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 $\delta^{18}O$ (H_2O-SO_4) 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).

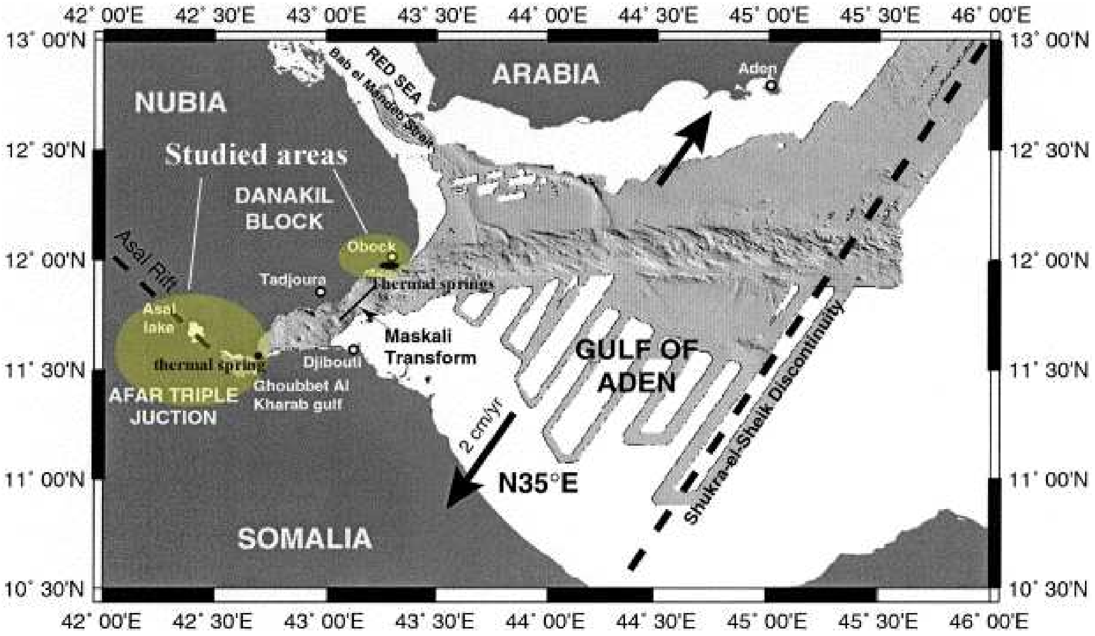

Figure 1: Location of the studied areas in the Republic of Djibouti and of the littoral thermal springs of Goubbet Channel and Obock. Black arrows show the direction of spreading between the Somalia and Arabia plates (figure extracted from Dauteuil et al., 2001)

The Asal-Ghoubbet emerged Rift occurs within the vast Danakils depression, an area still referred to as the Afar triangle (Fig. 1). In the southern part of this depression, within the frontiers of the Republic of Djibouti, this Rift forms a 12 km long axis which separates Asal Lake to the Northwest from the Gulf of Ghoubbet-Al Kharab to the Southeast. The Asal Lake is 155 m below sea level and is 9-10 km wide.

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 rhyolithes 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 Dahla 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.

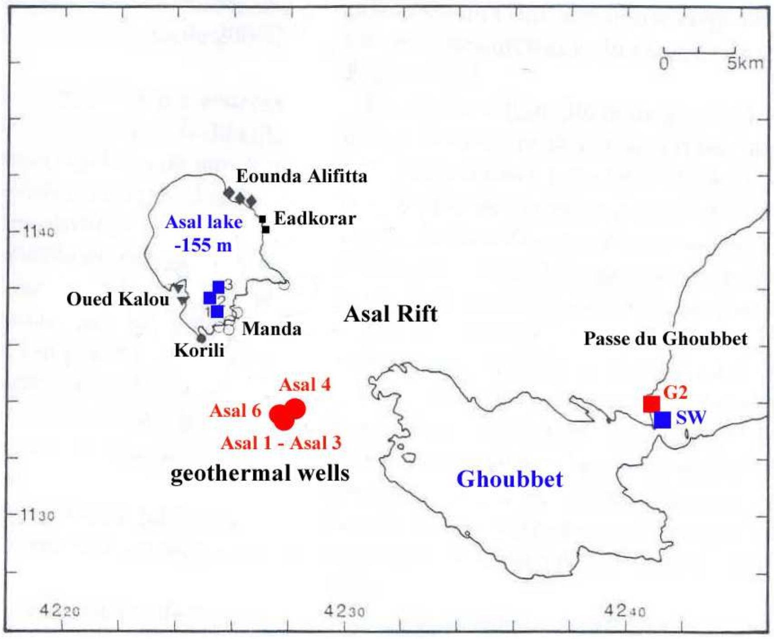

Figure 2: Location map of the geothermal wells studied in this study and of main thermal springs (Eounda Alifitta, Eadkorar, Manda, Korili, Oued Kalou, Ghoubbet Channel) in the Asal Rift and the North-Ghoubbet. Three water samples collected from Asal Lake and a sample of seawater (SW) were also integrated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

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 (Tab. 1; Sanjuan *et al.*, 1990). 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 SO_4, reacting with basalt (probably Gulf basaltic series 1 to 3 My old).

The graphical determination of the Na/Cl, Ca/Cl and SiO_2/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.

