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# Bibliographical review about Na/Li geothermometry and lithium isotopes applied to worldwide geothermal waters

Final report

BRGM/RP-57346-FR  
September 2009



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Study carried out in the framework of the HITI project, co-funded  
by the BRGM Research Division and the European Union (FP6)  
(contract n° 019913)

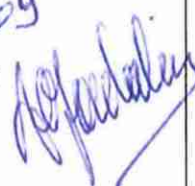
**B. Sanjuan, R. Millot**

**Checked by:**

Name : A. Gadalia

Date : 03/12/2009

Signature :



**Approved by:**

Name : F. Boissier

Date : 30/11/09

Signature :



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**Keywords:** sodium, lithium, lithium isotopes, geothermometer, geothermal waters, hydrothermal waters, oil-field basins, basalt, granite.

In bibliography, this report should be cited as follows:

Sanjuan B., Millot R. (2009) - Bibliographical review about Na/Li geothermometry and lithium isotopes applied to worldwide geothermal waters. Report BRGM/RP-57346-FR, 58 p., 1 tabl., 9 figs., 1 appendix.

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## Abstract

This study is performed within the framework of the FP6 European project HITI (High Temperature Instruments for supercritical geothermal reservoir characterization and exploitation). This research project, co-funded by EU and the different partners, aims to provide geophysical and geochemical sensors and methods to evaluate deep geothermal wells up to supercritical conditions ( $T > 370^{\circ}\text{C}$ ), which are more cost-effective than those of the conventional wells. A deep geothermal well is currently being drilled for this purpose into the Krafla area, Iceland, as part of the IDDP ("Iceland Deep Drilling Project") and with joint funding from Icelandic industry and science Institutes. Another deep well will be drilled in the Reykjanes peninsula, Iceland, within the framework of the same project. This study, a bibliographical review about the Na/Li geothermometer and lithium isotopes applied on the world geothermal waters, is the first step of the task envisaged by BRGM to use and validate the sodium-lithium (Na-Li) chemical geothermometer on Icelandic geothermal waters at temperatures ranging from 25 to  $500^{\circ}\text{C}$ .

In this study, more than 120 temperature and chemical data from world geothermal and oil-fields, sedimentary basins, oceanic ridges, emerged rifts and island arcs have been collected and investigated. These additional data have allowed to confirm and refine the three existing Na/Li thermometric relationships. Moreover, a new Na/Li thermometric relationship relative to the processes of seawater or dilute seawater-basalt interaction occurring in the oceanic ridges and emerged rifts is proposed. Even if the running of Na/Li is still poorly understood, the existence of a new thermometric relationship 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 reservoir rocks in contact with the geothermal fluids. For most of the geothermal waters in contact with volcanic rocks or granite in the deep reservoir, rock leaching and hydrothermal alteration (illite or smectite precipitation) are probably the main processes controlling the Li concentrations. Additional field and laboratory studies as well as a thermodynamic approach based on mineral dissolution-precipitation equilibrium reactions could help to support and confirm this assumption.

The scarcity of the  $\delta^7\text{Li}$  values analysed in the geothermal and oil-field fluids and the presently available data indicate that it is necessary to acquire additional data in both fluids and rocks to better understand the Li behaviour in the processes of water-rock interaction. However, as the dissolved Li during these processes seems to be controlled by several influent factors, it is recommended to study the Li behaviour at different temperatures for a same type of process of water-rock interactions. Among possible applications, the determination of  $\delta^7\text{Li}$  values in geothermal waters shows that these data can be used to determine the nature of the reservoir rocks in contact with these waters and indirectly estimate the depth of these reservoirs.

The Na/Li geothermometer, which is often less accurate than other classical geothermometers but can be more reliable in many cases, is then very useful for geothermal exploration. In order to improve the use of this geothermometer, additional developments in different environments and regions are necessary and 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 to improve the knowledge and to understand the running of this geothermometer.



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# 1. Introduction

## 1.1. FRAMEWORK OF THIS STUDY

This study is performed within the framework of the FP6 European project HITI (High Temperature Instruments for supercritical geothermal reservoir characterization and exploitation).

This research project, co-funded by EU and the different partners, aims to provide geophysical and geochemical sensors and methods to evaluate deep geothermal wells up to supercritical conditions ( $T > 370^{\circ}\text{C}$ ). Supercritical geothermal wells are presently non-conventional but may provide a very efficient way to produce electricity from a clean, renewable source. A deep geothermal well is currently being drilled for this purpose into the Krafla area, Iceland as part of the IDDP ("Iceland Deep Drilling Project") and with joint funding from Icelandic industry and science Institutes. Another deep well will be drilled in the Reykjanes peninsula, Iceland, within the framework of the same project.

Aimed to explore supercritical wells and to enhance production from them, the HITI project must develop, build and test in the field new surface and down-hole tools and approaches for deep high-temperature boreholes. The new set of tools and methods have been chosen to provide a basic set of data needed to describe either the supercritical reservoir structure and dynamics, or the evolution of the casing during production. The set of new instruments should tolerate high temperature and pressure in a highly corrosive environment. Slick-line tools up to  $500^{\circ}\text{C}$  and wire-line tools up to  $300^{\circ}\text{C}$  will be developed due to the present limitation in wire-line cables ( $320^{\circ}\text{C}$ ).

For reservoir characterisation (Work Package 3 - WP3), the measured quantities are temperature, pressure and pH (for fluid characterization, thermodynamic modelling of the reservoir and thermo-mechanical modelling of bore-hole integrity), natural gamma radiation and electrical resistivity (for basement porosity and alteration), acoustic signal (with borehole wall images for reservoir fracturing and in-situ crustal stresses), reservoir strativity and equilibrium (from geothermometers and organic tracers) and fluid sampling. For casing integrity, collar location, as well as thickness changes due to corrosion or plugging from mineral precipitation (from acoustic images again) will be measured. The new tools will be in-situ tested in existing Icelandic wells, including the IDDP hole.

One of the tasks envisaged by BRGM in the WP3 of HITI project is to use and validate the sodium-lithium (Na-Li) chemical geothermometer at temperatures ranging between 25 and  $500^{\circ}\text{C}$  in order to estimate the temperature of supercritical deep geothermal reservoirs such as they can exist in Iceland. This study, a bibliographical review about Na/Li geothermometry and lithium isotopes applied to worldwide geothermal waters, is the first step of this task.

## 1.2. OBJECTIVES OF THIS STUDY

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, geothermometers such as Na-K, Na-K-Ca, Na-K-Ca-Mg, K-Mg,  $\text{SiO}_2$  or  $\delta^{18}\text{O}(\text{H}_2\text{O})$ - $\delta^{18}\text{O}(\text{SO}_4)$ , based on empirical or semi-empirical laws, use data obtained from chemical and isotopic analyses performed on hot fluid samples collected either *in situ* or at surface. Unfortunately, the estimations of reservoir temperatures using these classical tools are not always concordant (Michard, 1979; Nicholson, 1993; Serra and Sanjuan, 2004).

Given this discordance and from numerous data obtained in several world geothermal fields (Fouillac and Michard, 1981) or in world geothermal and US oil-fields (Kharaka and Mariner, 1989), a new geothermometer was proposed for thermal and geothermal waters, based on three empirical and statistical Na/Li thermometric relationships. 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 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 such as Na/K. 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 ( $> 350^\circ\text{C}$ ).

The use and the validation of the Na-Li chemical geothermometer at temperatures ranging from 25 to  $500^\circ\text{C}$  is one of the tasks envisaged by BRGM in the WP3 of HITI project. This task aims to better understand the use and the running of the Na/Li geothermometer, and more especially, the behaviour of lithium and its isotopes (analysed by ICP-MS/MC), which can result relevant and decisive tools in numerous cases to estimate or validate the temperature of the fluids in the geothermal reservoirs. 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) was an excellent opportunity to test this geothermometer and to better understand its running.

Before starting the study of use and validation of the Na-Li chemical geothermometer at temperatures ranging from 25 to  $500^\circ\text{C}$  from Icelandic geothermal waters, it was necessary to carry out a bibliographical review integrating new hydrothermal, geothermal and oil-field data. This report presents the main results of this review, obtained using more than 120 additional data from world geothermal fields (New Zealand, USA, Japan, Mexico, Chile, Honduras, Philippines, Indonesia, Kenya, Ethiopia, Italy, France, Azores...), from oil-fields and sedimentary basins (USA, Israel, France, North Sea...), from oceanic ridges (Mid Atlantic Ridge, East Pacific Rise), emerged rifts (Djibouti, Iceland) and island arcs (Guadeloupe, Martinique, Dominica...). The three existing Na/Li thermometric equations are re-examined and a new equation relative to the seawater or dilute seawater-basalt interaction processes is proposed. The Li isotope data existing in the literature for hydrothermal, geothermal and oil-field areas are compiled and discussed.

## 2. Na/Li geothermometry

### 2.1. CLASSICAL GEOTHERMOMETERS

Since 1965, several chemical and isotopic geothermometers such as Na-K, Na-K-Ca, Na-K-Ca-Mg, K-Mg, SiO<sub>2</sub> or  $\delta^{18}\text{O}(\text{H}_2\text{O})-\delta^{18}\text{O}(\text{SO}_4)$  are commonly used in geothermal exploration (White, 1970; Fournier, 1979; Michard, 1979; Giggenbach, 1988; Nicholson, 1993; Serra and Sanjuan, 2004) but unfortunately, the estimates of reservoir temperatures using these classical tools are not always concordant.

The mixing of the deep geothermal fluids with surface waters or their cooling and the associated precipitation/dissolution processes during their rising to the surface can be responsible of these discordances. Other factors such as the presence of seawater, the water salinity or the nature of the rocks surrounding the reservoirs can also influence the estimated temperatures. For instance, the SiO<sub>2</sub> geothermometer underestimates the reservoir temperature when applied to deep geothermal fluids diluted by surface waters or after silica precipitation due to a fluid cooling. Conversely, for dilute thermal waters collected from volcanic or granite areas, the Na/K geothermometer often yields overestimated reservoir temperatures. The Na/K and Na/K/Ca geothermometers cannot be used with seawater.

### 2.2. THE Na/Li THERMOMETRIC RELATIONSHIPS EXISTING IN THE LITTERATURE

From numerous data obtained in several world geothermal fields mainly located in volcanic and granitic areas, Fouillac and Michard (1981) proposed a new geothermometer for thermal and geothermal waters based on two empirical and statistical thermometric Na/Li relationships (Na/Li being a molar ratio):

$$\log (\text{Na/Li}) = 1000/T(^{\circ}\text{K}) - 0.38 \text{ for Cl concentrations } < 0.3 \text{ M (black line in fig. 1)}$$

$$\log (\text{Na/Li}) = 1195/T(^{\circ}\text{K}) + 0.13 \text{ for Cl concentrations } \geq 0.3 \text{ M (red line in fig. 1)}$$

The mean square correlation coefficients are  $r^2 = 0.97$  and  $0.98$ , respectively.

Due to a rather low reactivity of lithium during the ascent of the geothermal waters up to the surface, the use of the Na/Li often gives more reliable deep temperature estimates than those of classical geothermometers such as Na/K. It also brings additional information. In contrast, the precision on the estimated temperatures using these two relationships was evaluated to  $\pm 20^{\circ}\text{C}$  (Michard, 1979) and is higher than that obtained using the Na/K or silica geothermometers.

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

$$\log (\text{Na/Li}) = 1590/T(^{\circ}\text{K}) - 1.299 \text{ (} r^2 = 0.91; \text{ green line in fig. 1)}$$

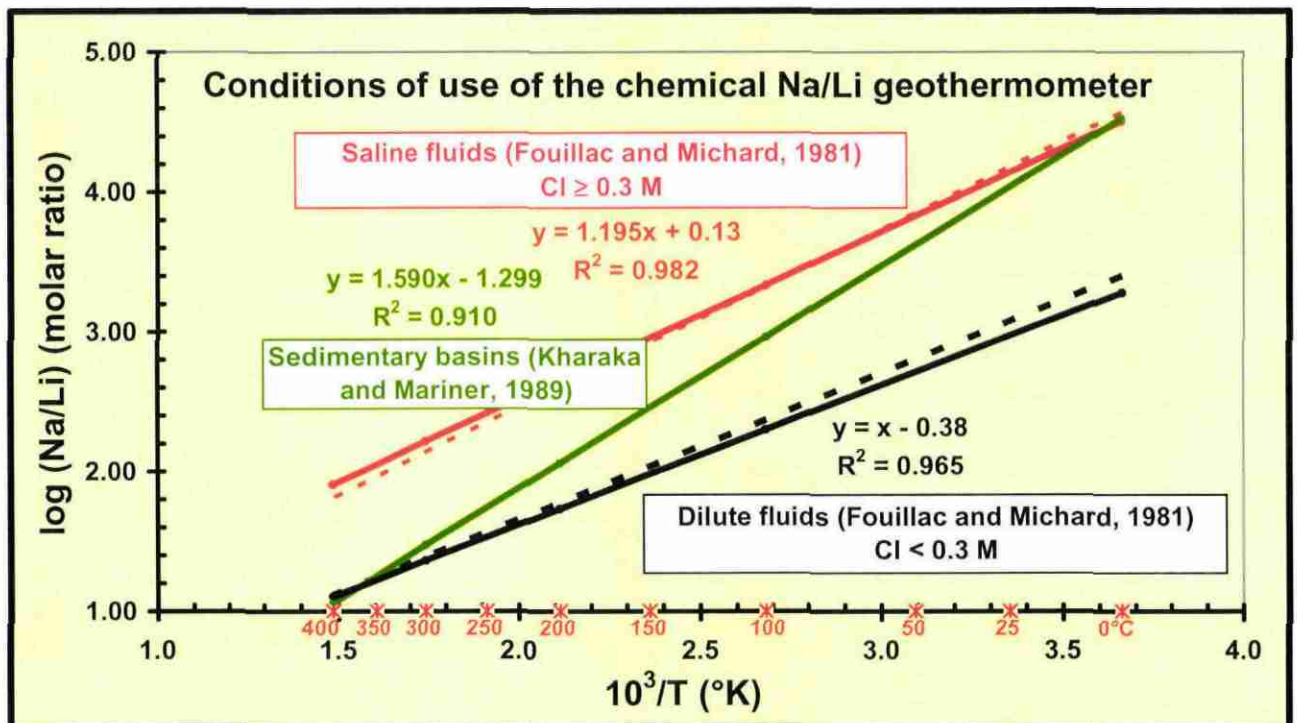


Figure 1 - Conditions of use of the chemical Na/Li geothermometer before this review.

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). Moreover, these three relationships seem to be essentially dependant on the fluid salinity and on the reservoir type (crystalline or sedimentary rocks).

As these relationships have been defined several years ago and very few revisions were performed since their determination, it was considered as useful to ameliorate the knowledge about this geothermometer by integrating new hydrothermal, geothermal and oil-field data from the literature before starting the study of use and validation of the Na-Li chemical geothermometer at temperatures ranging from 25 to 500°C from Icelandic geothermal waters.

