$T_{Na/K/Ca}$ °C	T_{Qz} °C	$T_{Qz\ vapor}$ °C	$T_{\delta^{18}O(H2O\text{-}SO4)}$ °C	$T_{sel.}$ °C	$1000/T_{sel.}$	log(Na/Li) molar
Krafla	**K-32**	10/10/2007	315	264	268	247	305	266		264	1.86	2.40
	K-34 (1999)	10/10/2007	308	277	278	250	276	244		270	1.84	2.36
	K-35 (2006)	10/10/2007	326	310	303	263	355	302		326	1.67	1.91
	K-13 (1980)	11/10/2007	327	209	226	210	253	226		215	2.05	2.72
	K-14	11/10/2007	324	259	265	229	151	144		260	1.88	2.48
	KS-01	13/06/2008	300	289	288	273	325	281		289	1.78	2.33
	K-05	13/06/2008	300	195	215	188	224	204		215	2.05	2.71
	K-24	13/06/2008	225	184	206	192	229	208	243	210	2.07	2.80
	K-27	13/06/2008	300	249	258	230	259	231	312	250	1.91	2.56
	K-37	12/06/2008	325	270	273	256	361	307	450	325	1.67	2.02
	K-39	01/2009	> 350	330	317	264	290	254				2.44
Namafjall	**B-09 (Sept. 1970)**	11/10/2007	262	229	242	213	248	222		229	1.99	2.69
	B-13	11/10/2007	334	293	290	267	303	264		293	1.77	2.25
Nesjavellir	**NJ-10**	11/06/2008	290	294	291	267	293	257	190	294	1.76	2.21
	NJ-14	11/06/2008	278	287	286	265	288	253		287	1.79	2.20
	NJ-16	11/06/2008	306	284	284	260	285	251	280	270	1.84	2.44
	NJ-19	11/06/2008	289	319	309	274	299	261		309	1.72	2.12
Hveragerdi	**HV-03**	12/10/2007	182 ?	210	226	211	238	215		200	2.11	2.93

$T_{Na/KM}$: Na/K geothermometer (Michard, 1979)

$T_{Na/KF}$: Na/K geothermometer (Fournier, 1979)

$T_{Qz\ vapor}$: Silica-quartz geothermometer taking into account the water vaporisation before water sampling (Fournier and Rowe, 1966)

All these results are in good agreement with the conclusions drawn by Arnorsson *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:

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

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.

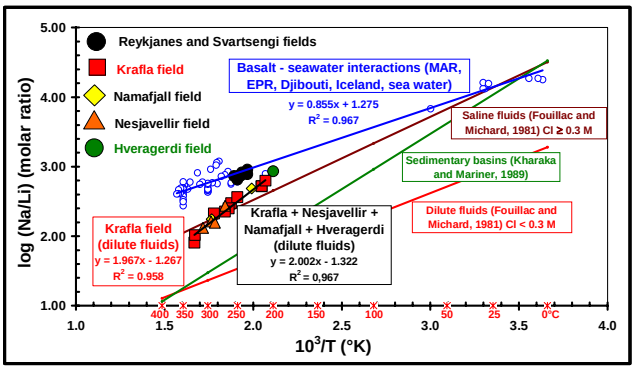

Figure 4: Sodium/Lithium thermometric relationships existing in the literature and new Na/Li relationships determined for Icelandic HT geothermal waters, during this study

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)

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

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):

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

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:

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

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:

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

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 came 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):

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

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 Arnorsson, 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 edge 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 rhyolites and associated thermal waters collected from the Valles caldera, New Mexico, and the Inyo domes chain, in the Long Valley caldera, California (USA). The thermal waters acquire both B and Li, but proportionately much more B (B/Li ratio is essentially constant at 4.0) because Li is trapped in altered products.