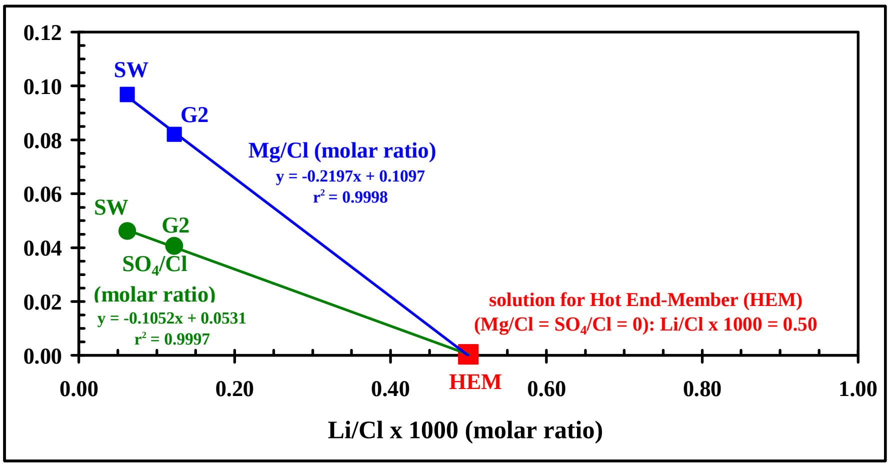

Figure 3: Determination of the Li/Cl ratio for the Hot End-Member (HEM) of the thermal spring Ghoubbet Channel (G2) using the Mg/Cl and SO4/Cl variations.

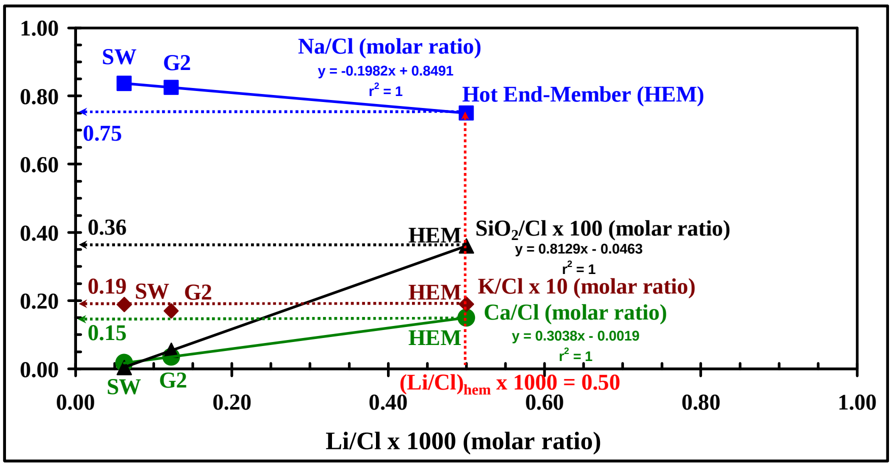

Figure 4: Determination of the Na/Cl, SiO2/Cl, Ca/Cl and K/Cl ratios for the hot end-member of the thermal spring G2 using the Li/Cl determined in figure 3.

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.).