As far as we are aware, only Verma and Santoyo (1997) proposed new improved equations of the geothermometric relationships determined by Fouillac and Michard (1981) on the basis of statistical treatment of data given by these authors and application of outlier detection and rejection as well as theory of error propagation. These equations are (fig. 1):

$$\log (\text{Na/Li}) = 1049/T(^{\circ}\text{K}) - 0.44 \text{ for Cl concentrations } < 0.3 \text{ M (black dashed line)}$$

$$\log (\text{Na/Li}) = 1267/T(^{\circ}\text{K}) - 0.07 \text{ for Cl concentrations } \geq 0.3 \text{ M (red dashed line).}$$

However, between 25 and 350°C, we can consider that these equations give similar estimations of temperature to those obtained using the relationships determined by Fouillac and Michard (1981). For the first equation, we have a maximum discrepancy of estimated temperature lower than 10°C in all the temperature range. For the second equation, the discrepancy of estimated temperature is lower than 15°C for most of the temperature values, except for the values ranging between 250 and 350°C for which it can reach up to 25°C. However, for these high temperatures, this discrepancy only corresponds to an uncertainty lower than 10%.

For 60 thermal springs located in granitic areas, Michard (1990) proposed a geothermometric relationship very close to that given by Fouillac and Michard (1981) for Cl concentrations lower than 0.3 M and still closer to that proposed by Verma and Santoyo (1997). The corresponding equation is:

$$\log (\text{Na/Li}) = 1040/T(^{\circ}\text{K}) - 0.43 \text{ (} r^2 = 0.91 \text{)}$$

### 2.3. MINERALOGICAL 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 ( $T > 400^{\circ}\text{C}$ ) did not give reliable results for Li. They considered that lithium behaves in hot waters as a "soluble" element, i.e. that 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  $500^{\circ}\text{C}$ . 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  $90^{\circ}\text{C}$  to 68% at  $220^{\circ}\text{C}$ .

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 ( $\text{B/Li} \approx 3$  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 ( $\text{B/Li}$  ratio is essentially constant at 4.0) because Li is trapped in altered products.

Sturchio and Chan (2003) again showed a loss of Li by incorporation into hydrothermal minerals in altered rhyolite, using relationships of Li and Cl concentrations for thermal waters collected in the Yellowstone National Park, Wyoming-Montana (USA), hydrothermal system. If Li is added to thermal waters only by leaching from rocks at high temperatures ( $\geq 350^{\circ}\text{C}$ ), as demonstrated experimentally (Ellis and Mahon, 1964; Seyfried *et al.*, 1984, 1998), Li removal from thermal waters occurs only at lower temperatures ( $\leq 350^{\circ}\text{C}$ ), when abundant phyllosilicates form as hydrothermal alteration products of obsidian. An analogous mode of redistribution of Li is documented in altered oceanic crust by Chan *et al.* (2002a). Because Li substitutes for Mg in the octahedral sites of phyllosilicates and other possible minerals (quartz, adularia, analcime), the mechanism for Li removal is most likely precipitation of minerals. It can be assumed that local isotopic equilibrium applies when Li is incorporated into these alteration minerals (Sturchio and Chan, 2003).

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  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  (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  $\text{K}^+$ -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).

## 2.4. RESULTS OBTAINED DURING THIS REVIEW

Relative to the previous studies, more than 120 additional data from worldwide geothermal fields (New Zealand, USA, Japan, Mexico, Chile, Honduras, Philippines, Indonesia, Kenya, Ethiopia, Italy, France, Azores...), from oil-fields and sedimentary basins (USA, Israel, France, North Sea...), from oceanic ridges (Mid Atlantic Ridge, East Pacific Rise), emerged rifts (Djibouti, Iceland), and island arcs (Guadeloupe, Martinique Dominica...) were investigated (see appendix 1 and bibliographical references therein). Relative to the geothermal waters, most of data were selected among water samples collected from geothermal wells in order to only consider waters representative of geothermal reservoirs. The water samples from thermal springs were generally discarded because it is likely that mixing processes with surface waters or mineral dissolution-precipitation reactions modify their deep chemical and isotopic compositions, during their cooling and rising to the surface. In these conditions, only some samples of not very modified thermal water were integrated.

### 2.4.1. Confirmation of the Na/Li thermometric relationships existing in the literature

The Na/Li thermometric relationships previously determined by Fouillac and Michard (1981) and Kharaka and Mariner (1989) (dashed lines in the figures 2a and 2b) were validated by numerous new data (see appendix 1), except for the data relative to the oceanic ridges (MAR and EPR) and emerged rifts (Djibouti, Iceland), which indicate lower Li concentrations and higher Na/Li ratios at a given temperature (figs. 2a and 2b), and for some rare data, not reported in appendix 1 and figures 2a and 2b.

By integrating the new data with the thermometric relationships determined by Fouillac and Michard (1981) and Kharaka and Mariner (1989), three straight lines were obtained with slightly different equations (solid lines in figures 2a and 2b). These equations are:

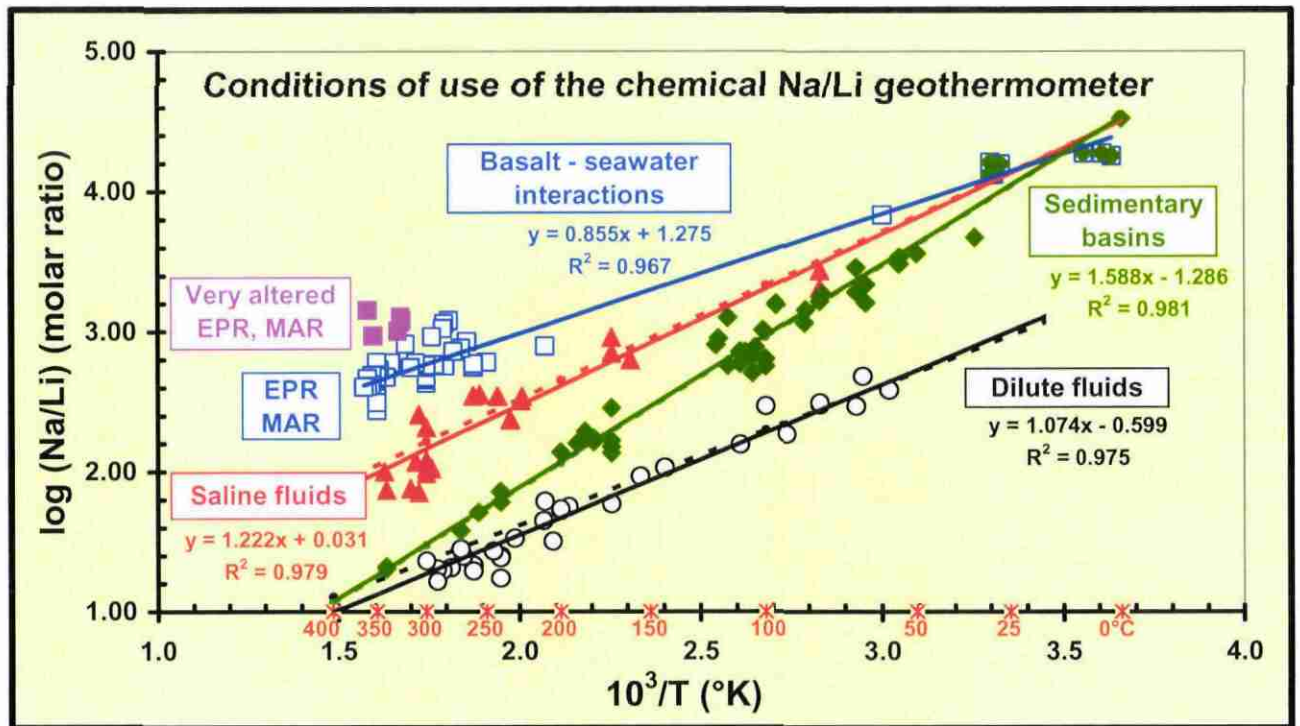
$$\log (\text{Na/Li}) = 1074/T(^{\circ}\text{K}) - 0.60 \text{ for Cl concentrations } < 0.3 \text{ M } (r^2 = 0.98; \text{ black line})$$

$$\log (\text{Na/Li}) = 1222/T(^{\circ}\text{K}) + 0.03 \text{ for Cl concentrations } \geq 0.3 \text{ M } (r^2 = 0.98; \text{ red line})$$

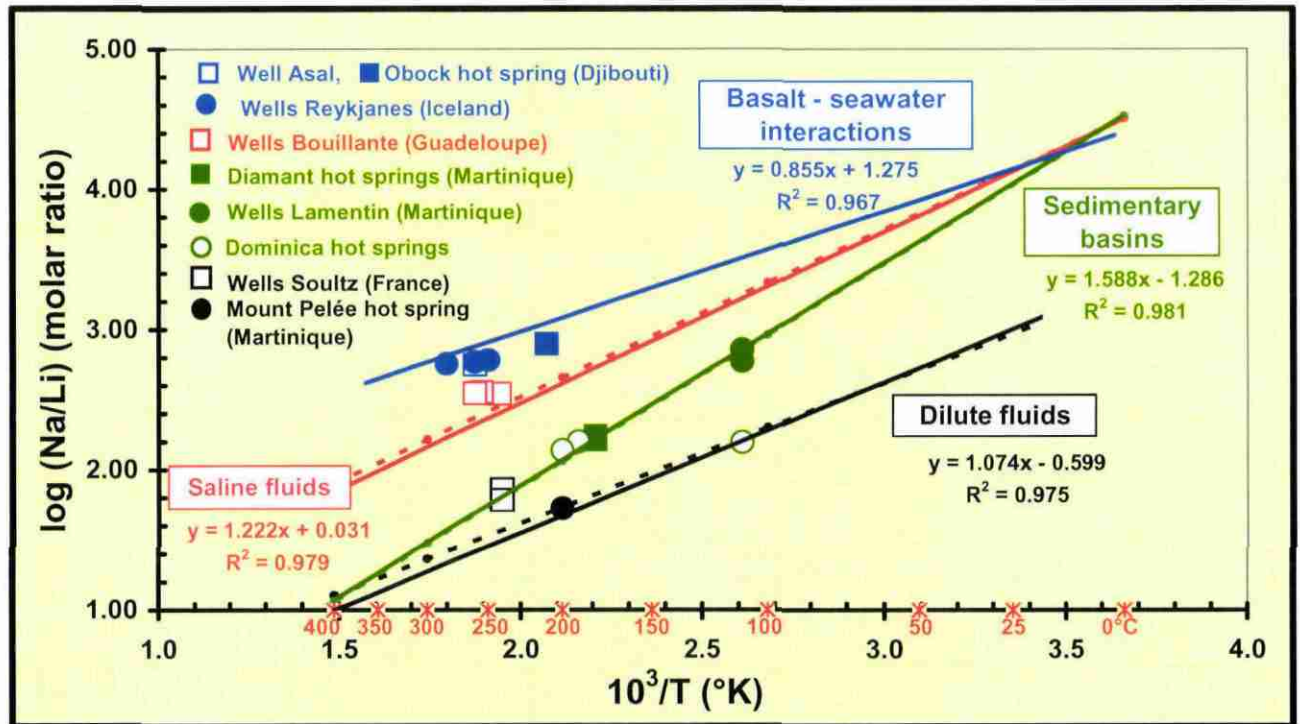
$$\log (\text{Na/Li}) = 1588/T(^{\circ}\text{K}) - 1.286 (r^2 = 0.98; \text{ green line})$$

The geothermal fluids produced in the area of the Caribbean island arc (Bouillante in Guadeloupe - Lamentin, Mount Pelée and Diamant in Martinique - Dominica; fig. 2b) agree with the three relationships, following their salinity and the nature of the rocks with which they interact (basalt, andesites, volcano-sedimentary rocks...). The geothermal waters collected from 5 km deep EGS wells, located at Soultz-sous-Forêts, in the Rhine Graben (Alsace, France), for which the bottom holes are located in a granite environment, agree with the relationship relative to the oil-fields and sedimentary basins (fig. 2b). In fact, the chemical and isotopic compositions of these waters suggest that they have a sedimentary origin (Triassic Buntsandstein formation) and have reached equilibrium at 220-240°C with these sedimentary rocks rather than granite (Sanjuan *et al.*, 2009).





a)



b)

Figure 2 - Conditions of use of the chemical Na/Li geothermometer after this review.

#### 2.4.2. A new Na/Li thermometric relationship

For the marine origin fluids discharged from the oceanic ridges (MAR and EPR) and emerged oceanic rifts (Djibouti, Iceland), except for some data relative to old and very altered EPR and MAR, which are depleted in lithium (pink colour in figure 2a), a new and relatively good thermometric relationship was obtained ( $r^2 = 0.97$ ; figs. 2a and 2b):

$$\log (\text{Na/Li}) = 855/T(^{\circ}\text{K}) + 1.275$$

The uncertainty on the temperature values estimated using this thermometric relationship is close to  $\pm 20^{\circ}\text{C}$ . This value was obtained by statistical treatment of the data.

This linear relationship can be considered as representative of the temperature influence on the seawater or dilute seawater-basalt interaction processes. According to the van't Hoff equation, the slope of straight lines as those observed in figures 2a and 2b can be used to estimate the standard enthalpy of the corresponding chemical equilibrium reactions, if the enthalpy is considered to be constant as a function of the temperature (Kharaka and Mariner, 1989). Consequently, the similarity of the slopes (855 and 1074) for two of the obtained straight lines in these figures suggests the existence of similar chemical processes controlling the concentrations of dissolved sodium and lithium.



## 3. Review of the isotopic Li data

### 3.1. LITHIUM ISOTOPE GEOCHEMISTRY

This light element has got two stable isotopes at different abundances: approximately  $^6\text{Li}$  7.5% and  $^7\text{Li}$  92.5%. Lithium is a lithophile element, highly soluble and moderately incompatible with magmatic processes. Moreover, the significant relative mass difference (17%) between the two isotopes can cause large mass fractionation during the natural geochemical processes.

Lithium occurs generally as a trace component of minerals (except a few rare Li minerals) where it tends to substitute for magnesium because of the similarity in ionic radii of Li and Mg. The Li concentrations in the waters are essentially controlled by water-rock interaction processes which depend on the mineral assemblage in contact with the waters, the chemical composition of these waters, dissolution-precipitation or exchange reactions, temperature, water-rock ratio, etc. In contrast, the Redox, organic complexation or speciation reactions have very limited effects on the Li concentrations in the waters.

At the present time, the magnitude of the Li isotopic fractionations associated to water-rock interaction processes and the factors controlling these fractionations are not always well constrained. However, studies carried out for altered rocks at low-moderate temperatures indicate that the Li isotopic fractionation associated to the water-rock interactions favours the enrichment of the heavy isotope  $^7\text{Li}$  in solution. The light isotope  $^6\text{Li}$  is preferentially retained by secondary alteration minerals when the latter are present. This behaviour is anomalous with respect to the normal trend of mass-dependent isotopic fractionation in which the heavier isotope is enriched in the solid phase.

As already reported by Tomascak (2004), most of the clearly identified isotopic fractionation processes involving lithium occurs close to the Earth's surface. The combination of low ionic charge, relatively small radius (0.068 nm, the smallest ionic radius of the alkali metals) and high degree of covalency in its bonds affords Li potential for considerable adaptability in numerous geochemical environments.

This element in aqueous solutions is highly hydrated relative to other alkali ions and ordinarily assumes tetrahedral hydrated coordination. In most solids, it may occupy either octahedrally or tetrahedrally coordinated sites. The occurrence of isotopic fractionation induced by crystallisation/re-crystallization, in which an energetic advantage is gained by the preferential incorporation of one isotope over another into a crystallographic site, is an important mechanism at the Earth's surface. Thermodynamic calculations (Yamaji *et al.*, 2001) confirm that Li exchange between solution and octahedral crystallographic sites favours the preferential incorporation of  $^6\text{Li}$  into the solids. This isotopic fractionation has been highlighted in numerous natural environments. It seems to be highly dependent on the reaction temperature and to a lesser extent, on the water-rock ratio.

