Lithium isotopic signature of high temperature geothermal fluids in volcanic arc islands (Guadeloupe and Martinique, French West Indies): an efficient tool to constrain the rock nature of the reservoirs and their depth

This study shows that the lithium (Li) isotope measurements performed in hot waters collected from deep production wells (Bouillante geothermal field, Guadeloupe) and thermal springs (Diamant area, Martinique) can be very useful to constrain the rock nature of the geothermal reservoirs and their depth without no sampling and analysis of reservoir rocks nor direct access by drilling, when the reservoir temperatures are known. In the Bouillante geothermal field, the reservoir temperature was measured at the bottom of the wells (250-260°C) and confirmed by chemical and gas geothermometers. In the Diamant area, it was estimated to be close to 180°C using most of the chemical and isotopic geothermometers. For each area, the Li isotopic signature of the reservoir rocks was estimated using the Li isotope signature of the hot waters and the temperature dependant isotopic Li fractionation equation experimentally determined for basalt-seawater interactions. This value close to δ^7Li = -2.6‰ ± 0.5 suggests that the main geothermal reservoirs in the Bouillante and Diamant areas are located in the transition zone, a zone which marks the contact between volcanic flows and the basaltic oceanic crust and is the center of intense fluid mixing and circulation. In the Bouillante geothermal field, this zone is probably present at a depth of 3-4 km.

Introduction

> Numerous geochemical tools, which are based upon the acquisition of chemical and isotopic data obtained from thermal waters, fumaroles or escapes of gases collected in surface conditions, or from fluids sampled in deep wells, are commonly used to study and better understand the high temperature geothermal reservoirs. If it is possible to characterize the fluids of the geothermal reservoirs and their deep circulation, estimate their residence time and the reservoir temperature (using chemical, isotopic or gas geothermometers, for example), few present geochemical tools are available to constrain the rock nature of these reservoirs and their depth, without no sampling and analysis of reservoir rocks nor direct access by drilling.

> In this study, we have investigated if the δ^7Li values measured in hot waters collected from deep production wells (Bouillante geothermal field, Guadeloupe; Figs. 1 and 2) and thermal springs (Diamant area, Martinique; Figs. 1 and 3) could be used to constrain these parameters.

Experimental data of seawater/basalt interactions at temperatures ranging from 25 to 250°C

> In order to determine the extent of Li isotope fractionation during seawater/basalt interactions as a function of temperature, laboratory experiments were performed by BRGM at different temperatures (25, 75, 200 and 250°C). The basalt chosen for these experiments was the JB-2 tholeiitic basalt (Japan Geological Survey) which is considered as a secondary reference material for Li isotopes (δ^7Li = 4.6‰ ± 0.9 and Li = 7.78 ppm). The selected seawater was the reference material IRMM BCR-403 (δ^7Li = +31.0‰ ± 0.5, Millot *et al.*, 2004; Li = 0.18 mg/l). The experiments were carried out with a seawater/basalt mass ratio of 10 and a seawater solution diluted at 60% (with ultrapure H_2O Milli-Q®) in order to match the natural conditions (water/rock ratio and seawater dilution) that are found in the Bouillante geothermal field. Run durations varied from 7 to 12 days for the experiments at 200 and 250°C to 245 days for the experiments at 25 and 75°C. The Li concentrations in the fluid aliquots were analyzed by ICP-MS (relative accuracy ± 5%) and the δ^7Li values were measured by using a Neptune Multi Collector ICP-MS (Thermo Fisher Scientific; Millot *et al.*, 2004). Typical in-run precision is about 0.1-0.2 ‰. For more experimental details, see Millot *et al.* (2007).

> The results obtained from these experiments are reported in Millot *et al.* (2007) and summarized in the figure 4. They are in good agreement with the other literature data. According to the data found in the BRGM experiments, Li isotopic fractionation ($\Delta_{solution - basalt}$) ranges from 19.5‰ at 25°C to 6.8‰ at 250°C, confirming that the heavy ^7Li isotope is preferentially released into solution. The corresponding linear correlation (Fig. 4) can be then expressed as:

$$\Delta_{solution - basalt} = 7790 / T (°K) - 7.85$$

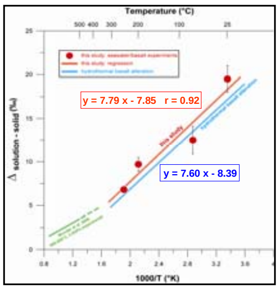

Fig. 4 - Li isotopic fractionation between solution and basalt ($\Delta_{solution - basalt}$) calculated from the BRGM experiments (red circles) versus the inverse of the temperature of interaction (1000/T, °K). The red line represents the correlation obtained from the BRGM data. The blue line corresponds to isotopic fractionation inferred from hydrothermal basalt interactions. The green line represents the experimental relationship determined by Wunder et al. (2006), between 500 and 900°C, and the dashed blue line is an extrapolation below 500°C (figure extracted from Millot et al., 2007)

Bouillante geothermal field (Guadeloupe)

> The Bouillante geothermal area where numerous hydrothermal events such as terrestrial and sub-marine hot waters, mud pools, steaming grounds and fumaroles occur, is located on the western coast of Basse Terre around the town of Bouillante (Fig. 2).

> The geothermal power plant located south of Bouillante Bay is exploited by Géothermie Bouillante S.A., a subsidiary company of the BRGM and EDF (Electricité de France) groups. Between 1996 and 2002, only the well BO-2, 330 m deep, was productive (150 tons/h of fluid whose 30 tons/h). Since 2005, the new geothermal power plant is fed by the wells BO-4, BO-5 and BO-6 which intersect a geothermal fluid (250-260°C) at a depth of 850-1100 m. These wells produce about 570 ton/h of fluid whose 115 tons/h of steam (corresponding to 15 MWe, around 8% of the annual electricity needs of the Guadeloupe island) and about 460 kg/h of non condensable gases, mainly constituted of 90-95% CO_2 and 2-3% H_2S.

> Since 1997, many scientific investigations about the Bouillante geothermal field are financially supported by BRGM and ADEME. Among them, the geochemical monitoring of the fluids discharged from the geothermal wells and main hot springs has shown that the deep geothermal fluid has an homogeneous chemical and isotopic composition, which suggests the existence of a large and common geothermal reservoir at the scale of the Bouillante area. This geothermal NaCl fluid with a TDS of 20 g/l and a pH value of 5.3 ± 0.3 is the result of a mixing of about 58% seawater and 42% surface fresh water, probably fed by rainfall on the western side of the Bouillante Pitons, which reacts with volcanic rocks at high temperatures (Sanjuan *et al.*, 2001; Mas *et al.*, 2006). The results obtained using chemical and gas geothermometers and geochemical modelling suggest that an equilibrium state at 250-260°C is reached with respect to a mineralogical assemblage, constituted of quartz, albite, K-feldspar, anhydrite, calcite, disordered dolomite, illite, smectite and zeolites (Sanjuan *et al.*, 2001).

Fig. 1 - Map showing the location of the Guadeloupe and Martinique islands (French overseas departments, West Indies) in the Caribbean volcanic insular arc.

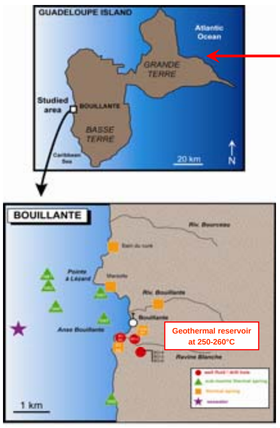

Fig. 2 - Map showing the location of the wells and main hot springs in the Bouillante geothermal field (Guadeloupe).

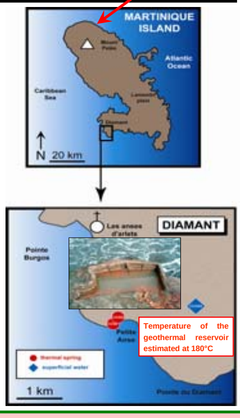

Fig. 3 - Map showing the location of the main hot springs in the Diamant area (Martinique).

Diamant geothermal area (Martinique)

> After the three exploration boreholes were drilled in the Lamentin plain in 2001, other geothermal exploratory investigations, funded by the Martinique Regional Council, European Union (FEDER), ADEME and BRGM, were carried out in 2003 in this area located in southern Martinique (Sanjuan *et al.*, 2005; Fig. 3).