Geothermal area	Sample	Fluid sampling	T	pH	Eh$_{nc}$	Na	K	Ca	Mg	Cl	Alk.	SO$_4$	SiO$_2$	Li	TDS	Na/K	Na/Li	$\delta^{18}O_{(SO4)}$	$\delta^{34}S_{(SO4)}$
		date	°C		mV	mg/l	mg/l	mg/l	mg/l	mg/l	meq/l	mg/l	mg/l	µg/l	g/l	molar	molar	‰	‰
Djibouti																			
Asal wells	**Asal 1**	1983	255			28507	4888	16393	24	77997	0.33	21.1	514	12976	128	10	663		
	Asal 3	9/11/1987	260	4.65		26254	4692	15431	23	72076		19.2	520	14156	119	10	560		
	Asal 3 (BH)	1/9/1988		5.22		26438	4497	14268	23	69842	0.11	44.2			115	10			
	Asal 6	10/1/1988	260	4.64		27588	4927	15511	23	74593	0.01	27.9	574	13878	123	10	600		
Asal Lake	**S1**	1987				81959	4340	2553	9795	173720				4857	272	32	5093		
	S2	1983	32	7.10		94718	4731	2469	11472	184001	2.05	4304	170	4649	302	34	6149		19.3
	S3	1983	32	7.00		101155	5161	2677	12493	198891	2.20	4400		5551	325	33	5500		18.9
Ghoubbet Channel thermal spring (Tadjourah)	**G2**	1987	60			11265	391	834	1172	20846		2296	19.2	500	36.8	49	6806		
Hot end-member	**HEMGC**	1987	160			10253	438	3571	0	21059		0	129	2061	35.5	40	1502		
Seawater	**SW-TA**	1987	30			11426	438	409	1398	21059		2632	1.20	257	37.4	44	13432		
Obock thermal springs	**O1**	1989	70	6.63		9541	579	1126	729	18081		1614	83.5	1388	31.8	28	2075	9.2	19.4
	O2	1989	63	6.70		10230	544	878	987	18896		2056	60.7	1041	33.7	32	2967	9.4	19.8
	O3	1989	74	6.52		10805	657	1050	792	19712		1777	92.5	1665	34.9	28	1958	9.2	20.2
	O4	1989	54	6.75		10230	559	902	941	19003		2037	63.1	1110	33.7	31	2781	9.1	20.2
Hot end-member	**HEMO**	1989	210			10529	1216	2409	0	20705		0	266	4025	35.1	15	790		
Seawater	**SW-OB**	1989	30	8.22		11495	442	449	1429	20705		3122	0.90	250	37.6	44	13878	9.1	19.9
Iceland																			
Svartsengi wells	**SV-07**	10/9/2007	244	6.15	-165	7043	1049	1128	0.4	13696	0.29	37.0	531	2580	23.5	11	824		
	SV-07	6/10/2008	244	6.09	-201	7483	997	1156	< 0.25	14942	0.32	32.6	465	2897	25.1	13	780	4.3	16.6
	SV-18	10/9/2007	244	7.29	-120	7498	1154	1163	0.5	14366	0.31	39.4	563	3060	24.8	11	740		
Reykjanes wells	**H2**	Bjornsson *et al.* (1972)	260			14506				19500				7440			588		
	H2	Olafsson and Riley (1978)	?	6.60		11930	1820	2239	12.7	23702		3.2	462	5950	40.2	11	605		
	H8	Olafsson and Riley (1978)	?	7.10		12730	1990	2249	9.8	25054		2.4	943	6590	43.0	11	583		
	H8	Tuesdell *et al.* (1981)	283			9629				18785			572	5100			570		
Reykjanes wells	**RN-10**	10/9/2007	319	4.95	-84	12644	1825	1886	2.1	25015	0.02	25.9	1023	5830	42.4	12	655		
	RN-21	6/10/2008		5.82	-6	12675	1748	1372	< 0.25	23795	0.19	20.9	789	5500	40.4	12	696	4.2	19.8
	RN-22	10/9/2007	305	5.17	-120	12263	1814	2087	2.4	23620	0.09	29.8	788	5068	40.6	11	730		
	RN-22	6/10/2008	305	5.17	114	13911	1763	1581	< 0.25	25293	0.11	25.3	800	5951	43.4	13	706	4.8	20.8
	RN-24	10/9/2007	286	5.66	-192	11310	1646	1889	1.0	21807	0.31	27.5	744	4700	37.4	12	726		
Seltjarnarnes wells	**SN-04**	6/5/2009	114	6.23	284	643	13	548	< 0.25	2020		340	109	63	3.7	84	3078		
	SN-05	6/5/2009	114	8.27	149	677	13	408	< 0.25	1870		259	105	61	3.3	91	3362		
Seawater (Grindavik)	**SW-GR**	6/10/2008	10			11427	374	386	1204	19108		2847	0.50	158	34.1	52	21829		

Table 2: Measured temperatures, temperatures of deep geothermal fluid estimated using chemical geothermometers and values of temperature selected for this study.

Geothermal area	Sample	T °C	$T_{Na/KM}$ °C	$T_{Na/KF}$ °C	$T_{Na/K/Ca}$ °C	$T_{K/Mg}$ °C	T_{Qz} °C	$T_{Qz\ vapor}$ °C	$T_{Chalc.}$ °C	$T_{Na/Li}$ °C	$T_{sel.}$ °C	$1000/T_{sel.}$	log(Na/Li) molar
Djibouti													
Asal wells	**Asal 1**	255	262	267	251	278	255			263	260	1.88	2.82
	Asal 3	260	268	271	253	277	256			287	260	1.88	2.75
	Asal 3 (BH)		261	266	251	274	256			286	260	1.88	
	Asal 6	260	268	271	254	280	266			277	260	1.88	2.78
Ghoubbet Channel thermal spring (Tadjourah)	**G2**	60	107	140	166	98	62			64	60	3.00	3.83
Tadjourah hot end-member	**HEMGC**	?	122	153	163		152			171	160	2.31	3.23
Obock thermal spring	**O3**	74	150	177	193	118	133			148			
Obock hot end-member	**HEMO**	?	213	229	223		201			240	210	2.07	2.90
Iceland													
Svartsengi wells	**SV-07**	244	243	253	240	310	258	230		235	243	1.94	2.92
	SV-07	244	230	242	233		246	221		242	235	1.97	2.89
	SV-18	244	248	256	243	309	264	234		248	245	1.93	2.87
Reykjanes wells	**H2**	260								279	260	1.88	2.77
	H2	?	247	255	246	241	245			275	250	1.91	2.78
	H8	?	250	258	249	252	318			281	292	1.77	2.77
	H8	283					265			284	283	1.80	2.76
Reykjanes wells	**RN-10**	319	239	250	245	292	328	283		265	283	1.80	2.82
	RN-21		234	245	246		298	261		256	261	1.87	2.84
	RN-22	305	243	252	245	288	298	260		250	260	1.88	2.86
	RN-22	305	224	237	240		300	262		255	262	1.87	2.85
	RN-24	286	241	251	243	310	292	256		251	256	1.89	2.86
Seltjarnarnes wells	**SN-04**	114	73	109	104		142	137	113	113	114	2.58	3.49
	SN-05	114	68	105	103		140	135	111	107	114	2.58	3.53

$T_{Na/KM}$: Na/K geothermometer (Michard, 1979)
$T_{Na/KF}$: Na/K geothermometer (Fournier, 1979)
$T_{Na/K/Ca}$: Na/K/Ca geothermometer (Fournier and Truesdell, 1973)
$T_{K/Mg}$: K/Mg geothermometer (Giggenbach, 1988)

$T_{Qz\ vapor}$: Silica-quartz geothermometer taking into account the water vaporisation before water sampling (Fournier and Rowe, 1966)
$T_{Chalcedony}$: Silica-Chalcedony geothermometer (Arnorsson, 1983)
$T_{Na/Li}$: 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.