Generally, for clay minerals as for hydrates in pure water, hydrated phases are more stable than the corresponding dehydrated phases. This is true for all the minerals of Mica and Celadonite types saturated by Li^+, Na^+, Mg^{2+} and Ca^{2+} (Tardy and Duplay, 1992). These minerals exhibit negative hydration energy so that they spontaneously hydrate in water. However, the contrary is observed for tetrahedrally charged K^+-Micas such as Muscovite, Ferri-Muscovite and Annite and these minerals do not spontaneously hydrate in water. The corresponding dehydrated phases are then more stable than the hydrated phases (Tardy and Duplay, 1992). A consequence of these results is when dehydration takes place by increase of temperature, potassium in competition with other ions is selected and clay minerals tend to form Illites (Tardy and Duplay, 1992). These minerals with relatively complex formulae were represented under the simplified form of $K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$ in the thermodynamic data base data0.com.R2 of the EQ3NR code (Wolery, 1995). As Muscovite ($KAl_3Si_4O_{10}(OH)_2$) 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_2O-Al_2O_3-SiO_2-H_2O (Manning, 2003; Sanjuan *et al.*, 2003).

Let us consider the following chemical reaction of mineral dissolution-precipitation:

$$\text{Na-mineral} + Li^+ = \text{Li-mineral} + Na^+$$

The equilibrium constant for this reaction at temperature T (K_T) is given by:

$$K_T = (Na^+)/(Li^+)$$

where (Na^+) and (Li^+) are the activities 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:

$$K_T \approx [Na^+]/[Li^+] \approx Na/Li$$

where $[Na^+]$ and $[Li^+]$ 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 to express 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:

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

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:

$\Delta H°_R/19.1478 \approx -2002$ (slope of the straight line in Figure 4) and:

$\log K_{298} + \Delta H°_R/5709 \approx -1.322$ (constant of the straight line in Figure 4)

This implies that $\Delta H°_R \approx -38334\ J.mol^{-1} \approx -38.3\ KJ.mol^{-1}$ and $\log K_{298} \approx 5.393$.

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:

$$\Delta G°_R = -\log K_{298} \times R \times 298.15 \times 2.303 \approx -30788\ J.mol^{-1} \approx -30.8\ KJ.mol^{-1}$$

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

$$NaAl_3Si_3O_{10}(OH)_2 + Li^+ = LiAl_3Si_3O_{10}(OH)_2 + Na^+$$

The corresponding $\Delta G°_R$ can be calculated using the following fundamental thermodynamic relationship:

$$\Delta G°_R = \Sigma\, n_i\, \Delta G°_{f\,(\text{right compounds})} - \Sigma\, n_i\, \Delta G°_{f\,(\text{left compounds})}$$
$$= \Delta G°_{f\,(\text{Li-Mica})} + \Delta G°_{f\,(Na^+)} - \Delta G°_{f\,(\text{Na-Mica})} - \Delta G°_{f\,(Li^+)}$$

where n_i is the reaction coefficient of each compound and $\Delta G°_f$ 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 3. Values of the standard molar Gibbs free energies of formation $\Delta G°_f$ found in the literature and selected for the compounds used in this study (last column).