Experimental and natural data found in the literature (Pistiner and Henderson, 2003; Huh *et al.*, 2001) suggest that the processes of mineral dissolution are not characterized by significant Li isotopic fractionation.

The adsorption on the mineral surfaces is a major mechanism of Li isotopic fractionation in the hydrosphere. Sorption of lithium from aqueous solution by mineral phases at the temperature of the Earth's surface has been highlighted by Taylor and Urey (1938) and Anderson *et al.* (1989). Sorption and retention of ions from aqueous solutions largely depend on both mineral surface chemistry and the chemical composition of the solutions. Although Taylor and Urey (1938) suggest that the magnitude of mass fractionation on desorption is equivalent to that on adsorption, natural and empirical data seem to indicate that this isotopic fractionation is not reversible (James and Palmer, 2000a). The irreversibility of this process is attributed to the Li incorporation into crystallographic structural sites rather than surface ion exchange sites, suggesting that the fractionation magnitude could be different following the considered mineral surfaces.

Li sorption experiments on several minerals (Pistiner and Henderson, 2003) have shown that Li isotopic fractionation does not occur when this element is not incorporated in the structure of the solid (physical sorption). When lithium is incorporated by stronger bounds (chemical sorption), an isotopic fractionation is observed which depends on the chemical structure of the minerals (Anghel *et al.*, 2002). The most significant Li isotopic fractionation factor ( $\alpha_{\text{solution-solid}} \approx 1.014$ ) was measured for gibbsite. For Li sorption processes between seawater and different solids (clay minerals such as kaolinite and vermiculite, freshwater sediments), Zhang *et al.* (1998) observed similar Li isotopic fractionation factor ( $\alpha_{\text{solution-solid}} \approx 1.022$ ).

### 3.2. LITHIUM ISOTOPE MEASUREMENTS

Accurate measurements of Li isotopic compositions in geological materials are of great interest in the Earth Sciences.

As for other low atomic number elements, the isotopic composition of lithium is usually expressed as delta units calculated from isotopic ratios relative to the composition of a specified reference sample. Over the last few decades, authors have frequently reported  $\delta^6\text{Li}$  values based on  $^6\text{Li}/^7\text{Li}$  ratios. However, since some years, the isotope geoscience community has adopted the  $\delta^7\text{Li}$  values based on  $^7\text{Li}/^6\text{Li}$  (Coplen, 1996; Carignan *et al.*, 2004; Millot *et al.*, 2004).  $\delta^7\text{Li}$  is defined as the deviation in parts per thousand relative to the L-SVEC certified reference material as follows:

$$\delta^7\text{Li} = \left( \left[ \left( \frac{^7\text{Li}}{^6\text{Li}} \right)_{\text{sample}} / \left( \frac{^7\text{Li}}{^6\text{Li}} \right)_{\text{L-SVEC}} \right] - 1 \right) \times 1000$$

The L-SVEC reference material (Flesh *et al.*, 1973) is a pure lithium carbonate originally prepared by NIST as a fine powder (SRM 8545) with an assigned  $\delta^7\text{Li}$  value of 0‰ ( $^7\text{Li}/^6\text{Li} = 12.02 \pm 0.03$ ). The IRMM-016 lithium carbonate is also available as a fine powder from the Institute of Reference Materials and Measurements (Geel, Belgium) and is isotopically identical to L-SVEC within analytical uncertainty (Lamberty *et al.*, 1987; Qi *et al.*, 1997).

Aside from L-SVEC and IRMM-016, no other reference samples for Li isotopes are available. Seawater ( $\delta^7\text{Li} \approx 31\text{‰}$ ) has been considered by many authors as a natural secondary standard and the Li isotope composition of seawater has been frequently reported in the literature (James and

Palmer, 2000b; Nishio and Nakai, 2002). However, no single seawater sample has been selected throughout the Li isotope community as a reference sample.

Over the last decades, lithium isotope compositions have been measured with a variable degree of accuracy and precision by different techniques. Early studies of Li isotope variations in natural materials were limited by the poor reproducibility of the methods employed in making the measurements. As described by Millot *et al.* (2004), the first precise Li isotope measurements were performed in the late 1980's by thermal ionisation mass spectrometry (TIMS) at the microgram level (Chan, 1987; Xiao and Beary, 1989) using the Li tetra-borate form for ionisation. Later, phosphoric acid was used as an activator, requiring smaller quantities of lithium (100 ng to 1 µg) and yielding an external reproducibility of between 0.7 and 1.5‰ for highly purified samples (You and Chan, 1996; Moriguti and Nakamura, 1998a; James and Palmer, 2000b).

The use of ICP-MS techniques represents a good alternative to TIMS. The high sensitivity of the quadrupole ICP-MS allows measurement of Li isotopes with an external reproducibility of 1.5-2‰ on quantities as low as 5 to 10 ng Li (Grégoire *et al.*, 1996; Kosler *et al.*, 2001).

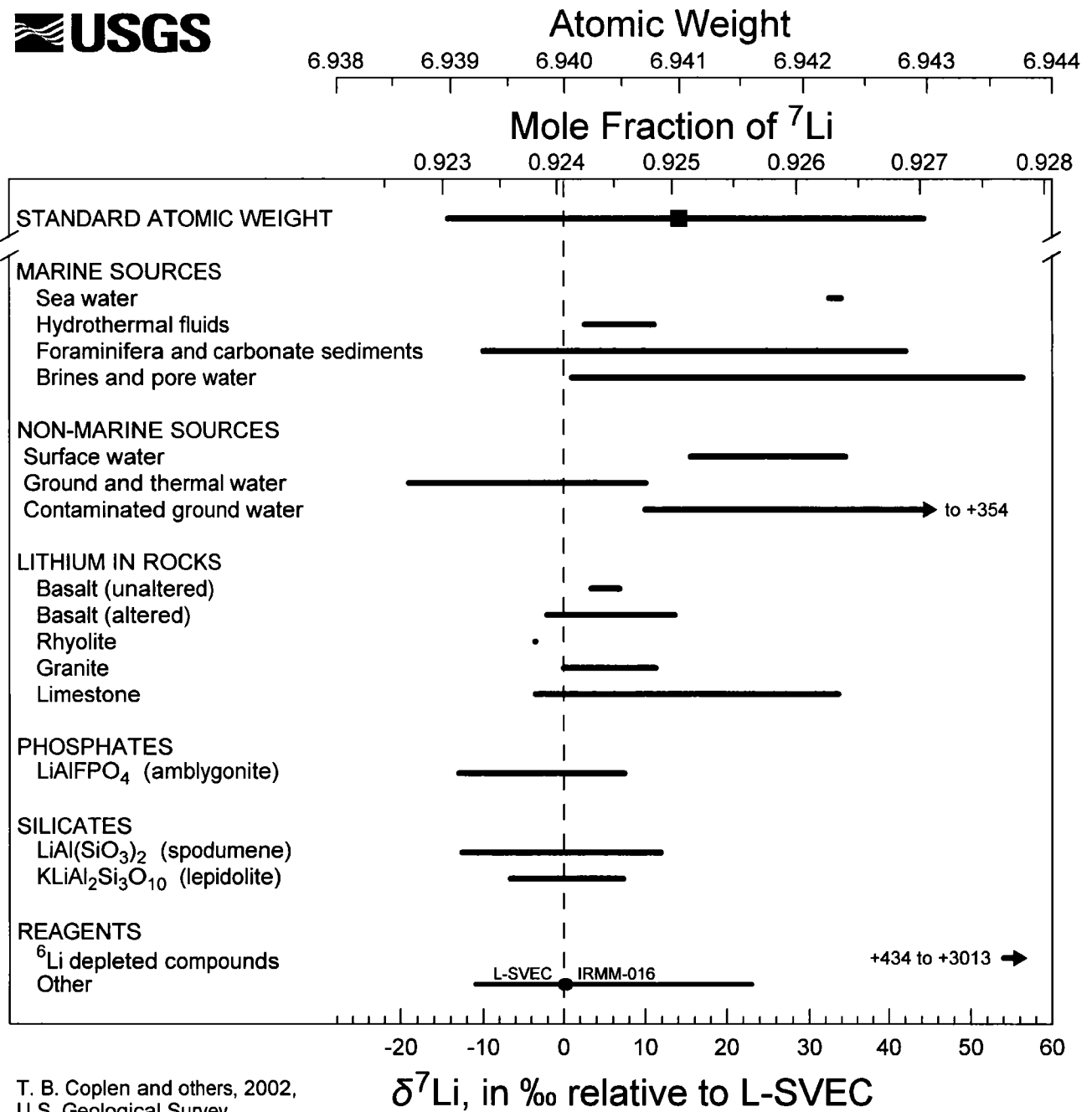
Recently, the use of Multi-Collector ICP-MS was shown to provide the most rapid and precise measurements of Li isotopes (external reproducibility of about 0.5-1‰; Tomascak *et al.*, 1999a; Nishio and Nakai, 2002; Bryant *et al.*, 2003a; Millot *et al.*, 2004). To date, the MC-ICP-MS approach combines advantages that no other technique can match in terms of accuracy, reproducibility, sensitivity and analysis throughput. As the achievable precision improves, more and more detailed geochemical problems can be realistically explored.

### 3.3. LITHIUM NATURAL ISOTOPIC VARIATIONS

Coplen *et al.* (2002) show that the range of natural variation of lithium isotopes for geological materials is very wide: about 60‰ (fig. 3). This is also illustrated by Tomascak (2004) in figure 4. Table 1 (after Tomascak, 2004) presents the reported isotopic compositions of a variety of standard materials in the literature.

Since the 1980's, precise Li isotope data collected for rocks, fluids, and marine sediments have provided significant constraints on the Li cycle in the marine environment, including sea-floor basalts, submarine hydrothermal systems, seawater, sediments, and riverine inputs, as well as on the contributions of subducted lithosphere to magmatism at convergent margins. The extent of Li isotope fractionation has not been explored as thoroughly in terrestrial rock-water systems as it has been in submarine systems. Few data exist in the literature about the Li isotopic compositions of the rocks of the continental crust.

Very recently, Teng *et al.* (2004) reported the concentrations and the isotopic compositions of different types of rocks (shales, loess and granites) in order to estimate the Li isotopic composition of the upper continental crust.



T. B. Coplen and others, 2002,  
U.S. Geological Survey  
Water-Resources Investigations  
Report 01-4222

Figure 3 - Variations of the lithium isotopic compositions in the natural environments (after Coplen et al., 2002).

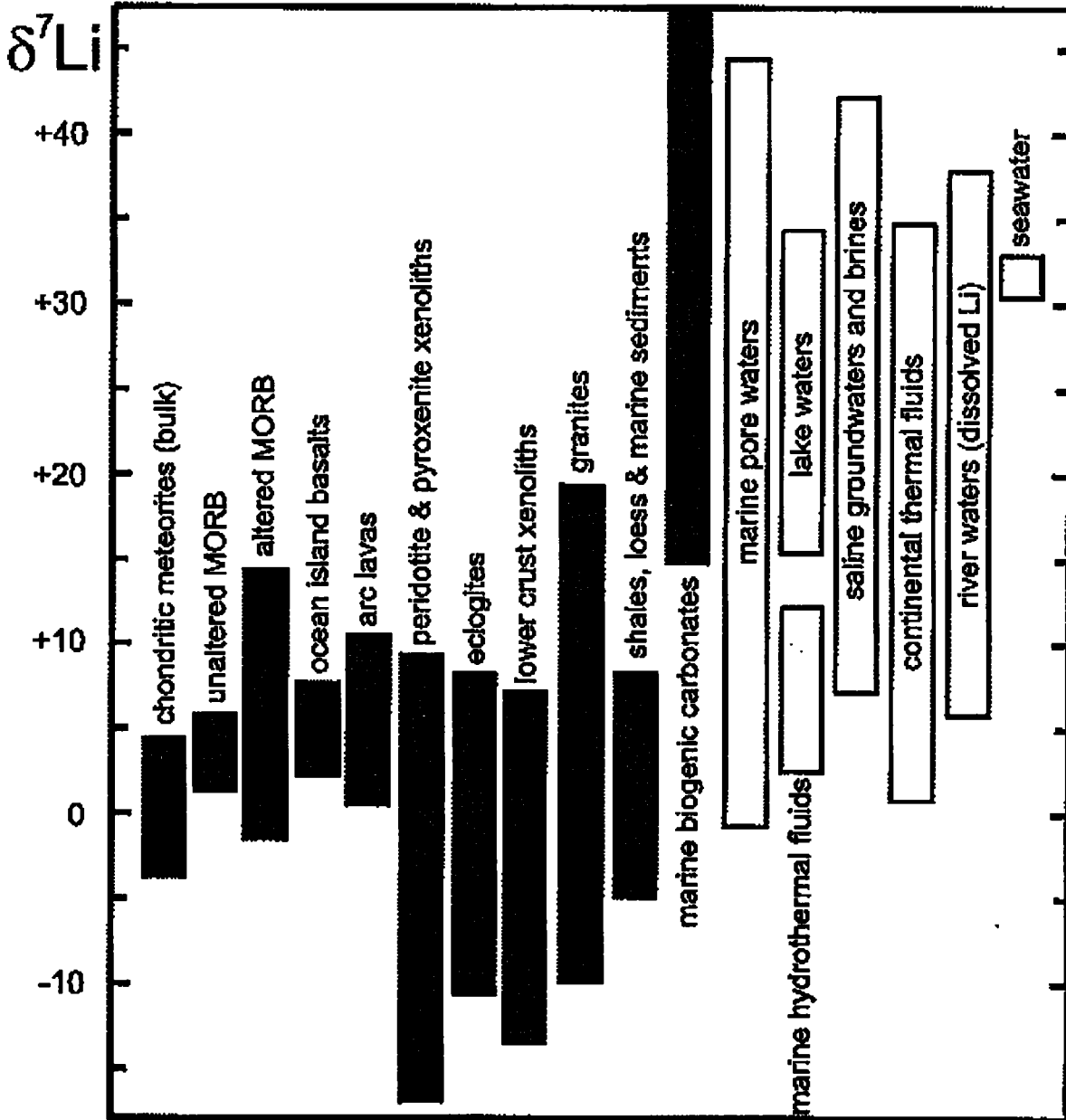


Figure 4 - Summary of lithium isotope compositions of Earth and planetary materials (after Tomascak, 2004). Filled bars are solid samples and open bars are liquids.