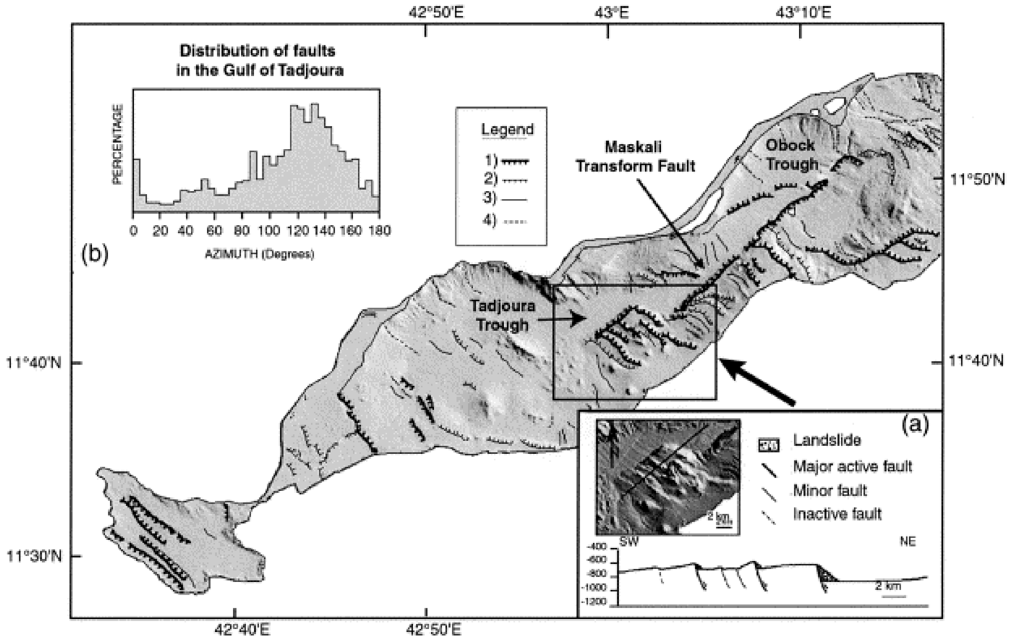

Figure 5: Fault pattern of the Gulf of Tadjourah deduced from detailed analysis of shaded relief, stereoscopic and acoustic reflectivity images. Four kinds of structures are identified (main active faults, minor active or inactive faults, inactive faults, and canyons) (figure extracted from Dauteuil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

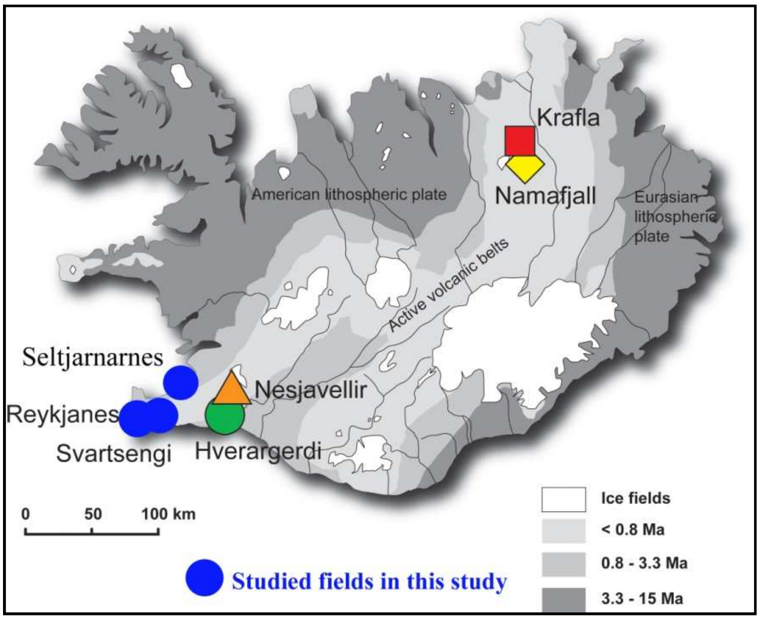

Figure 6: Location map of the three Icelandic geothermal fields selected for this study and of the other geothermal fields studied in the framework of the European project HITI (Sanjuan et al., 2010).

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:

- RN-10, RN-21, RN-22, and RN-24 in the Reykjanes geothermal field,
- SV-07 and SV-18 in the Svartsengi geothermal field,
- SN-04 and SN-05 in the Seltjarnarnes geothermal field.

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 Rifts 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 Rifts. 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).