Compound	Chemical formula	$\Delta G°f$ $KJ.mol^{-1}$	Authors	EQ3/6 data base	$\Delta G°f_{selected}$ $KJ.mol^{-1}$
Water	H_2O	-237.17	Johnson *et al.* (1992)	X	-237.17
		-237.10	Robie *et al.* (1978), Tardy and Duplay (1992)		
Aqueous Lithium ion	Li^+	-293.30	Robie *et al.* (1978), Tardy and Duplay (1992)		-293.30
		-292.60	Shock and Helgeson (1988) and Johnson *et al.* (1992)	X	
Aqueous Sodium ion	Na^+	-261.88	Wagman et al. (1976), Robie *et al.* (1978), Michard (1983), Shock and Helgeson (1988) and Johnson *et al.* (1992), Tardy and Duplay (1992)	X	-261.88
Albite	$NaAlSi_3O_8$	-3708.31	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	X	-3708.31
		-3713.47	Arnorsson and Stefasson (1999)		
		-3711.72	Robie *et al.* (1978), Berman (1988)		
		-3711.60	Robie and Hemingway (1995)		
		-3710.10	adjusted from Berman (1988) by Sverjensky *et al.* (1991)		
		-3706.69	Gottschalk (1997)		
		-3698.28	Naumov *et al.* (1971)		
K-Feldspar	$KAlSi_3O_8$	-3746.24	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	X	-3746.24
		-3752.11	adjusted from Berman (1988) by Sverjensky *et al.* (1991)		
		-3749.55	Arnorsson and Stefasson (1999)		
		-3749.30	Robie and Hemingway (1995)		
		-3747.23	adjusted from Helgeson *et al.* (1978) by Sverjensky *et al.* (1991)		
		-3745.42	Berman (1988)		
		-3744.41	Gottschalk (1997)		
		-3743.31	Michard (1983)		
		-3742.38	Robie *et al.* (1978)		
Illite	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	-5455.81	Wolery (1978)	X	-5455.81
Kaolinite	$Al_2Si_2O_5(OH)_4$	-3789.09	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	X	-3789.09
		-3807.44	Zen (1972), Tardy and Garrels (1974)		
		-3799.36	Robie *et al.* (1978)		
		-3789.87	Michard (1983)		
		-3780.24	Kittrick (1971)		
		-3778.15	Naumov *et al.* (1971)		
		-3771.46	Karpov and Kashik (1968)		
Li-Mica	$LiAl_3Si_3O_{10}(OH)_2$	-5596.80	estimated by Tardy and Duplay (1992)		-5596.80
Muscovite (K-Mica)	$KAl_3Si_3O_{10}(OH)_2$	-5591.10	estimated by Tardy and Duplay (1992)		-5591.10
		-5606.56	Zen (1972)		
		-5603.42	adjusted from Berman (1988) by Sverjensky *et al.* (1991)		
		-5600.67	Robie *et al.* (1978)		
		-5596.73	Berman (1988)		
		-5591.08	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	X	-5591.08
		-5588.43	adjusted from Helgeson *et al.* (1978) by Sverjensky *et al.* (1991)		
		-5586.31	Michard (1983)		
		-5554.26	Karpov and Kashik (1968)		
		-5552.17	Reesman and Keller (1968)		
Paragonite (Na-Mica)	$NaAl_3Si_3O_{10}(OH)_2$	-5565.90	estimated by Tardy and Duplay (1992)		-5565.90
		-5570.38	adjusted from Berman (1988) by Sverjensky *et al.* (1991)		
		-5563.69	Berman (1988)		
		-5558.86	Thompson (1974)		
		-5556.35	Zen (1972), Tardy and Garrels (1974)		
		-5548.03	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	X	
		-5547.98	Karpov and Kashik (1968)		
		-5514.51	Zen (1972)		
Quartz	SiO_2	-856.24	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	X	-856.24
		-856.51	Naumov *et al.* (1971)		
		-856.34	Michard (1983)		
		-856.29	Robie *et al.* (1978)		

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 molal 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 alumino-silicate 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 cristallinity 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 $\Delta G°_R$ 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)*:

$2\ NaAlSi_3O_8$ (Albite) + $KAl_3Si_3O_{10}(OH)_2$ (Muscovite) + $Al_2Si_2O_5(OH)_4$ (Kaolinite) + Li^+

= $KAlSi_3O_8$ (K-Feldspar) + $NaAl_3Si_3O_{10}(OH)_2$ (Na-Mica) + $LiAl_3Si_3O_{10}(OH)_2$ (Li-Mica) + 2 SiO_2 (Quartz) + H_2O + Na^+,

we find a corresponding $\Delta G°_R$ 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 $\Delta G°_R$ 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 illitic and Mica minerals, at high temperature. This equilibrium reaction is also in good agreement with the linear correlation found between the Na/Li and Na/K 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 $\Delta H°_R$ and log K_{298}, as previously:

$\Delta H°_R/19.1478 \approx -1000$ (slope of the straight line in Figure 4) and:

$\log K_{298} + \Delta H°_R/5709 \approx -0.38$ (constant of the straight line in Figure 4)

This implies that $\Delta H°_R \approx -19148\ J.mol^{-1} \approx -19.2\ KJ.mol^{-1}$ and $\log K_{298} \approx 2.974$. We can also determine the value for the corresponding $\Delta G°_R$ following the thermodynamic relation:

$$\Delta G°_R = -\log K_{298} \times R \times 298.15 \times 2.303 \approx -16978\ J.mol^{-1} \approx -17.0\ KJ.mol^{-1}$$

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 $\Delta G°_R$ value is the following one *(reaction 3)*:

$NaAlSi_3O_8$ (Albite) + $Al_2Si_2O_5(OH)_4$ (Kaolinite) + Li^+

= $LiAl_3Si_3O_{10}(OH)_2$ (Li-Mica) + 2 SiO_2 (Quartz) + H_2O + Na^+

Indeed, a $\Delta G°_R$ 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 illitic and Mica alteration.