> The only thermal spring in this area has several discharge points near the seaside from which two water samples were collected (Fig. 3). The chemical and isotopic analyses done on these samples have shown that the deep geothermal fluid is a NaCl water with a high salinity (TDS ≈ 20 g/l) and a reconstructed pH value close to 5.3. Abundant magmatic CO_2 gas emanations ($\delta^{13}C$ = -4.4‰) and hydrothermal deposits (mainly carbonates, iron hydroxides, sulfates and clays) are associated with this fluid. The location of the thermal spring, the nature of this fluid and its high salinity indicate a probable marine contribution (about 50%?) associated to a dilution by fresh waters, but a magmatic origin is also assumed given its exceedingly low δD value (-22‰) compared to the values usually analyzed in the waters of Martinique and the lesser Antilles (Sanjuan *et al.*, 2005). The geochemical data of this fluid, and especially the use of the chemical and isotopic geothermometers, suggest that this fluid has reacted with volcanic rocks in a geothermal reservoir at about 180°C, whose the depth is unknown.

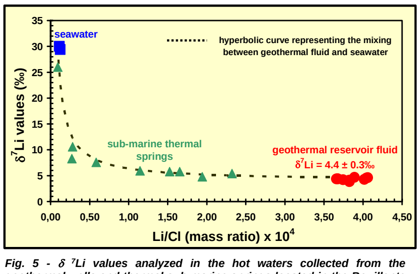

Fig. 5 - δ^7Li values analyzed in the hot waters collected from the geothermal wells and thermal sub-marine springs located in the Bouillante site plotted as a function of the Li/Cl ratios.

Main results obtained in this study

> The δ^7Li values measured in the fluids collected from the geothermal wells and main thermal springs located in the Bouillante site confirm the homogeneity of the composition of the deep geothermal fluid and the existence of a common and large reservoir (Fig. 5).

> Using the temperature dependant isotopic Li fractionation equation experimentally determined for basalt-seawater interactions (Fig. 4), the δ^7Li values analyzed in the geothermal fluids (4.4 ± 0.3‰ for Bouillante and 6.5 ± 0.3‰ for Diamant) and the reservoir temperatures, a value of δ^7Li = -2.6 ± 0.5‰ is found for the isotopic signature of the reservoir volcanic rocks (Fig. 6). According to Chan *et al.* (2002), this value suggests that the main geothermal reservoirs of Bouillante and Diamant are located in the transition zone that marks the contact between volcanic flows and basaltic dikes and is a region of fluid mixing. Li enrichment is accompanied by relatively low isotopic compositions, which indicates the influence of basalt-derived Li during mineralization and alteration. In the Bouillante geothermal field, this transition zone is probably present at a depth of about 3-4 km (Andreieff *et al.*, 1987).

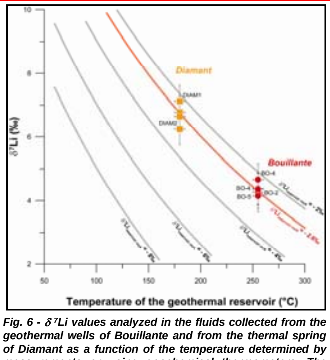

Fig. 6 - δ^7Li values analyzed in the fluids collected from the geothermal wells of Bouillante and the thermal spring of Diamant as a function of the temperature determined by measurements or using geochemical thermometers. The parametric curves (grey) correspond to δ^7Li values of the reservoir rocks calculated using the temperature dependant Li isotopic fractionation equation obtained from the experimental data (figure extracted from Millot et al., 2007).

Main Conclusions

> This study shows that the Li concentrations and δ^7Li values analyzed in the hot fluids can be used not only to identify geothermal reservoirs and estimate their temperature but can also be a powerful tool to constrain the nature and the type of the reservoir rocks (and indirectly the reservoir depth). So, the main geothermal reservoirs of Bouillante and Diamant, at temperatures of about 260 and 180°C respectively, and with a δ^7Li value estimated at -2.6‰ for the reservoir rocks, would be located in the transition zone which marks the contact between volcanic flows and basaltic dikes and is a region of fluid mixing. In the Bouillante geothermal field, this zone is probably present at a depth of about 3-4 km.

> Additional water/rock interaction experiments (fresh water/basalt, seawater and fresh water/andesite, etc.) similar to those presented in this study and more isotopic Li data on the hot fluids of other geothermal reservoirs are necessary to complete this study and improve our understanding of Li behavior in island arc geothermal systems.

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