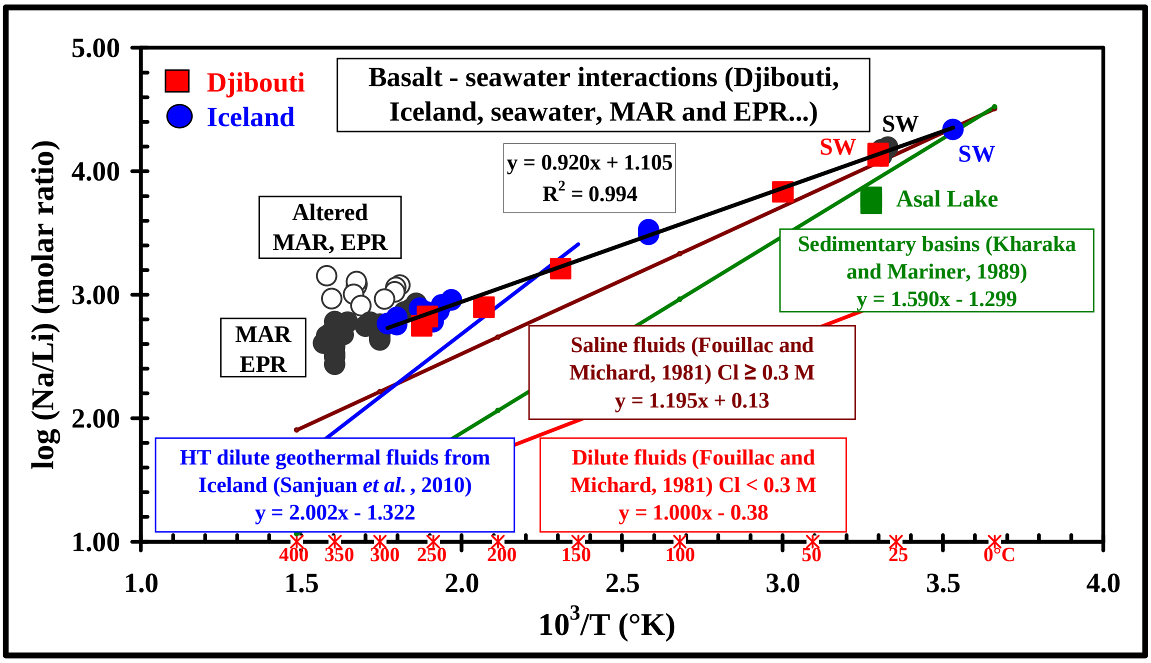

Figure 7: Sodium/Lithium geothermometric relationships existing in the literature and new Na/Li relationship determined for geothermal fluids derived from basalt-seawater interaction processes in this study.

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):

$$T\ (°K) = 855 / [\log\ (Na/Li) - 1.275] \qquad (r^2 = 0.967)$$

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):

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

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

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

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 ($KAl_3Si_4O_{10}(OH)_2$) 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). Consequently, muscovite replaced illite in the thermodynamic calculations of this study.

If we consider the following equilibrium reaction:

$$NaAlSi_3O_8 \text{ (albite)} + KAlSi_3O_8 \text{ (K-feldspar)} + 2\ Al_2Si_2O_5(OH)_4 \text{ (Kaolinite)} + Li^+ = KAl_3Si_3O_{10}(OH)_2 \text{ (Muscovite)}+ LiAl_3Si_3O_{10}(OH)_2 \text{ (Li-Mica)} + 4\ SiO_2 \text{ (Quartz)} + 2\ H_2O + Na^+,$$

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 Na and Li are essentially in form of Na^+ and Li^+ and the activity coefficients for these ions are very close, 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 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:

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

If we compare the Na/Li thermometric relationship obtained in paragraph 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:

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

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

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

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:

$$\Delta G°_R = -\log K_{298} \times R \times 298.15 \times 2.303 \approx -23924\ J.mol^{-1} \approx -23.9\ KJ.mol^{-1}.$$

The $\Delta G°_R$ of this reaction can be also calculated using the following fundamental thermodynamic relationship:

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

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.

We can then write:

$$\begin{aligned}\Delta G°_R &= \Delta G°_{f\,(muscovite)} + \Delta G°_{f\,(Li\text{-}mica)} + 4\,\Delta G°_{f\,(quartz)} + 2\,\Delta G°_{f\,(H2O)} + \Delta G°_{f\,(Na^+)} \\ &\quad - \Delta G°_{f\,(albite)} - \Delta G°_{f\,(K\text{-}feldspar)} - 2\,\Delta G°_{f\,(kaolinite)} - \Delta G°_{f\,(Li^+)} \\ &= -23.1\ \mathrm{KJ.mol^{-1}}.\end{aligned}$$

Most of the $\Delta G°_f$ 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 $\Delta G°_f$ 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 alumino-silicate 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 $\Delta G°_R$ 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 $\Delta H°_R$ value relative to the considered equilibrium 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.