The $\Delta H°_R$ 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:

$$\Delta H°_R = \Sigma\, n_i\, \Delta H°_{f\ (right\ compounds)} - \Sigma\, n_i\, \Delta H°_{f\ (left\ compounds)}$$

where n_i is the reaction coefficient of each compound.

Normally, the $\Delta H°_R$ 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 $\Delta H°_R$ 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 $\Delta H°_f$ found in the literature and selected for the compounds used in this study (last column).

Compound	Chemical formula	$\Delta H°f$ KJ.mol^{-1}	Authors	EQ3/6 data base	$\Delta H°f_{selected}$ KJ.mol^{-1}
Water	H_2O	-285.84	Robie *et al.* (1978), Johnson *et al.* (1992)	X	-285.84
Aqueous Lithium ion	Li^+	-278.45	Shock and Helgeson (1988) and Johnson *et al.* (1992)	X	-278.45
Aqueous Sodium ion	Na^+	-240.30	Robie *et al.* (1978), Shock and Helgeson (1988) and Johnson *et al.* (1992)	X	-240.30
Albite	$NaAlSi_3O_8$	-3931.62	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	X	-3931.62
		-3936.86	Arnorsson and Stefansson (1999)		
		-3935.00	Robie and Hemingway (1995)		
		-3935.12	Robie *et al.* (1978), Berman (1988)		
		-3931.10	Michard (1983)		
		-3930.12	Gottschalk (1997)		
K-Feldspar	$KAlSi_3O_8$	-3971.40	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	X	-3971.40
		-3974.89	Arnorsson and Stefansson (1999)		
		-3974.60	Robie and Hemingway (1995)		
		-3972.38	Sverjensky *et al.* (1991)		
		-3970.79	Berman (1988)		
		-3969.59	Gottschalk (1997)		
		-3967.74	Robie *et al.* (1978)		
		-3967.31	Michard (1983)		
Illite	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	-5835.29	Wolery (1978)	X	-5835.29
Kaolinite	$Al_2Si_2O_5(OH)_4$	-4109.61	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	X	-4109.61
		-4120.11	Robie *et al.* (1978)		
		-4116.05	Michard (1983)		
		-4086.09	Naumov *et al.* (1971)		
Li-Mica	$LiAl_3Si_3O_{10}(OH)_2$	-5992.00	no data found in the literature - proposed in this study		-5992.00
Muscovite (K-Mica)	$KAl_3Si_3O_{10}(OH)_2$	-5971.60	Krupka *et al.* (1979), value also selected by Vieillard (1994)		-5971.60
		-5977.77	Roux and Hovis (1996)		
		-5976.74	Robie *et al.* (1978), Berman (1988)		
		-5972.28	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	X	
		-5970.45	Haselton *et al.* (1995)		
		-5968.12	Sverjensky et al.(1991)		
		-5967.50	Michard (1983)		
		-5958.40	calculated by Vieillard (1994)		
		-5954.87	calculated by Vieillard (1994)		
Paragonite (Na-Mica)	$NaAl_3Si_3O_{10}(OH)_2$	-5949.01	Robie and Hemingway (1984) for ordered Paragonite, value also selected by Vieillard (1994)		-5949.01
		-6012.83	calculated by Vieillard (1994) for ordered Paragonite		
		-5944.20	Berman (1988)		
		-5937.52	Roux and Hovis (1996)		
		-5933.07	Robie and Hemingway (1984) for disordered Paragonite, value also selected by Vieillard (1994)		
		-5928.57	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	X	
		-5917.93	calculated by Vieillard (1994) for disordered Paragonite		
Quartz	SiO_2	-910.65	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	X	-910.65
		-910.94	Naumov *et al.* (1971)		
		-910.70	Robie *et al.* (1978)		
		-910.67	Michard (1983)		

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:

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

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:

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

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.

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