Table 1 - Reported lithium isotope compositions for international rock standards (after Tomascak, 2004).

| <i>Name</i> | <i>Producer*</i> | <i>Material</i>       | $\delta^7\text{Li}$ | <i>Source**</i> |
|-------------|------------------|-----------------------|---------------------|-----------------|
| BHVO-1      | USGS             | basalt, Hawaii        | +5.2 ± 0.5 (4)      | 1               |
| BHVO-1      |                  |                       | +5.1 ± 0.4 (2)      | 2               |
| BHVO-1      |                  |                       | +5.0 ± 1.9 (8)      | 3               |
| BHVO-1      |                  |                       | +5.8 ± 1.9 (3)      | 4               |
| JB-2        | GSJ              | basalt, Japan         | +6.8 ± 0.3 (3)      | 4               |
| JB-2        |                  |                       | +5.1 ± 1.1 (4)      | 5               |
| JB-2        |                  |                       | +4.3 ± 0.3 (5)      | 6               |
| JB-2        |                  |                       | +4.9 ± 0.7 (5)      | 7               |
| JB-2        |                  |                       | +5.1 ± 0.4 (3)      | 8               |
| JB-3        | GSJ              | basalt, Japan         | +3.9 ± 0.3 (3)      | 6               |
| SRM-688     | NIST             | basalt, Nevada        | +2.8 ± 1.1 (1)      | 5               |
| JGb-1       | GSJ              | gabbro, Japan         | +6.2 ± 2.5 (3)      | 4               |
| DR-N        | ANRT             | diorite, France       | +2.3 ± 1.1 (3)      | 4               |
| JA-1        | GSJ              | andesite, Japan       | +5.8 ± 0.7 (5)      | 6               |
| G-2         | USGS             | granite, Rhode Island | -0.3 ± 0.4 (3)      | 2               |
| G-2         |                  |                       | -1.2 ± 0.6 (3)      | 4               |
| JR-2        | GSJ              | rhyolite, Japan       | +3.9 ± 0.4 (3)      | 1               |
| JR-2        |                  |                       | +3.9 ± 0.4 (1)      | 2               |
| JR-2        |                  |                       | +3.8 ± 1.0 (3)      | 4               |
| JG-2        | GSJ              | granite, Japan        | -0.7 ± 0.4 (2)      | 2               |
| JG-2        |                  |                       | +0.4 ± 1.0 (4)      | 3               |
| JG-2        |                  |                       | -0.4 ± 0.2 (3)      | 4               |
| UB-N        | ANRT             | serpentine, France    | -2.7 ± 1.1 (4)      | 4               |
| UB-N        |                  |                       | -2.6                | 9               |
| SCo-1       | USGS             | shale, Wyoming        | +5.3 ± 1.5 (3)      | 4               |

Note: uncertainties are those listed in the cited source or recalculated from data therein, 2 $\sigma$  population, where available; number in parentheses is number of analyses factored into this precision, where given

\*Producers: USGS = United States Geological Survey; GSJ = Geological Survey of Japan; NIST = National Institute of Standards and Technology (USA); ANRT = Association Nationale de la Recherche Technique (France)

\*\*Sources: 1 = Chan and Frey (2003); 2 = Pistiner and Henderson (2003); 3 = Bouman et al. (2002); 4 = James and Palmer (2000a); 5 = Tomascak et al. (1999a); 6 = Nishio and Nakai (2002); 7 = Moriguti and Nakamura (1998a); 8 = Chan et al. (2002c); 9 = Benton et al. (in review)

Before studying the worldwide geothermal systems for which there is very few Li isotopic data, we have estimated that it was interesting to examine some fields of application of the Li isotope geochemistry. In particular, we have collected some information about rocks such as basalts, granites or sediments, which often constitute the geothermal reservoirs and are issued from different origin processes (mantellic, crustal or Earth's surface processes). The hydrothermal alteration of the oceanic crust by marine fluids is well-documented in the literature and is very useful for geothermal applications. Many of these data were directly collected from the recent and very complete bibliographic study carried out by Tomascak (2004).

### 3.3.1. Unaltered basalts (mantle processes) and volcanic rocks

The mantle, although Li-poor relative to the continents (3-6 ppm in normal MORB and about 1 ppm in depleted peridotites; Ryan and Langmuir, 1987), is a significant reservoir due to its large volume.

The studies carried out by Chan *et al.* (1992; 1993) suggested that the Li concentrations and  $\delta^7\text{Li}$  values of unaltered recent basalts from Mid-Ocean Ridges (MORB) were relatively homogeneous (5.4-6.0 ppm and 3.4 to 4.7‰, respectively). However, subsequent studies have increased the global range of samples, the diversity of bulk compositions analysed, and the isotopic range ( $\delta^7\text{Li}$  values from 1.5 to 5.6‰; Tomascak and Langmuir, 1999; Tomascak, 2004), which could be interpreted as reflecting heterogeneity in mantle sources of these rocks.

Mantle composition can also be assessed through examination of lavas from other oceanic settings. In a study of well-characterized Hawaiian lavas, Chan and Frey (2003) found a total range in  $\delta^7\text{Li}$  that overlaps the range for MORB (2.5 to 5.7‰). However, these data, when compared with other isotopic and elemental parameters, suggested incorporation of recycled altered oceanic crust into the source of the Hawaiian plume. Other data from Kilauea volcano (Tomascak *et al.*, 1999b) did not show significant variations ( $\delta^7\text{Li} \approx 4‰$ ). The authors conclude that Li isotopic fractionation was absent during the lava formation at 1050-1200°C. On the whole, the analyses of lavas collected from ocean islands (hot spots; Nishio *et al.*, 2003; Ryan and Kyle, 2000) and back-arc basins (Nishio *et al.*, 2002) have indicated  $\delta^7\text{Li}$  values in agreement with the observed range for normal MORB.

As mentioned by Tomascak (2004), unmetasomatized peridotite xenoliths are additional potential sources of information on Li isotopes in the upper mantle. To date, the xenolith data set is very sparse, owing largely to the analytical challenges of these low Li-abundance, Mg, Fe-enriched materials. Chan *et al.* (2002c) determined that an unaltered peridotite from Zabargad Island had  $\delta^7\text{Li} = 5.0‰$ , identical to the value reported for peridotites from the same area. Oceanic peridotite xenoliths from La Palma showed a range of values ( $\delta^7\text{Li} = 4$  to  $7‰$ ), overlapping and slightly higher than the normal MORB range. In spite of the analytical challenges presented by ultramafic rocks, more data from these materials are crucial to an understanding of Li in the mantle, and in resolving questions about the appropriateness of the accepted MORB mantle range.

Lithium isotope characteristics of subduction zones have been considered in multiple thorough studies. Although the role of isotopically light sediments cannot be disregarded, altered oceanic crust is likely to be a primary source of Li to most subduction zone fluids (Tatsumi *et al.*, 1986). Thus, these fluids should be isotopically heavier than MORB. The residue from this dehydration process may, therefore, be enriched in light Li relative to MORB.

The first studies of Li isotopes in subduction zones concentrated on young convergent margin lavas. Moriguti and Nakamura (1998b) reported correlated Li isotope ( $\delta^7\text{Li}$  from 1.1 to 7.6‰) and fluid-mobile element (notably boron) concentration variations in the Izu arc, south-eastern Japan, consistent with significant incorporation of Li from altered oceanic crust into arc lava sources (fig. 5). A similar trend has been reported in samples of basalts and basaltic andesites from Mt. Shasta, California ( $\delta^7\text{Li}$  from 2.5 to 6.5‰; Magna *et al.*, 2003). North-eastern Japan arc lavas have isotopic compositions like MORB ( $\delta^7\text{Li}$  from 1.5 to 5.5‰; Moriguti and Nakamura, 2003). Bouman and Elliott (1999) suggested that isotopic relations for Marianas samples ( $\delta^7\text{Li}$  from 0.7 to 7.6‰) could be satisfied by differences in inputs from isotopically light subducted sediments and isotopically heavier subducted altered oceanic crust. The  $\delta^7\text{Li}$  values generally observed in global arc lavas are shown in figure 6.

Samples of fresh volcanic lavas collected in the geothermal areas of Bouillante and Diamant, located in the Guadeloupe and Martinique Islands, respectively, which belong to the Caribbean island arc, indicated Li concentrations of 7-13 ppm and  $\delta^7\text{Li}$  values of 3-5‰ (BRGM data) whereas more heterogeneous data were found for samples of hydrothermally altered lavas: Li concentrations of 5-24 ppm and  $\delta^7\text{Li}$  values ranging from -3.3 to 10.5‰ (BRGM data). A Li concentration of 15 ppm and a  $\delta^7\text{Li}$  value of 5.4‰ were analysed on a sample of fresh micro-syenite collected in the Reunion Island (BRGM data), a Hot Spot in the Indian Ocean.

In the geothermal area of Lamentin (Martinique Island), which also belongs to the Caribbean island arc and where alternated volcano-sediments formations occurs at sub-surface, all the  $\delta^7\text{Li}$  values analysed in core samples collected from 1 km-deep drill-holes are negative and range from -4.7 to -0.8‰ (BRGM data). These negative values can be very probably attributed to the presence of sediments (see section 3.3.3). The corresponding Li concentrations vary from 11 to 74 ppm.

### 3.3.2. Granites (continental crust)

Estimates of the Li isotopic composition of granitic rocks from various regions span a very wide range. A number of granitic and rhyolitic rock standards have been analysed, and they showed generally light but variable isotopic compositions:  $\delta^7\text{Li} = -1.2$  to  $3.9\text{‰}$  (tabl. 1; James and Palmer, 2000a; Bouman *et al.*, 2002; Chan and Frey, 2003; Pistiner and Henderson, 2003). The only large studies of granitic rocks to date examined rocks from eastern Australia, finding a range in  $\delta^7\text{Li}$  from -1.4 to  $8.0\text{‰}$  (Bryant *et al.*, 2003b; Teng *et al.*, 2004). Of these, the granites derived from predominantly meta-sedimentary source rocks had lighter average compositions ( $\delta^7\text{Li} = -1.4$  to  $2.1\text{‰}$ ) than I-type granites ( $1.9$  to  $8.0\text{‰}$ ). Composite samples of granitic rocks from throughout China also had light isotopic compositions ( $-3.4$  to  $3.0\text{‰}$ ; Teng *et al.*, 2004).

Four core samples of fresh granite collected from deep geothermal wells located at Soultz-sous-Forêts (Alsace, France) indicate Li concentrations of 29-69 ppm and  $\delta^7\text{Li}$  values ranging from -0.6 to  $2.1\text{‰}$  (BRGM data). Three core samples of hydrothermally altered granite have Li concentrations of 16-23 ppm and  $\delta^7\text{Li}$  values ranging from -3.5 to  $4.0\text{‰}$  (BRGM data).

Individual samples of isotopically heavier granitic rocks have also been reported from the Canadian Shield ( $\delta^7\text{Li} = 7.3$  to  $11.3\text{‰}$ ; Bottomley *et al.*, 2003) and from the Isle of Skye, Scotland ( $\delta^7\text{Li} = 8.1\text{‰}$ ; Pistiner and Henderson, 2003). These are all rocks with long near-surface histories and modal Chlorite or Epidote, suggesting their isotopic compositions may not be pristine, igneous values.

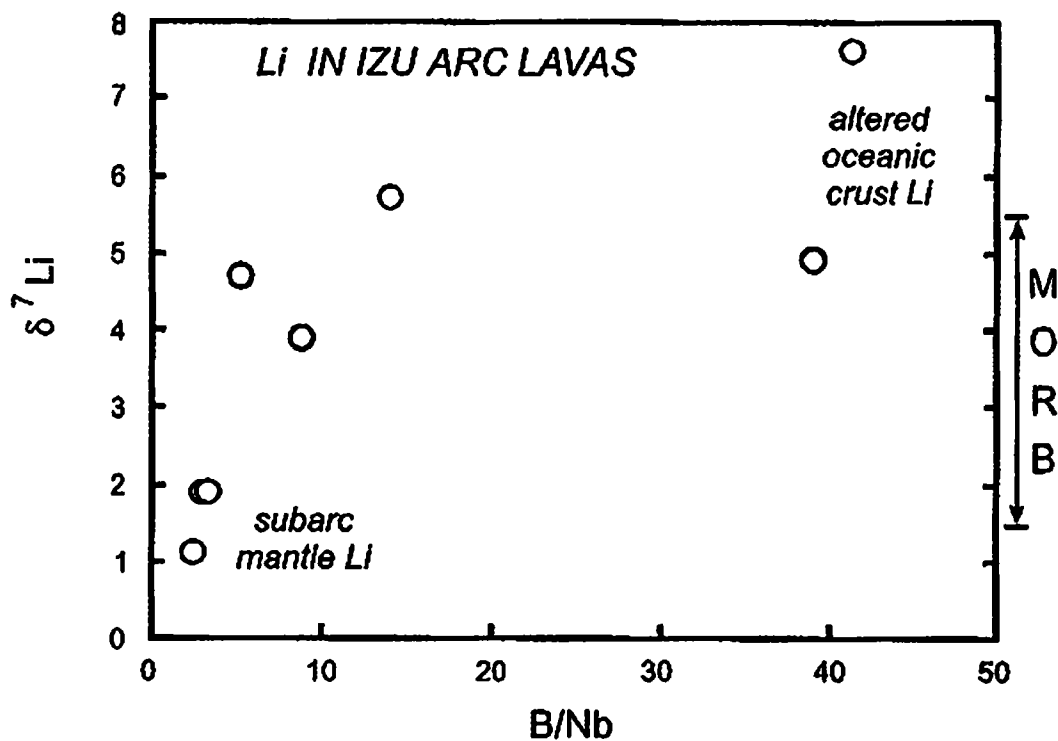


Figure 5 - Plot of Li isotopic composition versus B/Nb for a suite of samples from the Izu arc (after Moriguti and Nakamura, 1998b).

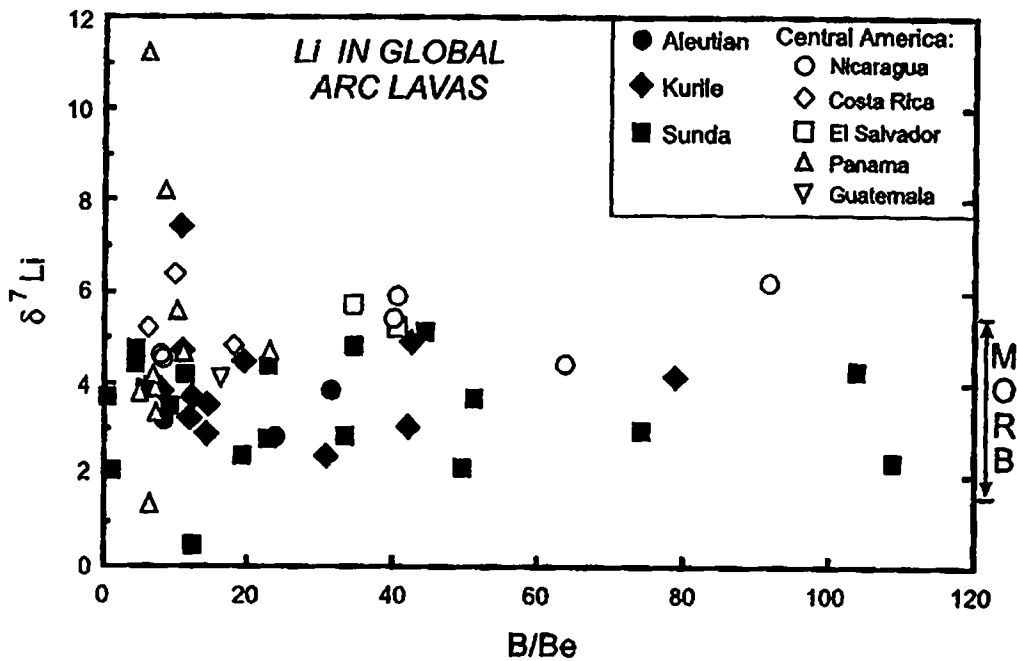


Figure 6 - Plot of Li isotopic composition versus B/Be for several suites of volcanic arc lavas (after Tomascak, 2004).