We can then write:

$$\begin{aligned}\Delta H°_R &= \Delta H°_{f\,(muscovite)} + \Delta H°_{f\,(Li\text{-}mica)} + 4\,\Delta H°_{f\,(quartz)} + 2\,\Delta H°_{f\,(H2O)} + \Delta H°_{f\,(Na^+)} - \Delta H°_{f\,(albite)} - \Delta H°_{f\,(K\text{-}feldspar)} - 2\,\Delta H°_{f\,(kaolinite)} - \Delta H°_{f\,(Li^+)} \\ &= -17.5\ \mathrm{KJ.mol^{-1}}.\end{aligned}$$

As for the $\Delta G°_f$, the $\Delta H°_f$ 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 $\Delta H°_f$ value selected for muscovite was determined by Vieillard (1994) and is very close to that of the EQ3/6 data base (Tab. 4). The $\Delta H°_f$ 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 $\Delta H°_f$ values (Sanjuan *et al.*, 2010), the value determined for $\Delta H°_R$ 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 $\Delta G°_R$ values and strengthen the conclusions drawn up from these last. It is concordant with the $\Delta H°_f$ value estimated for Li-mica by Sanjuan *et al.* (2010).

Table 3: Values of the standard molar Gibbs free energies of formation $\Delta G°_f$ selected for the compounds used in this study.

Compound	Chemical formula	Authors	$\Delta G°f_{selected}$ KJ.mol^{-1}	EQ3/6 data base
Water	H_2O	Johnson *et al.* (1992)	-237.17	X
Aqueous Lithium ion	Li^+	Robie *et al.* (1978), Tardy and Duplay (1992)	-293.30	
Aqueous Sodium ion	Na^+	Shock and Helgeson (1988) and Johnson *et al.* (1992)	-261.88	X
Albite	$NaAlSi_3O_8$	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	-3708.31	X
K-Feldspar	$KAlSi_3O_8$	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	-3746.24	X
Illite	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	Wolery (1978)	-5455.81	X
Kaolinite	$Al_2Si_2O_5(OH)_4$	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	-3789.09	X
Li-Mica	$LiAl_3Si_3O_{10}(OH)_2$	estimated by Tardy and Duplay (1992)	-5596.80	
Muscovite (K-Mica)	$KAl_3Si_3O_{10}(OH)_2$	estimated by Tardy and Duplay (1992)	-5591.10	X
Quartz	SiO_2	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	-856.24	X

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

Compound	Chemical formula	Authors	$\Delta H°f_{selected}$ KJ.mol^{-1}	EQ3/6 data base
Water	H_2O	Robie *et al.* (1978), Johnson *et al.* (1992)	-285.84	X
Aqueous Lithium ion	Li^+	Shock and Helgeson (1988) and Johnson *et al.* (1992)	-278.45	X
Aqueous Sodium ion	Na^+	Robie *et al.* (1978), Shock and Helgeson (1988) and Johnson *et al.* (1992)	-240.30	X
Albite	$NaAlSi_3O_8$	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	-3931.62	X
K-Feldspar	$KAlSi_3O_8$	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	-3971.40	X
Illite	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	Wolery (1978)	-5835.29	X
Kaolinite	$Al_2Si_2O_5(OH)_4$	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	-4109.61	X
Li-Mica	$LiAl_3Si_3O_{10}(OH)_2$	no data found in the literature - proposed in this study	-5992.00	
Muscovite (K-Mica)	$KAl_3Si_3O_{10}(OH)_2$	Krupka *et al.* (1979), value also selected by Vieillard (1994)	-5971.60	
Quartz	SiO_2	Helgeson *et al.* (1978) and Johnson *et al.* (1992)	-910.65	X

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, Svartsengi 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 the knowledge and understanding of the running of this geothermometer.

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Appendix 1

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.