### 3.3.3. Sedimentary rocks

Lithium isotope studies of sediments and sedimentary rocks have thus far concentrated on marine clastic and carbonate materials. No systematic description of the effects of diagenetic processes on sediments has been made. Clay rich sediments are important to Li budgets in near-surface systems, as they concentrate Li relative to marine carbonates, which are among the most Li-impoverished materials in the crust (Ronov *et al.*, 1970). Lacustrine carbonates have higher Li concentrations than their marine counterparts, and minerals generated in evaporitic environments are commonly enriched in Li (Tardy *et al.*, 1972; Calvo *et al.*, 1995).

The first modern publication of Li isotope data from sediments came from Chan *et al.* (1994), who reported the isotopic compositions of unaltered turbidites from DSP Hole 477 and 477A, from the Gulf of California. These samples have been reanalysed, yielding lighter values. Similarly, Chan and Frey (2003) suggested a range for marine clastic sediments ( $\delta^7\text{Li} = -1.0$  to  $5.6\text{‰}$ ) based on new data and re-analysis of samples previously considered to be isotopically heavy.

Contact metamorphosed, hydrothermally altered and Greenschist facies metamorphosed equivalents of these sediments showed a wide range of generally lighter compositions ( $\delta^7\text{Li}$  as low as  $-1.3\text{‰}$ ), and all altered samples had lower Li contents by  $> 1.4\text{x}$ , consistent with removal of Li during  $> 300^\circ\text{C}$  alteration.

Sediments ranging from clay-rich to carbonate-rich from ODP Sites 1039 and 1040, outboard of Costa Rica, had variable isotopic compositions, unrelated to their bulk chemistry ( $\delta^7\text{Li} = 9.5$  to  $23.3\text{‰}$ ; Chan and Kastner, 2000). Turbidites and underlying ash-rich mudstones at ODP Site 808, southwest of Japan, defined a similarly large range in isotopic compositions ( $\delta^7\text{Li} = -1.0$  to  $8.0\text{‰}$ ; You *et al.*, 1995). James *et al.* (1999) reported  $\delta^7\text{Li}$  values for variably altered sandy to silty turbidites to hemipelagic muds from ODP Site 1038, off the coast of northern ( $-0.5$  to  $5.6\text{‰}$ ).

Data for shales range from  $\delta^7\text{Li} = 4.5$  to  $8.0\text{‰}$  for formations in the western U.S. (James and Palmer, 2000a; Sturchio and Chan, 2003), to light values for the Shimano shale, Japan ( $\delta^7\text{Li} = -2.7$  to  $-1.5\text{‰}$ ; Moriguti and Nakamura, 1998b). These ranges overlap measurements from the one large-scale study of sedimentary materials to date (Teng *et al.*, 2004). This study reported data for five loess localities ( $\delta^7\text{Li} = -3.1$  to  $4.8\text{‰}$ ) and for nine shales ( $\delta^7\text{Li} = -3.2$  to  $3.9\text{‰}$ ) used in the compilation of the Post-Archean average Australian Shale Composition (PASC) of Nance and Taylor (1976). Composite samples of well-characterized sedimentary rocks from throughout China give a similar range of values ( $\delta^7\text{Li} = -5.2$  to  $1.2\text{‰}$ ; Teng *et al.*, 2004). The isotopically light values from these sedimentary rocks contrast with a measurement of Vicksburg, Mississippi loess ( $\delta^7\text{Li} \approx 15\text{‰}$ ; Huh *et al.*, 1998).

According to Tomascak (2004), minerals derived from evaporation of saline solutions have not been extensively examined. Evaporitic salts from the western U.S. Great Basin concentrated  $^7\text{Li}$  ( $\delta^7\text{Li}$  from  $31.8$  to  $32.6\text{‰}$ ; Tomascak *et al.*, 2003). Evaporation of thermal waters from Yellowstone yielded Travertine with extremely low  $\delta^7\text{Li}$  ( $-4.8\text{‰}$ ; Sturchio and Chan, 2003), offset from its coexisting fluid by  $-11.1\text{‰}$ . Such evaporites, where preserved in the sedimentary record, could afford an opportunity to examine variations in spring water compositions and hence information on hydrothermal processes over time.

To understand the role of subducted sediments in arc magmatism and the formation of the continental crust, Chan *et al.* (2006) have determined the Li isotopic composition of marine sediments subducting at several trenches, as well as from non convergent margin settings. The bulk Li isotopic composition of global sediments varies widely ( $\delta^7\text{Li} = -4.3$  to  $14.5\text{‰}$ ), reflecting sediment type, provenance, and diagenetic processes. Among detrital sediments ( $\delta^7\text{Li} = -1.5$  to  $5\text{‰}$ ), clay-rich variants are generally isotopically lighter than sands owing to isotopic fractionation during continental weathering. Sediments derived from mature continental crust are especially light. Volcanogenic sediments can have either heavier or lighter isotopic compositions than the mantle depending on alteration effects. Biogenic carbonate and silica are susceptible to re-crystallization, which results in heavier isotopic compositions ( $\delta^7\text{Li} = 6$  to  $14.5\text{‰}$ ). The lightest composition was observed in hydrothermally leached sediments ( $\delta^7\text{Li} = -4.3\text{‰}$ ). Slowly accumulated metalliferous sediments display anomalously high  $\delta^7\text{Li}$  values (6 to  $10\text{‰}$ ) due to incorporation of seawater-derived Li. On the basis of this and previous studies, integrated  $\delta^7\text{Li}$  values for subducted sediment-derived Li also vary from arc to arc, ranging from  $-0.4$  to  $9.0\text{‰}$ .

Chan *et al.* (2006) conclude that, although clay-rich sediments can contribute to the Li light isotopic composition of continental crustal rocks, their study suggests diverse compositions of sedimentary rocks. Incorporation of sedimentary components in the formation of granite rocks may give rise to greater heterogeneity in the composition of the upper continental crust than is currently estimated.

### 3.3.4. Hydrothermally altered oceanic crust

Chan *et al.* (1992) have shown that the alteration of the oceanic crust by seawater at low temperature was able to generate  $\delta^7\text{Li}$  values up to  $14\text{‰}$  for the oldest basalts (46 My). Given the difference in Li concentration between MORB and sea floor altered MORB (which are commonly higher than 12 ppm; Chan *et al.*, 1992), small contributions of altered oceanic crust could have a substantial impact on the measured Li isotopic composition of sea floor lavas.

#### ***a) Laboratory experiments and Li isotopic fractionation as a function of the temperature***

Laboratory experiments have been carried out in order to gain insight on Li isotope behaviour during interaction of high temperature fluids and various materials. All the experimental evidence shows extraction of Li from basalt, altered basalt and sediments even at temperatures  $< 100^\circ\text{C}$ . Lithium was incorporated into clays (smectites, illites, etc.) at temperatures up to  $150^\circ\text{C}$  during basalt alteration (Seyfried *et al.*, 1984; James *et al.*, 2003) and even, at a lesser extent, at temperatures up to  $250^\circ\text{C}$  (Millot *et al.*, 2009), with affinity proportional to the fluid/rock ratio, such that Li was simultaneously added to and removed from fluids. Under high temperature, solid-dominated hydrothermal conditions ( $350^\circ\text{C}$ ), Li was universally removed from materials and kept in solution, rather than in alteration minerals. A high mobility of this element was observed.

The Li isotopic fractionation  $\Delta^7\text{Li}_{\text{solution-altered rock}}$  (in per mil) is defined as follows:

$$\Delta^7\text{Li}_{\text{solution-altered rock}} = 1000 \text{Ln} (\alpha_{\text{solution-altered rock}})$$

where  $\alpha_{\text{solution-altered rock}} = \left(\frac{^7\text{Li}/^6\text{Li}}{\text{solution}}\right) / \left(\frac{^7\text{Li}/^6\text{Li}}{\text{altered rock}}\right)$  is the Li isotopic fractionation factor.

If  $\delta^7\text{Li}_{\text{solution}}$  and  $\delta^7\text{Li}_{\text{altered rock}}$  are sufficiently low, we have:

$$\begin{aligned}\Delta^7\text{Li}_{\text{solution-altered rock}} &\approx 1000 \ln (1 + [(\delta^7\text{Li}_{\text{solution}} - \delta^7\text{Li}_{\text{altered rock}}) / 1000]) \\ &\approx \delta^7\text{Li}_{\text{solution}} - \delta^7\text{Li}_{\text{altered rock}}\end{aligned}$$

Most of the Li isotopic fractionation values reported in the literature comes from studies of interaction between seawater and more or less altered basalts. The isotopic fractionation factors inferred from these studies give  $\Delta^7\text{Li}_{\text{solution-altered rock}}$  values of 4‰ at 350°C, 9‰ at 160°C and 19‰ at 2°C (Chan and Edmond, 1988; Chan *et al.*, 1992; 1993; 1994; James *et al.*, 1999). These values are represented in figure 7 as “hydrothermal basalt alteration” for which the following empirical equation was reported by James *et al.* (1999):

$$\Delta^7\text{Li}_{\text{solution-altered rock}} = 7600 / T(^{\circ}\text{K}) - 8.39$$

Chan *et al.* (1994) also showed that the Li isotopic composition of the fluids decreased with increasing temperature.

The experimental results found by Millot *et al.* (2009) involving dilute seawater and basalt (water-rock ratio:  $w/r = 10$ ) at temperatures ranging from 25 to 250°C are in good agreement with the relationship “hydrothermal basalt alteration”, estimated from data inferred from natural systems (see fig. 7). The equation of the empirical relationship obtained by Millot *et al.* (2009) is:

$$\Delta^7\text{Li}_{\text{solution-altered rock}} = 7847 / T(^{\circ}\text{K}) - 8.093 \quad (r^2 = 0.93)$$

Wunder *et al.* (2006) have recently reported a temperature-dependent relationship of Li isotopic fractionation determined from experiments between Li-bearing Clinopyroxene and aqueous fluids at temperatures between 500 and 900°C at 2.0 GPa. According to these authors, there is fractionation (about 1‰), even at very high temperature (900°C). This relationship, shown in figure 7 for comparison (dashed-line corresponds to an extrapolation for temperatures below 500°C), cannot be directly compared with the other ones because the experimental conditions (temperature and pressure range, initial solids, water-rock ratio, etc.) are very different.

### **b) Alteration conditions of the upper oceanic crust**

Chan *et al.* (2002a) present Li concentrations and isotopic profiles through the upper 2 km of oceanic crust, which represent a record of the alteration conditions and Li exchange processes as a function of depth.

In the upper part of the volcanic section, the unaltered basalts have typical Li concentrations and  $\delta^7\text{Li}$  values found for fresh MORB (Chan *et al.*, 1992). Interaction of these basalts with seawater at low temperatures (< 100°C) leads to alteration phases, especially red halos and breccias, which are enriched in Li (5.6-27.3 ppm) and isotopically heavier ( $\delta^7\text{Li}$  from 6.6 to 20.8‰) relative to fresh MORB. Seawater Li can be incorporated into alteration clays by substituting for Mg in the octahedral site. Secondary minerals including saponite, celadonite, and phillipsite present in the altered extrusive rocks can serve as host minerals. Because seawater is isotopically heavier than MORB by about 28‰ (Chan and Edmond, 1988; You and Chan, 1996), Li uptake with attendant isotopic fractionation results in an increase in  $\delta^7\text{Li}$  in the weathered basalt.

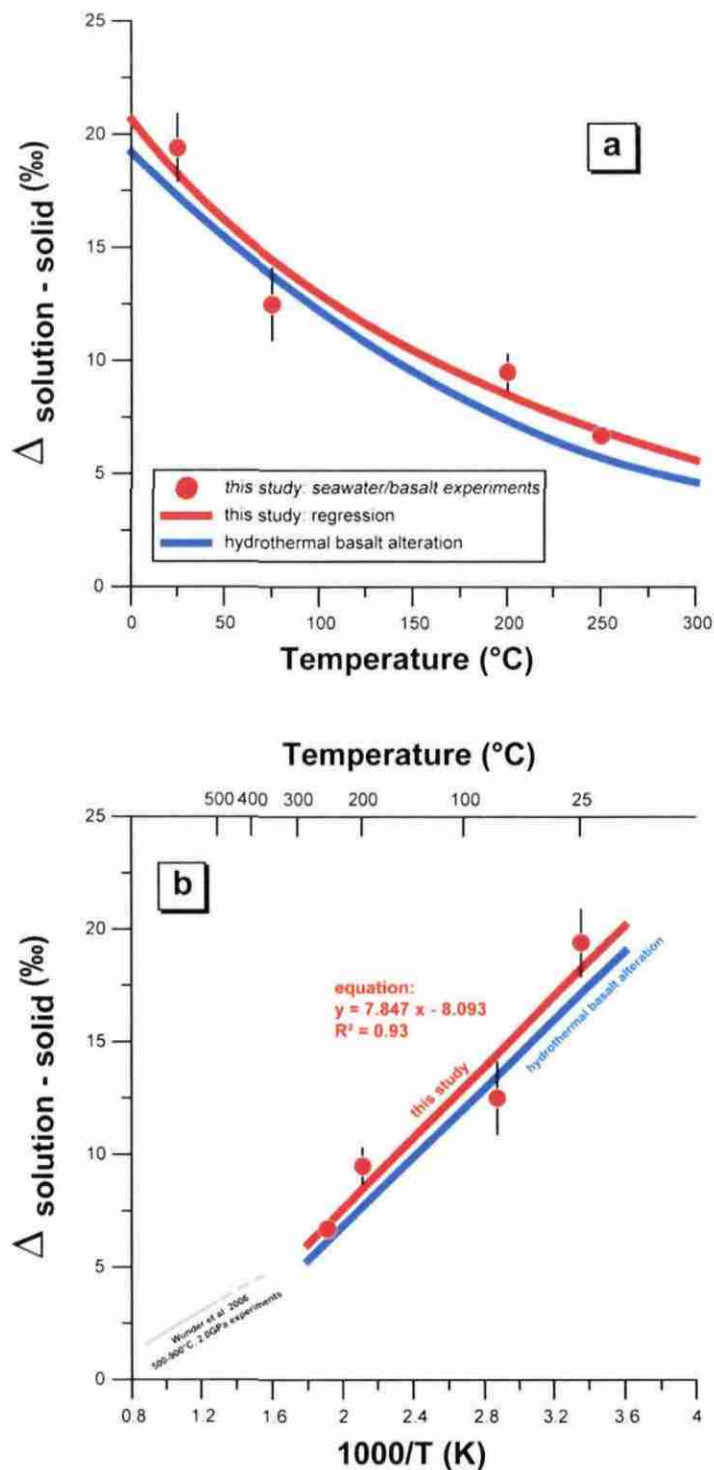


Figure 7 - (a) Lithium isotopic fractionation between solution and solid ( $\Delta_{\text{solution} - \text{solid}}$ ) determined in our experiments vs. the interaction temperature (red circles and red curve). (b) Lithium isotopic fractionation between solution and solid ( $\Delta_{\text{solution} - \text{solid}}$ ) calculated in our experiments (red circles) vs. the inverse of the temperature of interaction ( $1000/T$ , °K). The red line represents the correlation obtained in our experiments (after Millot et al., 2009).



In contrast to the upper volcanic section, the rocks from the lower portion (up to 150°C) fall in the domain of unaltered MORB because of reduced permeability, restricted fluid flow and rock-dominated conditions. The transition zone, which marks the contact between volcanic flows and dikes and is a zone where up-welling hydrothermal fluids mixed with cold seawater, is characterized by enrichment of Li but light isotopic composition (between -0.8 and 2.1‰) resulting from precipitation from mixtures of seawater and Li-rich hydrothermal fluids. Rocks are hydrothermally altered at a wide range of temperatures (100-380°C) but predominantly at sub-Greenschist to Greenschist conditions. The main secondary minerals include chlorite, mixed-layer smectite, actinolite, quartz and pyrite.