Hydrothermal springs	T	1000/T	pH	Na	Li	Cl	SiO_2	Alk.	Na/Li	log (Na/Li)	Li/Na x 1000	Li/Cl x 1000	Na/Cl	δ^7Li	T Sil.-Qz	Reference
	°C	$°K^{-1}$		mg/l	mg/l	mg/l	mg/l	mg/l HCO_3						‰	°C	
Vent fluids Bent Hill (Middle Valley Ridge, 1990)	265	1.86	5.13	7242	2.57	14607	619	88	851	2.93	1.17	0.90	0.76		273	Butterfield *et al.* (1994)
Guaymas Basin hydrothermal solution 9 (Gulf of California, USA)	270	1.84	5.90	11035	4.37	20598	559		762	2.88	1.31	1.08	0.83	10.0	263	Von Damm *et al.* (1985) - Chan *et al.* (1994)
Vent fluids Dead Dog (Middle Valley Ridge, 1990)	276	1.82	5.50	9150	3.82	20492	637	122	724	2.86	1.38	0.95	0.69		276	Butterfield *et al.* (1994)
Vent 6X (Escanaba Through, Gorda Ridge hydrothermal system, 1988)	300	1.74	5.40	12874	8.92	23683	415	189	435	2.64	2.30	1.93	0.84	9.1	236	Campbell et al. (1994)
Vent 6X (Escanaba Through, Gorda Ridge hydrothermal system, 2000)	300	1.74	< 5.81	12460	8.74	22406	382	< 145	430	2.63	2.32	1.99	0.86		229	Von Damm *et al.* (2005)
Vent 6X (Escanaba Through, Gorda Ridge hydrothermal system, 2002)	300	1.74	< 5.75	12736	7.70	22725	379	< 128	499	2.70	2.00	1.73	0.86		228	Von Damm *et al.* (2005)
Guaymas Basin hydrothermal fluid 7 (Gulf of California, USA)	300	1.74	5.90	11265	7.47	20598	769		455	2.66	2.20	1.85	0.84		295	Von Damm (1988)
Guaymas Basin hydrothermal fluid (South Field, Gulf of California, USA, 1982)	300	1.74	5.90	11265	7.36	20917	775	641	462	2.66	2.16	1.80	0.83	5.0	296	Campbell *et al.* (1988b) - Chan *et al.* (1993)
Guaymas Basin hydrothermal fluid (South Field, Gulf of California, USA, 1985)	300	1.74	5.90	10851	6.89	20563	811	586	475	2.68	2.10	1.71	0.81	2.6	301	Campbell *et al.* (1988b) - Chan *et al.* (1994)
Guaymas Basin hydrothermal fluid (East Hill, Gulf of California, USA, 1982)	300	1.74	5.90	11150	6.06	21236	829	494	556	2.74	1.80	1.46	0.81	7.6	303	Campbell *et al.* (1988b) - Chan *et al.* (1994)
Guaymas Basin hydrothermal fluid (East Hill, Gulf of California, USA, 1985)	300	1.74	5.90	11219	5.89	21378	829	543	575	2.76	1.74	1.41	0.81	10.2	303	Campbell *et al.* (1988b) - Chan *et al.* (1994)
Vent fluid 6 at 11°N (East Pacific Rise)	310	1.71	3.10	6667	3.36	11983	859		599	2.78	1.67	1.43	0.86	10.7	307	Bowers *et al.* (1988) - Chan *et al.* (1993)
Guaymas Basin hydrothermal solution 4 (Gulf of California, USA)	315	1.70	5.90	11150	6.06	21236	829		556	2.74	1.80	1.46	0.81		303	Von Damm (1988)
MARK-1 vent fluid (Mid-Atlantic Ridge)	335	1.64	3.70	11702	5.89	19818	1100	< 4	600	2.78	1.67	1.52	0.91	6.3	336	Campbell *et al.* (1988b) - Chan *et al.* (1993)
OBS (21°N, East Pacific Rise, 1985)	340	1.63	3.40	10093	6.43	17727	1057		474	2.68	2.11	1.85	0.88	8.9	332	Campbell *et al.* (1988b) - Chan *et al.* (1993)
Vent fluid 1 at 11°N (East Pacific Rise)	347	1.61	3.10	10851	6.13	19960	1130		534	2.73	1.87	1.57	0.84	10.9	340	Bowers et al. (1988) - Chan et al. (1993)
MARK-2 vent (Mid-Atlantic Ridge)	350	1.60	3.90	11725	5.85	19818	1094	< 15	605	2.78	1.65	1.51	0.91	8.5	336	Campbell *et al.* (1988a) - Chan *et al.* (1993)
Clambake (Ridge crest hydrothermal activity at Galapagos Spreading Center)	350	1.60		11196	7.92	21095	1316		427	2.63	2.34	1.92	0.82		359	Edmond *et al.* (1979)
Garden of Eden (Ridge crest hydrothermal activity at Galapagos Spreading Center)	350	1.60		10368	7.92	19251	1316		395	2.60	2.53	2.10	0.83		359	Edmond *et al.* (1979)
Dandelions (Ridge crest hydrothermal activity at Galapagos Spreading center)	350	1.60		7196	7.92	14004	1316		274	2.44	3.65	2.89	0.79		359	Edmond *et al.* (1979)
Oyster Beds (Ridge crest hydrothermal activity at Galapagos Spreading Center)	350	1.60		5954	4.78	11416	1316		376	2.58	2.66	2.14	0.80		359	Edmond *et al.* (1979)
OBS (21°N, East Pacific Rise, 1981)	350	1.60	3.40	9932	6.18	17337	1057	< 24	485	2.69	2.06	1.82	0.88	9.2	332	Von Damm *et al.* (1985) - Chan *et al.* (1993)
NGS (21°N, East Pacific Rise, 1981)	350	1.60	3.80	11725	7.17	20527	1172	< 12	494	2.69	2.03	1.78	0.88	10.0	344	Von Damm *et al.* (1985) - Chan *et al.* (1993)
NGS (21°N, East Pacific Rise, 1985)	350	1.60		11656	7.57	20421	1166		465	2.67	2.15	1.89	0.88		344	Campbell *et al.* (1988b)
SW (21°N, East Pacific Rise, 1981)	350	1.60	3.60	10093	6.24	17585	1039	< 18	488	2.69	2.05	1.81	0.89	9.6	330	Von Damm *et al.* (1985) - Chan *et al.* (1993)
SW (21°N, East Pacific Rise, 1985)	350	1.60	4.00	10621	6.72	18613	1033	< 10	477	2.68	2.10	1.85	0.88	8.6	329	Campbell *et al.* (1988b)
HG (21°N, East Pacific Rise, 1981)	350	1.60	3.30	10184	9.17	17585	937	< 31	335	2.53	2.98	2.67	0.89	6.6	317	Von Damm *et al.* (1985) - Chan *et al.* (1993)
HG (21°N, East Pacific Rise, 1985)	350	1.60	3.60	10414	10.05	17939	1009	< 24	313	2.50	3.20	2.86	0.90	6.8	326	Campbell *et al.* (1988b) - Chan *et al.* (1993)
OBS (21°N, East Pacific Rise, 1981)	355	1.59	3.60	10093	6.24	17585	1040		488	2.69	2.05	1.81	0.89		330	Von Damm *et al. (* 1985)
Vent fluid 5 from the Broken Spur site (29°N Mid-Atlantic Ridge)	356	1.59		9679	6.98	16627			418	2.62	2.39	2.14	0.90			James *et al.* (1995)
Plume (Southern Juan de Fuca Ridge)	360	1.58	3.20	18300	11.92	38537	1400		463	2.67	2.16	1.58	0.73		368	Von Damm and Bischoff (1987)
Vent fluid 3 from the Broken Spur site (29°N Mid-Atlantic Ridge)	360	1.58		9702	7.17	16627			409	2.61	2.45	2.20	0.90			James *et al.* (1995)
Vent fluid 4 from the Broken Spur site (29°N Mid-Atlantic Ridge)	364	1.57		9633	7.18	16627			405	2.61	2.47	2.21	0.89			James *et al.* (1995)
Vent fluid from the Menez Gwen Field (Mid-Atlantic Ridge, 37°50'N, Mean values, 1993)	*280*	*1.81*	*4.20*	*7242*	*1.82*	*13259*	*601*		*1198*	*3.08*	*0.83*	*0.70*	*0.84*		*270*	*Charlou et al. (2000)*
Vent fluid from the Menez Gwen Field (Mid-Atlantic Ridge, 37°50'N, Menez flank site, 1993)	*284*	*1.79*	*4.20*	*7196*	*1.90*	*13508*	*619*		*1142*	*3.06*	*0.88*	*0.72*	*0.82*		*273*	*Charlou et al. (2000)*
Hydrothermal fluid from the 17°S active site on the North Fiji Basin Ridge (SW Pacific)	*285*	*1.79*	*4.70*	*4828*	*1.39*	*9041*	*841*		*1050*	*3.02*	*0.95*	*0.78*	*0.82*		*305*	*Grimaud et al. (1993)*
Brandon vent - brine Be.5 (Southern East Pacific Rise)	*295*	*1.76*	*3.30*	*10322*	*3.39*	*19747*	*751*		*920*	*2.96*	*1.09*	*0.88*	*0.81*		*293*	*Von Damm et al. (2003)*
13°N hydrothermal site (East Pacific Rise)	*320*	*1.69*	*3.20*	*12874*	*4.77*	*26235*	*1322*		*814*	*2.91*	*1.23*	*0.93*	*0.76*		*360*	*Michard et al. (1984)*
Vent fluid from the Lucky Strike Field (Mid-Atlantic Ridge, 37°17'N, Eiffel Tower site, 1994)	*324*	*1.67*	*3.70*	*7977*	*1.98*	*14784*	*799*		*1213*	*3.08*	*0.82*	*0.69*	*0.83*		*299*	*Charlou et al. (2000)*
Vent fluid from the Lucky Strike Field (Mid-Atlantic Ridge, 37°17'N, Eiffel Tower site, 1993)	*325*	*1.67*	*4.07*	*8161*	*2.10*	*15528*	*943*	*< 1.2*	*1172*	*3.07*	*0.85*	*0.69*	*0.81*		*318*	*Von Damm et al. (1998)*
Vent fluid from the Lucky Strike Field (Mid-Atlantic Ridge, 37°17'N, Mean values)	*325*	*1.67*	*3.65*	*8966*	*2.13*	*16486*	*865*		*1270*	*3.10*	*0.79*	*0.66*	*0.84*		*308*	*Charlou et al. (2000)*
Vent fluid from the Lucky Strike Field (Mid-Atlantic Ridge, 37°17'N, 2608 Vent site, 1996)	*328*	*1.66*	*3.78*	*9633*	*2.89*	*18648*	*1051*	*< 35*	*1005*	*3.00*	*1.00*	*0.79*	*0.80*		*331*	*Von Damm et al. (1998)*
Vent fluid 2 at 13°N (East Pacific Rise)	*354*	*1.59*	*3.10*	*12667*	*4.11*	*25243*	*1166*		*931*	*2.97*	*1.07*	*0.83*	*0.77*		*344*	*Bowers et al. (1988)*
Hydrothermal fluid from Trans-Atlantic Geotraverse (TAG, 26°08'N)	*360*	*1.58*		*13426*	*2.85*	*23364*	*1322*		*1421*	*3.15*	*0.70*	*0.62*	*0.89*	*11.5*	*360*	*Campbell et al. (1988a) - Chan et al. (1994)*
Seawater (Diamant, Martinique)	29	3.32	8.19	11400	0.23	20200	0.19	143	14960	4.17	0.07	0.06	0.87	30.5		Sanjuan *et al.* (2003)
Seawater (Bouillante, Guadeloupe)	29	3.31	8.23	11000	0.25	20181	0.43	169	13280	4.12	0.08	0.06	0.84	29.3		Sanjuan (2001)
Seawater (Lamentin, Martinique)	29	3.31	8.20	11400	0.23	21307		148	14960	4.17	0.07	0.06	0.83	30.1		Sanjuan *et al.* (2002)
Lake Bogoria (Kenya)	27	3.33	10.10	39300	0.76				15608	4.19	0.06					Cioni *et al.* (1992)

$T_{Sil.-Qz}$: temperature estimated using the Silica-quartz geothermometer (Fournier and Rowe, 1966).