Below the transition zone, the sheeted dikes exhibit decreasing Li concentration with depth. Interaction of seawater-derived hydrothermal fluids at high temperatures and low water-rock ratios results in depletion of Li and light isotopic composition in the Greenschist and sub-amphibolite facies rocks. The range of  $\delta^7\text{Li}$  (-1.7 to 7.9‰) may be explained by varying fluid composition, temperature-dependent isotopic fractionation, and water-rock ratio. Throughout the upper dike complex, Li isotopic compositions are lighter than fresh MORB ranging from -1.7 to 2.4‰. In the deeper dike section,  $\delta^7\text{Li}$  values range from 0.7‰ to MORB-like values. The general trend toward heavier isotopic composition at depths reflects reduced isotopic fractionation at higher temperature.

The water-rock interactions in the dike complex may be examined using the model of Magenheim *et al.* (1995). In this model, the calculation of the water-rock ratio is made by using infinitely small dissolution and precipitation steps. The rock is incrementally destroyed, and Li is partitioned into the fluid and alteration phases. The relationship of the integrated concentration of the two isotopes X and Y in solution with water-rock ratio is described in the following two equations:

$$r/w = -1/K \times \ln[(X_r - KX)/(X_r - KX_0)] \quad (1)$$

$$r/w = -\alpha/K \times \ln[(Y_r - KY/\alpha)/(Y_r - KY_0/\alpha)] \quad (2)$$

$X_0$  and  $Y_0$  are the initial concentrations of the two isotopes in the starting solution. K is the distribution coefficient of an isotope between the solution and the altered phase, so that:

$$X_{\text{alt}} = KX \text{ and } Y_{\text{alt}} = KY/\alpha$$

In this model calculation, the Li concentration and  $\delta^7\text{Li}$  for the fresh rock are taken as 3 ppm and 4‰, consistent with the least altered rocks. Since K and  $\alpha$  are dependent on temperature, different values are assumed to accommodate the temperature ranges of the upper and lower dike sections. The distribution coefficients based on the experimentally determined values for chlorite (Berger *et al.*, 1988) are adopted as an approximation. K = 0.40-0.23 for the temperature range of 260-400°C are used for the dike section. The isotopic fractionation factors of Li are estimated from high-temperature vent fluids (Chan *et al.*, 1993), using  $\alpha = 1.006-1.003$  for temperatures of 260-400°C. With these parameters and seawater as an initial solution,  $\delta^7\text{Li}$  of the fluids and the alteration phases with which they are equilibrated can be calculated. Because the composition of down-flowing seawater may change by reaction with basalts, it was also considered an initial solution with an evolved composition having half of the original seawater Li concentration and a  $\delta^7\text{Li}$  of 44‰, much like the sediment pore fluids where Li is depleted by volcanic ash alteration (Zhang *et al.*, 1998).

The calculated  $\delta^7\text{Li}$  of the alteration phase as a function of water-rock ratios and temperature are shown in figure 8. The model calculations show that  $\delta^7\text{Li}$  in the alteration phases decreases with decreasing water-rock ratio. At very low water-rock ratios where rock dominates,  $\delta^7\text{Li}$  increases to approach the rock composition. At a given water-rock ratio, precipitates formed at lower temperatures have a lighter isotopic composition due to larger isotopic fractionation. The evolved fluid yields lower  $\delta^7\text{Li}$  in the altered phases compared to seawater, but the differences are very small at water-rock ratios  $< 1$  (fig. 8).

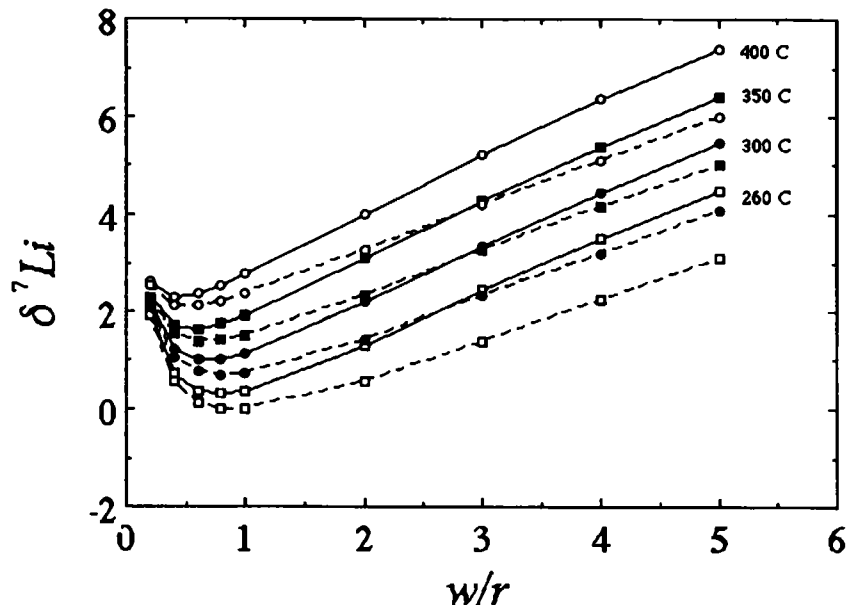


Figure 8 - Calculations of  $\delta^7\text{Li}$  change in alteration phase with  $w/r$  ratios during interaction of basalt with seawater at high temperatures, according the model of Maggenheim *et al.* (1995) (after Chan *et al.*, 2002). Solid lines are model curves with seawater as the starting fluid and dashed lines are for an evolved seawater fluid as the initial fluid.

Rocks at the top of the dike section have lower  $\delta^7\text{Li}$  values (-1.7 and -1.4‰) than predicted by the model. These enrichments can be explained by equilibration with the up-welling hydrothermal fluids at moderate temperatures, hence greater isotopic fractionation, much like that in the transition zone. In the deeper dike section,  $\delta^7\text{Li}$  values of highly altered (light gray) rocks range from 0.7‰ to 2.7‰. This range of isotopic compositions can be produced by reaction of the rocks with seawater at temperatures of 260-400°C and water-rock ratios less than 1 (fig. 8). Oxygen isotope systematics also indicates water-rock ratios of 0.1-1.5 for the dike section (Alt *et al.*, 1986).

Chan *et al.* (2002a) conclude that crustal rocks of different alteration zones exhibit distinct characteristics in Li abundance and isotopic composition, making Li a sensitive indicator of the conditions and history of alteration. The data provide a rock-based constraint on the Li budget in the ocean. Flux calculations were carried out based on the Li contents and proportions of various alteration types. Overall the upper 1.8 km is a sink for oceanic Li with a heavy isotopic signature. Various alteration zones of the oceanic crust are isotopically distinct from the upper mantle. Li isotope systematics may therefore be applied to examine the source components of arc magmas and possibly recycling of crustal material in the deep mantle.

The upper sheeted dike complex of the oceanic crust located just below the transition zone between andesite volcanic lava flows and basaltic dikes, in which Li is extracted by hydrothermal fluid circulation, can be characterized by lighter Li isotopic values (from -5 to 1‰; Chan *et al.*, 1996), indicating retention of  $^6\text{Li}$  by the altered rocks. According to Chan *et al.* (1992) who analyzed an altered metabasalt (abundance of chlorite with minor amphibole) from the ocean floor of the MAR median valley, with a  $\delta^7\text{Li}$  value of -2.1‰, “Li is not quantitatively extracted by the circulating fluid but may be partially retained in the greenschist facies minerals during hydrothermal activity, the lighter isotope being preferentially taken up in the solid phase”.

Subsequent reports of hydrothermally or greenschist facies metamorphosed sediments and basalt in the oceanic crust demonstrate reduction in lithium concentrations and a general trend toward lighter isotopic compositions (Chan *et al.*, 1994; You *et al.*, 1995; James *et al.*, 1999).

### 3.3.5. Serpentinization of mantle rocks

In oceanic fracture zones as well as in actively-upwelling forearc mud volcanoes, seawater or other marine fluids interact directly with mantle rocks. Serpentinization of mantle rocks at temperatures broadly < 350°C involves influx of water, as well as general increase in lithium concentration in the newly-formed hydrous assemblage. Considering the low temperatures involved, Li isotope exchange during seawater-mantle interaction can be expected. Results from dredged serpentinites (Decitre *et al.*, 2002) and from forearc mud volcanoes (Savov *et al.*, 2002; Benton *et al.*, 1999) gave a consistent picture of fluid evolution during progressive interaction. Serpentinites in both studies were enriched in Li over unmetasomatized mantle rocks and were isotopically heterogeneous, ranging from much lighter than ordinary mantle rocks to slightly heavier ( $\delta^7\text{Li} = -6.1$  to 14.2‰ for bulk analyses, -19 to 28‰ for *in-situ* analyses). Despite the differences in nature of formation of these two suites of serpentinites, the samples that showed the most coherent relations between elemental and isotopic data had a coincident mean  $\delta^7\text{Li} = 7 \pm 5\%$ , which was interestingly similar to the average composition of sea floor hydrothermal vent fluids ( $8 \pm 4\%$ ).

In table 1, a value of  $\delta^7\text{Li} = -2.7\%$  is given for an international serpentine standard. Metasomatized mantle xenoliths, thought to derive ultimately from subduction-zone mantle that was affected by components (fluids and/or melts) discharged from the subducting lithosphere, are additional windows into mass transfer at convergent margins and into elemental cycling in the mantle. Pyroxenite veins from peridotites on Zabargad Island were dominantly isotopically heavier than their normal-mantle hosts ( $\delta^7\text{Li} = 8.6$  to 11.8‰), but also showed light values (-4.2‰; Brooker *et al.*, 2000). These signatures were interpreted to derive from metasomatism of subarc mantle by materials related to Pan-African subduction. Metasomatized xenoliths studied by Nishio *et al.* (2004) show a diversity of Li isotopic compositions ( $\delta^7\text{Li} = -17.1$  to 6.8‰), some of these correlated with variations in radiogenic isotopes. Other examples of light  $\delta^7\text{Li}$  values, especially in pyroxenes or phlogopite ( $\delta^7\text{Li}$  up to -17 and -20‰), can be found in the literature for xenoliths or peridotites (Zindler and Hart, 1986; Jeffcoate *et al.*, 2007; Parkinson *et al.*, 2007; Tang *et al.*, 2007; Ionov and Seitz, 2008). These results show that strongly isotopically fractionated Li from crustal sources plays a role in the mantle. Processes active in subduction zones appear to be cardinal in the control of the Li isotopic composition of different parts of the mantle. However, significant variations of  $\delta^7\text{Li}$  in lava-hosted suites could be also related to different cooling times for thicker and thinner flows (re-distribution of Li between minerals, diffusive fractionation of Li isotopes with a magnitude depending on modal ratios of olivine and pyroxenes, grain size and other factors).

### 3.4. ISOTOPIC LI DATA RELATIVE TO THE GEOTHERMAL WATERS

Contrary to the marine hydrothermal fluids associated to the mid-ocean ridges or subduction areas, few Li isotopic data exist for the fluids of the geothermal systems.

#### 3.4.1. Marine hydrothermal fluids

Numerous Li isotopic data relative to the marine hydrothermal fluids were found in the literature (see table in appendix 1; fig. 9). The up-welling fluids are a significant source of Li to the oceans, although the magnitude of the hydrothermal flux is not precisely quantified (Elderfield and Schultz, 1996). Lithium is enriched in high temperature (350°C) vent fluids by a factor of 20-50 relative to seawater (Edmond *et al.*, 1979; Von Damm, 1995). Global mean of  $\delta^7\text{Li}$  for high temperature mid-ocean ridge vent fluids is  $7.5 \pm 1.6\text{‰}$  (Chan *et al.*, 1993; Bray, 2001) and the isotopic compositions of hydrothermal fluids are not affected by phase separation (James *et al.*, 1999). A value of 8.1‰ is proposed by Tomascak (2004). The constancy of fluid  $\delta^7\text{Li}$  is interpreted to be the result of isotopic equilibrium between the hydrothermal fluids and Greenschist facies alteration mineral assemblage (Bray, 2001).

The Li isotopic compositions of marine hydrothermal vent fluids range from MORB-like to heavier compositions with an average value of 5.1‰ (Tomascak, 2004). Fluids from vents in various settings can show a degree of isotopic variability with values extending from the MORB range to several per mil heavier ( $\delta^7\text{Li}$  from 2.6 to 11.6‰; fig.9; Chan and Edmond, 1988; Chan *et al.*, 1993; 1994; Bray, 2001; Foustoukos *et al.*, 2003). In areas where subsurface mixing of hydrothermal fluids and cold seawater is important, isotopic signature of the fluids would be modified by precipitation of secondary minerals and heavier isotopic compositions in the resulting colder diffuse flows are expected.

In view of the absence of correlation between  $\delta^7\text{Li}$  and spreading rate, Chan *et al.* (1993) suggested that circulating mid-ocean ridge hydrothermal fluids derived most of their Li from young, deep unaltered basaltic crust (lower dikes), and not from older, sea floor altered basalts. The altered basalts have higher Li concentrations and markedly heavier isotopic signatures compared to unaltered basalts. High temperature fluids from systems capped with thick sediment cover showed similar concentration and isotopic ranges as those from ridge areas that lack sediment cover, requiring the development of the isotopic signature by deeper processes that are not vitally affected by shallow materials that are enriched in Li available for hydrothermal leaching (Chan *et al.*, 1994).

Lithium concentration and isotopic composition of the reacted fluids seem to depend on the temperature, substrate composition, water-rock ratio and degree of hydrothermal interaction. At high temperature (> 200°C), seawater would extract Li from basalts, while at low temperatures (< 150°C), Li would be removed from seawater into alteration phases.

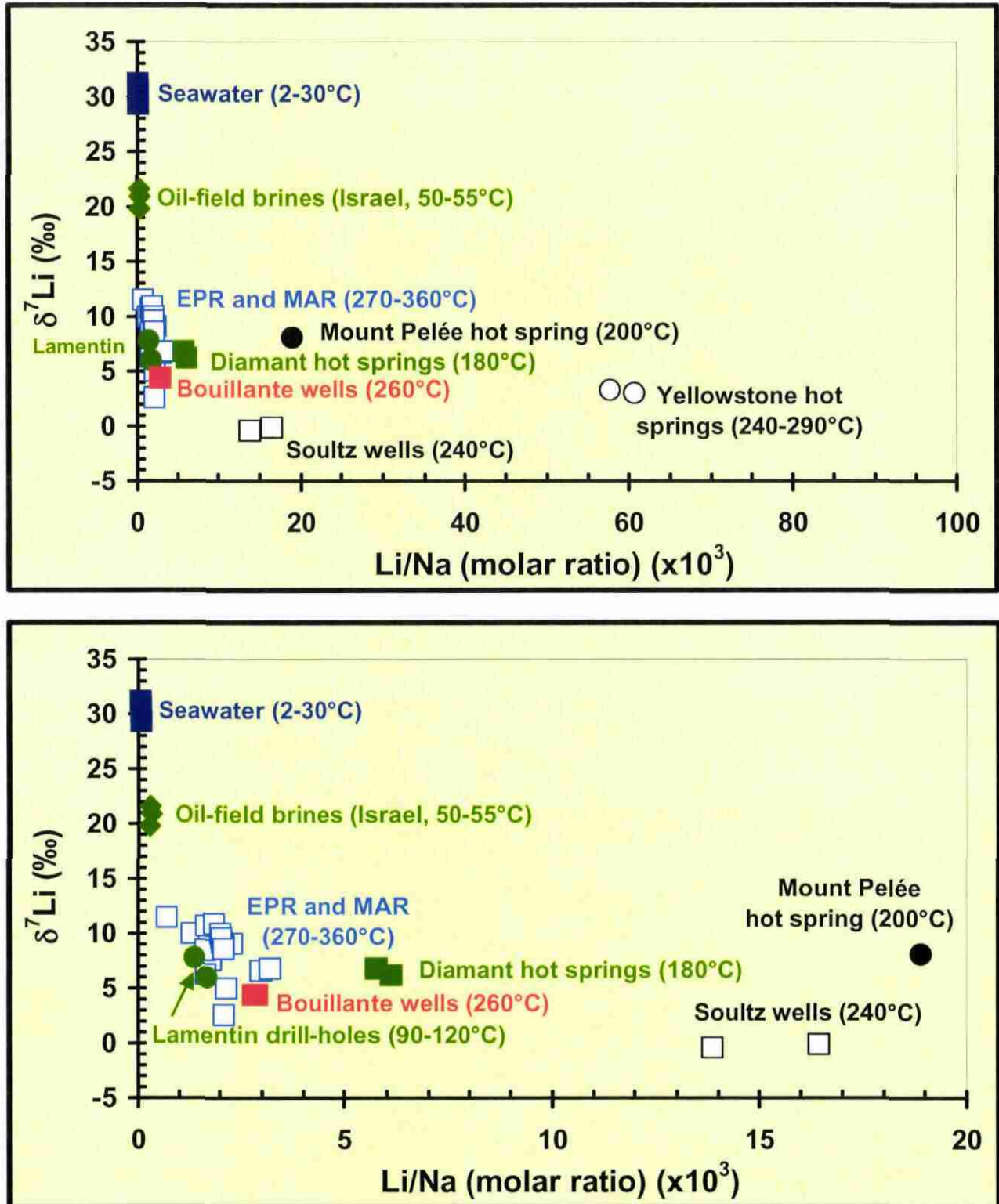


Figure 9 - Variation of  $\delta^7\text{Li}$  values as a function of the molar Li/Na ratios for some marine hydrothermal waters (EPR and MAR), oil-field brines and geothermal waters.

### 3.4.2. Geothermal fluids

The rare  $\delta^7\text{Li}$  isotopic values relative to the geothermal fluids range from -1 to 34.8‰. Some data are reported in appendix 1 and figure 9. Continental hot spring waters, where essentially undiluted, have high Li concentrations (most in the range 0.1 to 10 ppm; Brondi *et al.*, 1973; White *et al.*, 1976; Shaw and Sturchio, 1992). Although they showed a large range in Li isotopic composition ( $\delta^7\text{Li}$  from 1.0 to 34.8‰; Bullen and Kharaka, 1992; Falkner *et al.*, 1997; Sturchio and Chan, 2003; Tomascak *et al.*, 2003), the majority of these fluids were fairly similar to marine hydrothermal vent fluids in terms of Li concentration and isotopic composition (average  $\delta^7\text{Li}$  = 5.1 vs. 7.5-8.1‰ in vent fluids). Extensive hydrothermal alteration will yield fluids with isotopic compositions that approach those of the materials from which Li is originally leached. Extant evidences from the eastern Sierra Nevada and Long Valley, California, and Yellowstone, Wyoming (USA), are consistent with local geology having Li isotope characteristics congruent with the thermal fluids emanating from springs in these areas. The isotopically light sources of thermal waters at Yellowstone, lighter than any of the potential source materials of the area, would be satisfied by the high temperature dissolution of pre-existing alteration minerals in altered volcanic rocks, analogous to the laboratory results of granite dissolution by Pistiner and Henderson (2003).

Sturchio and Chan (2003) successfully interpreted the Li isotope variations of thermal waters (from 1.0 to 6.5‰) and various rock types from drill cores and outcrops in the Yellowstone National Park, Wyoming-Montana (USA), hydrothermal system, using simple isotopic fractionation models for closed- and open-system Li isotope exchange, with mass transfer constraints from Li/Cl ratios of thermal waters. These data and models show that Li isotope ratios provide a sensitive indicator of active hydrothermal alteration. Mass balance considerations indicate that the long-term discharge of Li from the Yellowstone hydrothermal system may be sustained in large part by deep input of high-salinity magmatic brine.

Combinations of mineral reactions at lower temperatures and mixing with more dilute fluids (surface fresh waters, for example) are likely to result in the variations in concentration and isotopic composition in many of the continental thermal spring waters but not seen in their marine relatives. In volcanic islands such as La Réunion, Guadeloupe or Martinique (France), the river and surface waters have  $\delta^7\text{Li}$  values ranging from 10 to 25‰ (BRGM data). The dilute thermal waters which generally have high proportions of surface waters indicate  $\delta^7\text{Li}$  signatures varying from - 1 to 18‰ in these areas. Those with the highest Li concentrations and for which the chemical geothermometers yield the highest estimated reservoir temperatures (up to 200°C) have  $\delta^7\text{Li}$  values ranging from 2.0 to 8.6‰ (BRGM data).

Lithium isotope measurements in seawater derived waters discharged from geothermal wells, thermal and submarine springs located in volcanic island arc areas in Guadeloupe (the Bouillante geothermal field) and Martinique (Lamentin plain and the Diamant areas) show that, for a given site, the Li isotopic signature of the deep geothermal fluid is homogeneous and probably comes from a common reservoir (Millot *et al.*, 2009). So, all the well fluids in the Bouillante geothermal field, constituted of about 58% seawater and 42% fresh surface water having reacted with volcanic rocks at 250-260°C, present  $\delta^7\text{Li}$  signatures between 4.2 and 4.8‰, with an average value of  $\delta^7\text{Li}$  =  $4.4 \pm 0.4$ ‰ (fig. 9). It is also demonstrated that, in this geothermal field, the fluids collected from the thermal submarine springs ( $\delta^7\text{Li}$  ranging from 4.8 to 26.1‰) are the result of mixing between the deep geothermal fluid and seawater.

The deep saline geothermal waters collected from the wells drilled in the Lamentin area, which are also made up of a mixture of seawater and fresh surface water having reacted with volcanic rocks at 90-120°C, are significantly different from the Bouillante fluid samples with respect to their  $\delta^7\text{Li}$  signature, with values varying from 6.0 to 7.8‰ and an average value of 6.7‰ (fig. 9). The saline waters collected from the thermal spring located in the Diamant area indicate similar  $\delta^7\text{Li}$  values ranging from 6.2 to 6.8‰ (fig. 9). However, the temperature of the deep reservoir estimated using chemical geothermometers (180-200°C) would be higher than that of the Lamentin reservoir.

Using the experimental data relative to the lithium isotope fractionation between dilute seawater and basalt at temperatures ranging from 25 to 250°C, Millot *et al.* (2009) estimated a  $\delta^7\text{Li}$  value of about -2.4‰ for the volcanic rocks of the Bouillante geothermal reservoir and concluded that this reservoir could be located at the upper sheeted basaltic dike complex of the oceanic crust, just below the transition zone between andesite volcanic flows and basaltic dikes, at a depth greater than 3 km. Concerning the Diamant and Lamentin areas, the geological and geochemical data as well as the  $\delta^7\text{Li}$  values of -2.4‰ and -5 to -6‰, estimated for the reservoir rocks, respectively, suggest that the geothermal fluids could be partially in equilibrium with sedimentary rocks.

The geothermal fluids discharged from the wells of Soultz-sous-Forêts (Alsace, France) indicate high Li concentrations of about 115 to 160 mg/l (Sanjuan *et al.*, 2009). Their  $\delta^7\text{Li}$  values range from -0.4 to -0.1‰ (fig. 9). The good results obtained using Na/Li and Mg/Li geothermometers, especially developed for sedimentary basin waters (Kharaka *et al.*, 1982; Kharaka and Mariner, 1989), and the poor temperature results obtained using Na/Li, Sr/K, Na/Cs and Na/Rb geothermometers (Fouillac and Michard, 1981; Michard, 1990), all developed for volcanic and granitic areas, suggest that most of the equilibrium reactions at 220-240°C occur in a sedimentary rather than a granite reservoir (Sanjuan *et al.*, 2009). Moreover, according to the experimental and literature data obtained for the lithium isotopic fractionation at 230°C (Chan *et al.*, 1994; James *et al.*, 1999; Millot *et al.*, 2009), the  $\delta^7\text{Li}$  value estimated for the rock in equilibrium with the deep native geothermal brine would be lower than -6‰ (Sanjuan *et al.*, 2009). This value is not characteristic of granites ( $\delta^7\text{Li}$  ranges from 0 to 10‰) but would rather correspond to that of carbonated sediments (Coplen *et al.*, 2002; Tomascak, 2004). From all these studies, it can be concluded that lithium isotopic systematics is a powerful tool to infer the origin of the waters and the nature of the reservoir rocks at a given temperature.

Oil-field brines have been suggested as a natural resource for Li owing to their very high concentrations (Collins, 1976). Chan *et al.* (2002b) investigated Li isotopes in oil-field brines from Israel. The Ca-chloride brines from the Heletz-Kokhav oil-field were Li-rich (1.0 to 2.3 ppm) and showed a range in Li isotopic composition ( $\delta^7\text{Li}$  from 18.2 to 30.8‰) lighter than modern seawater, unlike the Yellowknife basement or Sudbury brines located in Canadian mines ( $\delta^7\text{Li}$  from 33.2 to 41.8‰ and from 27.9 to 42.6‰, respectively; Bottomley *et al.*, 2003), consistent with predominance of preserved marine Li. Evolution of these brines from seawater through a process of mineral reactions, evaporation and dilution was interpreted from the Li isotope and elemental data. The studies of Bottomley *et al.* (1999) and Chan *et al.* (2002b) succinctly illustrated the variable nature of Li in even broadly similar environments: in one case, Li was taken up in secondary minerals, leaving a solution that was isotopically heavier than modern seawater; in the other case, Li was interpreted to have been removed from sediments, leaving a solution isotopically lighter than seawater.

## 4. Conclusions

In this study, the integration of more than 120 additional temperature and chemical data collected from world geothermal and oil-fields, sedimentary basins, oceanic ridges, emerged oceanic rifts and island arcs, has allowed to confirm and refine the three existing Na/Li thermometric relationships. A new Na/Li thermometric relationship relative to the processes of seawater or diluted seawater-basalt interaction occurring in the oceanic ridges and emerged oceanic rifts is proposed.

Even if the running of Na/Li is still poorly understood, the existence of a new thermometric relationship 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 reservoir rocks in contact with the geothermal fluids. For most of the geothermal waters in contact with volcanic rocks or granite in the deep reservoir, rock leaching and hydrothermal alteration (illite or smectite precipitation) are probably the main processes controlling the Li concentrations. Additional field and laboratory studies as well as a thermodynamic approach based on mineral dissolution-precipitation equilibrium reactions could help to support and confirm this assumption.

The scarcity of the  $\delta^7\text{Li}$  values analysed in the geothermal and oil-field fluids and the presently available data indicate that it is necessary to acquire additional data in both fluids and rocks to better understand the Li behaviour in the processes of water-rock interaction. However, as the dissolved Li during these processes seems to be controlled by several influent factors, it is recommended to study the Li behaviour at different temperatures for a same type of process of water-rock interactions (see the new Na/Li thermometric relationship obtained for the processes of seawater or dilute seawater-basalt interaction occurring in the oceanic ridges and emerged oceanic rifts). So, a study as that envisaged within the framework of the HITI project for Icelandic dilute geothermal waters in contact with volcanic rocks at temperatures ranging from 50 to 325°C is an excellent opportunity to advance in this field. Some studies in which  $\delta^7\text{Li}$  values were analysed in geothermal waters show that this type of information can be used to determine the nature of the reservoir rocks in contact with these waters and indirectly estimate the depth of the geothermal reservoirs.

The Na/Li geothermometer, which is often less accurate than other classical geothermometers but can be more reliable in many cases, is consequently very useful for geothermal exploration. In order to improve the use of this geothermometer, this study shows that additional developments 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 to improve 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 geothermal, hydrothermal marine, oil-field and sedimentary basins waters**







# Bibliographical review about Na/Li geothermometry and lithium isotopes applied to worldwide geothermal waters

| Well or thermal spring  | T °C | 1000/T °K <sup>-1</sup> | pH     | Na mg/l | Li mg/l | Na/Li | log (Na/Li) molar | Li/Na x 1000 molar | δ <sup>7</sup> Li ‰ | SiO <sub>2</sub> mg/l | T sil. °C | Cl mg/l | Alk. mg/l HCO <sub>3</sub> | Reference  |
|---|------|-------------------------|--------|---------|---------|-------|-------------------|--------------------|---------------------|-----------------------|-----------|---------|----------------------------|--|
| Hot fluid from Tadjourah springs (Djibouti)   | 60   | 3.00                    |        | 11285   | 0.50    | 6908  | 3.83              | 0.15               | na                  | 19                    | 62        | 20846   |                            | Sarjuan <i>et al.</i> (1990)                               |
| Hot fluid from Obock springs (Djibouti)   | 210  | 2.07                    | na     | 10529   | 4.02    | 791   | 2.90              | 1.26               | na                  | 266                   | 200       | 20705   |                            | Houssien <i>et al.</i> (1993)                              |
| Drillhole H2 (Reykjanes, Iceland)   | 250  | 1.91                    | 6.6    | 11930   | 5.95    | 605   | 2.78              | 1.65               | na                  | 462                   | 245       | 23702   |                            | Otafsson and Riley (1978)                                  |
| Well Aaal 3 (Djibouti)  | 260  | 1.88                    | 4.65   | 26254   | 14.16   | 580   | 2.75              | 1.79               | na                  | 514                   | 255       | 22076   |                            | Sarjuan <i>et al.</i> (1990)                               |
| Well Reykjanes (Bjornsson <i>et al.</i> , 1972)   | 260  | 1.88                    |        | 14506   | 7.44    | 588   | 2.77              | 1.70               | na                  |                       |           | 19500   |                            | Fouillac and Michard (1981)                                |
| Vent fluids Bent Hill (Middle Valley Ridge, 1996)   | 265  | 1.86                    | 5.13   | 7242    | 2.57    | 851   | 2.93              | 1.17               | na                  | 619                   | 273       | 14607   | 88                         | Butterfield <i>et al.</i> (1994)                           |
| Guaymas Basin hydrothermal solution 6 (Gulf of California, USA)                               | 270  | 1.84                    | 5.9    | 11035   | 4.37    | 762   | 2.88              | 1.31               | na                  | 559                   | 263       | 20598   |                            | Von Damm <i>et al.</i> (1985a)                             |
| Vent fluids Dead Dog (Middle Valley Ridge, 1990)  | 276  | 1.82                    | 5.50   | 9150    | 3.82    | 724   | 2.86              | 1.38               | na                  | 637                   | 276       | 20452   | 122                        | Butterfield <i>et al.</i> (1994)                           |
| Vent fluid from the Menz Gwen Field (Mid-Atlantic Ridge, 37°50'N, Mean values, 1993)          | 280  | 1.81                    | 4.2    | 7242    | 1.82    | 1198  | 3.08              | 0.83               | na                  | 601                   | 270       | 13259   |                            | Charlou <i>et al.</i> (2000)                               |
| Well H8 (Reykjanes, Iceland, Amorseon)  | 283  | 1.80                    |        | 9629    | 5.10    | 570   | 2.76              | 1.75               | na                  | 572                   | 265       | 18785   |                            | Truesdell <i>et al.</i> (1981)                             |
| Vent fluid from the Menz Gwen Field (Mid-Atlantic Ridge, 37°50'N, Menz flank site, 1993)      | 284  | 1.79                    | 4.2    | 7196    | 1.90    | 1142  | 3.06              | 0.88               | na                  | 619                   | 273       | 13508   |                            | Charlou <i>et al.</i> (2000)                               |
| Hydrothermal fluid from the 17°S active site on the North Fiji Basin Ridge (SW Pacific)       | 285  | 1.79                    | 4.7    | 4828    | 1.39    | 1050  | 3.02              | 0.95               | na                  | 841                   | 305       | 9041    |                            | Grimaud <i>et al.</i> (1993)                               |
| Drillhole H8 (Reykjanes, Iceland)   | 292  | 1.77                    | 7.1    | 12730   | 6.59    | 583   | 2.77              | 1.72               | na                  | 943                   | 318       | 25054   |                            | Otafsson and Riley (1978)                                  |
| Brandon vent - brine Be.5 (Southern East Pacific Rise)  | 295  | 1.76                    | 3.3    | 10322   | 3.39    | 920   | 2.96              | 1.08               | na                  | 751                   | 293       | 19747   |                            | Von Damm <i>et al.</i> (2003)                              |
| Vent 6X (Escanaba Through, Gorda Ridge hydrothermal system, 1988)                             | 300  | 1.74                    | 5.40   | 12874   | 8.92    | 435   | 2.64              | 2.30               | 9.1                 | 415                   | 236       | 23683   | 189                        | Campbell <i>et al.</i> (1994)                              |
| Vent 6X (Escanaba Through, Gorda Ridge hydrothermal system, 2000)                             | 300  | 1.74                    | < 5.81 | 12460   | 8.74    | 430   | 2.63              | 2.32               | na                  | 382                   | 229       | 22406   | < 145                      | Von Damm <i>et al.</i> (2005)                              |
| Vent 6X (Escanaba Through, Gorda Ridge hydrothermal system, 2002)                             | 300  | 1.74                    | < 5.75 | 12736   | 7.70    | 499   | 2.70              | 2.00               | na                  | 379                   | 228       | 22725   | < 128                      | Von Damm <i>et al.</i> (2005)                              |
| Guaymas Basin hydrothermal fluid 7 (Gulf of California, USA)                                  | 300  | 1.74                    | 5.9    | 11265   | 7.47    | 455   | 2.66              | 2.20               | na                  | 769                   | 295       | 20598   |                            | Von Damm (1988)  |
| Guaymas Basin hydrothermal fluid (South Field, Gulf of California, USA, 1982)                 | 300  | 1.74                    | 5.9    | 11265   | 7.38    | 462   | 2.66              | 2.16               | 5.0                 | 775                   | 296       | 20917   | 641                        | Campbell <i>et al.</i> (1988b) - Chan <i>et al.</i> (1993) |
| Guaymas Basin hydrothermal fluid (South Field, Gulf of California, USA, 1985)                 | 300  | 1.74                    | 5.9    | 10851   | 6.99    | 475   | 2.68              | 2.10               | 2.6                 | 811                   | 301       | 20563   | 586                        | Campbell <i>et al.</i> (1988b) - Chan <i>et al.</i> (1993) |
| Guaymas Basin hydrothermal fluid (East Hill, Gulf of California, USA, 1982)                   | 300  | 1.74                    | 5.9    | 11150   | 6.06    | 556   | 2.74              | 1.80               | 7.6                 | 829                   | 303       | 21236   | 494                        | Campbell <i>et al.</i> (1988b) - Chan <i>et al.</i> (1993) |
| Guaymas Basin hydrothermal fluid (East Hill, Gulf of California, USA, 1985)                   | 300  | 1.74                    | 5.9    | 11219   | 5.89    | 575   | 2.76              | 1.74               | 10.2                | 829                   | 303       | 21378   | 543                        | Campbell <i>et al.</i> (1988b) - Chan <i>et al.</i> (1993) |
| Vent fluid 6 at 11°N (East Pacific Rise)  | 310  | 1.71                    | 3.1    | 6667    | 3.36    | 599   | 2.78              | 1.67               | 10.7                | 859                   | 307       | 11993   |                            | Bowers <i>et al.</i> (1988) - Chan <i>et al.</i> (1993)    |
| Guaymas Basin hydrothermal solution 4 (Gulf of California, USA)                               | 315  | 1.70                    | 5.9    | 11150   | 6.06    | 556   | 2.74              | 1.80               | na                  | 829                   | 303       | 21236   |                            | Von Damm (1988)  |
| 13°N hydrothermal site (East Pacific Rise)  | 320  | 1.69                    | 3.2    | 12874   | 4.77    | 814   | 2.91              | 1.23               | na                  | 1322                  | 360       | 26235   |                            | Michard <i>et al.</i> (1984)                               |
| Vent fluid from the Lucky Strike Field (Mid-Atlantic Ridge, 37°17'N, Eiffel Tower site, 1994) | 324  | 1.67                    | 3.7    | 7977    | 1.98    | 1213  | 3.08              | 0.82               | na                  | 799                   | 299       | 14784   |                            | Charlou <i>et al.</i> (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    | 1172  | 3.07              | 0.85               | na                  | 943                   | 318       | 15528   | < 1.2                      | Von Damm <i>et al.</i> (1998)                              |
| Vent fluid from the Lucky Strike Field (Mid-Atlantic Ridge, 37°17'N, Mean values)             | 325  | 1.67                    | 3.65   | 8966    | 2.13    | 1270  | 3.10              | 0.79               | na                  | 865                   | 308       | 16486   |                            | Charlou <i>et al.</i> (2000)                               |
| Vent fluid from the Lucky Strike Field (Mid-Atlantic Ridge, 37°17'N, 2608 Vent site, 1996)    | 326  | 1.66                    | 3.78   | 9633    | 2.89    | 1005  | 3.00              | 1.00               | na                  | 1051                  | 331       | 18648   | < 35                       | Von Damm <i>et al.</i> (1996)                              |
| MARK-1 vent fluid (Mid-Atlantic Ridge)  | 335  | 1.64                    | 3.7    | 11702   | 5.89    | 600   | 2.78              | 1.67               | 6.3                 | 1100                  | 336       | 19818   | < 4                        | Campbell <i>et al.</i> (1988a) - Chan <i>et al.</i> (1993) |
| OBS (21°N, East Pacific Rise, 1985)   | 340  | 1.63                    | 3.4    | 10093   | 6.43    | 474   | 2.68              | 2.11               | 8.9                 | 1057                  | 332       | 17727   |                            | Campbell <i>et al.</i> (1988b) - Chan <i>et al.</i> (1993) |
| Vent fluid 1 at 11°N (East Pacific Rise)  | 347  | 1.61                    | 3.1    | 10851   | 6.13    | 534   | 2.73              | 1.87               | 10.9                | 1130                  | 340       | 19606   |                            | Bowers <i>et al.</i> (1988) - Chan <i>et al.</i> (1993)    |
| MARK-2 vent (Mid-Atlantic Ridge)  | 350  | 1.60                    | 3.9    | 11725   | 5.85    | 605   | 2.78              | 1.65               | 8.5                 | 1094                  | 336       | 19818   | < 15                       | Campbell <i>et al.</i> (1988a) - Chan <i>et al.</i> (1993) |
| Clambake (Ridge crest hydrothermal activity at Galapagos Spreading Center)                    | 350  | 1.60                    |        | 11196   | 7.92    | 427   | 2.63              | 2.34               | na                  | 1316                  | 359       | 21095   |                            | Edmond <i>et al.</i> (1979)                                |
| Garden of Eden (Ridge crest hydrothermal activity at Galapagos Spreading Center)              | 350  | 1.60                    |        | 10368   | 7.92    | 395   | 2.60              | 2.53               | na                  | 1316                  | 359       | 19251   |                            | Edmond <i>et al.</i> (1979)                                |
| Dandelions (Ridge crest hydrothermal activity at Galapagos Spreading center)                  | 350  | 1.60                    |        | 7196    | 7.92    | 274   | 2.44              | 3.65               | na                  | 1316                  | 359       | 14004   |                            | Edmond <i>et al.</i> (1979)                                |
| Oyster Beds (Ridge crest hydrothermal activity at Galapagos Spreading Center)                 | 350  | 1.60                    |        | 5934    | 4.78    | 376   | 2.58              | 2.66               | na                  | 1316                  | 359       | 11416   |                            | Edmond <i>et al.</i> (1979)                                |
| OBS (21°N, East Pacific Rise, 1981)   | 350  | 1.60                    | 3.4    | 9932    | 6.18    | 485   | 2.69              | 2.06               | 9.2                 | 1057                  | 332       | 17337   | < 24                       | Von Damm <i>et al.</i> (1985a) - Chan <i>et al.</i> (1993) |
| NGS (21°N, East Pacific Rise, 1981)   | 350  | 1.60                    | 3.8    | 11725   | 7.17    | 494   | 2.69              | 2.03               | 10.0                | 1172                  | 344       | 20527   | < 12                       | Von Damm <i>et al.</i> (1985a) - Chan <i>et al.</i> (1993) |
| NGS (21°N, East Pacific Rise, 1985)   | 350  | 1.60                    |        | 11656   | 7.57    | 465   | 2.67              | 2.15               | na                  | 1166                  | 344       | 20421   |                            | Campbell <i>et al.</i> (1988b)                             |
| SW (21°N, East Pacific Rise, 1981)  | 350  | 1.60                    | 3.6    | 10093   | 6.24    | 488   | 2.69              | 2.05               | 9.6                 | 1039                  | 330       | 17585   | < 18                       | Von Damm <i>et al.</i> (1985a) - Chan <i>et al.</i> (1993) |
| SW (21°N, East Pacific Rise, 1985)  | 350  | 1.60                    | 4.9    | 10621   | 6.72    | 477   | 2.68              | 2.10               | 8.6                 | 1033                  | 329       | 18613   | < 10                       | Campbell <i>et al.</i> (1988b)                             |
| HG (21°N, East Pacific Rise, 1981)  | 350  | 1.60                    | 3.3    | 10184   | 9.17    | 335   | 2.53              | 2.98               | 6.6                 | 937                   | 317       | 17585   | < 31                       | Von Damm <i>et al.</i> (1985a) - Chan <i>et al.</i> (1993) |
| HG (21°N, East Pacific Rise, 1985)  | 350  | 1.60                    | 3.6    | 10414   | 10.05   | 313   | 2.50              | 3.20               | 6.8                 | 1009                  | 326       | 17939   | < 24                       | Campbell <i>et al.</i> (1988b) - Chan <i>et al.</i> (1993) |
| Vent fluid 2 at 13°N (East Pacific Rise)  | 354  | 1.59                    | 3.1    | 12867   | 4.11    | 931   | 2.97              | 1.07               | na                  | 1166                  | 344       | 25243   |                            | Bowers <i>et al.</i> (1988)                                |
| OBS (21°N, East Pacific Rise, 1981)   | 355  | 1.59                    | 3.6    | 10093   | 6.24    | 488   | 2.69              | 2.05               | na                  | 1040                  | 330       | 17585   |                            | Von Damm <i>et al.</i> (1985a)                             |
| Vent fluid 5 from the Broken Spur site (29°N Mid-Atlantic Ridge)                              | 356  | 1.59                    |        | 9679    | 6.98    | 418   | 2.62              | 2.39               | na                  |                       |           | 16627   |                            | James <i>et al.</i> (1995)                                 |
| Hydrothermal fluid from Trans-Atlantic Geotraverse (TAG, 26°08'N)                             | 360  | 1.58                    |        | 13426   | 2.85    | 1421  | 3.15              | 0.70               | 11.5                | 1322                  | 360       | 23364   |                            | Campbell <i>et al.</i> (1988a) - Chan <i>et al.</i> (1994) |
| Plume (Southern Juan de Fuca Ridge)   | 360  | 1.58                    | 3.2    | 18300   | 11.92   | 463   | 2.67              | 2.16               | na                  | 1400                  | 368       | 38537   |                            | Von Damm and Bischoff (1987)                               |
| Vent fluid 3 from the Broken Spur site (29°N Mid-Atlantic Ridge)                              | 360  | 1.58                    |        | 9702    | 7.17    | 409   | 2.61              | 2.45               | na                  |                       |           | 16627   |                            | James <i>et al.</i> (1995)                                 |
| Vent fluid 4 from the Broken Spur site (29°N Mid-Atlantic Ridge)                              | 364  | 1.57                    |        | 9633    | 7.18    | 405   | 2.61              | 2.47               | na                  |                       |           | 16627   |                            | James <i>et al.</i> (1995)                                 |
| Sea water   | 2    | 3.63                    | 7.80   | 10697   | 0.18    | 17846 | 4.25              | 0.06               | 31.2                | 10.2                  |           | 19180   |                            | Von Damm <i>et al.</i> (2005)                              |
| Sea water (Goldberg, 1965)  | 4    | 3.61                    |        | 10500   | 0.17    | 18642 | 4.27              | 0.05               | na                  | 6.0                   |           | 18980   | 140                        | Truesdell <i>et al.</i> (1981)                             |
| Sea water (average composition)   | 8    | 3.56                    |        | 10500   | 0.17    | 18642 | 4.27              | 0.05               | na                  |                       |           |         |                            | Kharaka and Marner (1989)                                  |
| Sea water (Diamant, Martinique)   | 29   | 3.32                    | 8.19   | 11400   | 0.23    | 14960 | 4.17              | 0.07               | 30.5                | 0.19                  |           | 20200   | 143                        | Sarjuan <i>et al.</i> (2003)                               |
| Sea water (Bouillante, Guadeloupe)  | 29   | 3.31                    | 8.23   | 11000   | 0.25    | 13280 | 4.12              | 0.06               | 29.3                | 0.43                  |           | 20181   | 169                        | Sarjuan (2001)   |
| Sea water (Lamenin, Martinique)   | 29   | 3.31                    | 8.20   | 11400   | 0.23    | 14960 | 4.17              | 0.07               | 30.1                |                       |           | 21307   | 148                        | Sarjuan <i>et al.</i> (2002)                               |
| Sea water (Asal-Tadjourah, Djibouti)  | 30   | 3.30                    |        | 11426   | 0.26    | 13264 | 4.12              | 0.08               | na                  | 1.20                  |           | 21059   |                            | Sarjuan <i>et al.</i> (1990)                               |
| Sea water (Obock, Djibouti)   | 30   | 3.30                    | 8.22   | 11495   | 0.22    | 16137 | 4.21              | 0.06               | na                  | 0.90                  |           | 20705   |                            | Houssien <i>et al.</i> (1993)                              |
| Lake Bogoria (Kenya)  | 27   | 3.33                    | 10.10  | 39300   | 0.76    | 15608 | 4.19              | 0.06               | na                  | 378                   | 103       |         |                            | Cori <i>et al.</i> (1992)                                  |

T sil. (°C): temperature estimated using the silica geothermometer (Fournier and Rowe, 1966)



**Centre scientifique et technique**  
**Département GTH**  
3, avenue Claude-Guillemin  
BP 36009 – 45060 Orléans Cedex 2 – France – Tél. : 02 38 64 34 34