Earth and Planetary Science Letters 411 (2015) 62–71

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Lithium isotopes in hydrothermally altered basalts from Hengill (SW Iceland)

A. Verney-Carron[a,*], N. Vigier[a,1], R. Millot[b], B.S. Hardarson[c]

[a] CRPG-CNRS, 15, rue Notre Dame des Pauvres, 54501 Vandœuvre lès Nancy Cedex, France
[b] BRGM, Laboratory Division, Isotope Geochemistry, 3 avenue Claude Guillemin, BP 36009, 45060 Orléans Cedex, France
[c] ISOR, Iceland Geosurvey, Grensasvegur 9, 108 Reykjavik, Iceland

ARTICLE INFO

Article history:
Received 29 April 2014
Received in revised form 14 October 2014
Accepted 28 November 2014
Available online 15 December 2014
Editor: G.M. Henderson

Keywords:
lithium isotopes
chemical weathering
basalt
hydrothermal fluids
Iceland

ABSTRACT

The Li isotope signatures of hydrothermal fluids are remarkably constant (δ^7Li $= 8.0 \pm 1.9$‰) irrespective of the water/rock ratio (W/R), permeability, temperature or fluid involved (seawater or meteoric). High temperature hydrothermal fluids represent the second most significant source of Li to the ocean, yet the homogeneity of the Li isotopic signatures of this source remains to be explained and in this context, the lack of data for the corresponding altered phases is problematic. We measured Li contents and Li isotope signatures (as well as mineralogy, composition and local fluid temperature) in hyaloclastites collected from a borehole in the Hellisheidi geothermal system (Iceland) which have been altered by high temperature aqueous fluids (from 170 to 300 °C). Li is more enriched in the solid phases than the other alkali metals, highlighting its greater ability to be incorporated into secondary phases, especially at high temperatures (>250 °C). Mass balance calculations show that the low Li concentrations in hydrothermal fluids are best explained by a high water/rock ratio and a high permeability of this system. The Li isotopic signature of the altered hyaloclastites (δ^7Li between +1.9 and +4.0‰) remains close to the fresh basalt at deep levels and high temperatures (290–300 °C) (as measured δ^7Li range between +3.7 and +4.0‰), and decreases at shallower depths and lower temperatures (150–270 °C) (δ^7Li between +1.9 and +3.1‰). A mass balance model involving basalt dissolution, secondary phase formation, and successive isotope equilibrium during the migration and the cooling of the percolating fluid was developed. The corresponding apparent mineral-fluid Li isotope fractionation factors resulting from precipitation of secondary phases ($\Delta^7\mathrm{Li}_{minerals\text{-}fluid}$) range between 0‰ at 300 °C and −8.5‰ at 170 °C and highlight a key role of chlorite. Applying the same approach to mid-ridge oceanic hydrothermal systems allows the relatively homogeneous isotope signatures of high temperature fluids of various locations to be explained.

1. Introduction

High temperature (HT) hydrothermal fluids represent a major source of lithium to the ocean. The Li isotope signature of the ocean is controlled by a balance between the main Li sources (rivers and HT fluids) and the Li isotopic fractionation during Li removal resulting from weathering and formation of authigenic phases in the ocean (Chan et al., 1992; Elderfield and Schultz, 1996; Huh et al., 1998; Zhang et al., 1998; Misra and Froelich, 2012).

Hydrothermal activity supplies dissolved Li from the rocks to oceanic waters (Edmond et al., 1979) and geothermal and submarine hydrothermal fluids collected in different geological or tectonic contexts are usually enriched in Li, displaying concentrations between 0.14 and 9.7 ppm (Chan et al., 1993, 1994; Foustoukos et al., 2004; Millot et al., 2010; Misra and Froelich, 2012) (see Fig. 1a for more details). In comparison, the Li content of seawater is 0.18 ppm (e.g. Riley and Tongudai, 1964) and is 1.5 ppb on average in rivers (Huh et al., 1998). However, the Li hydrothermal flux to the ocean is difficult to estimate because of the uncertainties related to hydrothermal heat and water fluxes (Alt, 2003) and to the large range in Li concentrations measured in submarine hydrothermal fluids, which is not simply correlated to the fluid temperature (Fig. 1a). Moreover, the distribution of Li in the deep oceanic crust

---

[*] Corresponding author. Present address: LISA, UMR CNRS 7583, UPEC, UPD, 61, avenue du Général de Gaulle, 94010 Créteil, France. Tel.: +33 1 45 17 66 08; fax: +33 1 45 17 15 64.
E-mail address: aurelie.verney@lisa.u-pec.fr (A. Verney-Carron).
[1] Now at: Laboratoire d'Océanographie de Villefranche, Villefranche sur Mer, France.

http://dx.doi.org/10.1016/j.epsl.2014.11.047

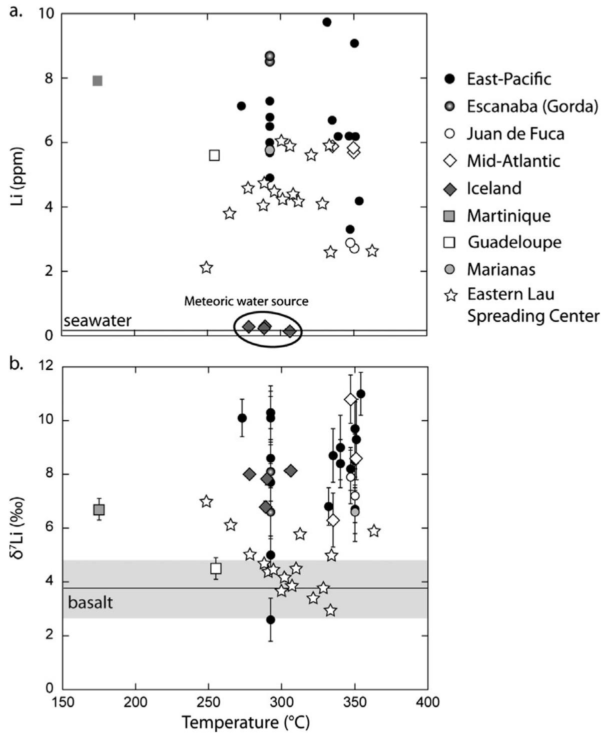

Fig. 1. (a) Li concentration (in ppm) and (b) Li isotopic composition (δ^7Li in ‰) of hydrothermal fluids as a function of temperature in basaltic host rocks. References are: Chan et al. (1993, 1994) for East–Pacific (Guaymas), Escanaba, Mid-Atlantic, and Marianas; Foustoukos et al. (2004) for Juan de Fuca ridge; Mottl et al. (2011) for Eastern Lau Spreading Center; Millot et al. (2009) for Iceland; Millot et al. (2010) for Martinique and Guadeloupe (high-temperature hydrothermal fluids from well fluids). Li content of seawater and δ^7Li of MORB (Tomascak et al., 2008) were added for comparison.

is poorly known, and the proportion of Li that is recycled through the hydrothermal systems is not well quantified.

In contrast with Li concentrations, the Li isotopic composition of subaerial and submarine hydrothermal fluids ($\delta^7\mathrm{Li}_{hydr}$) varies within a moderate range with an average value of $+8.0 \pm 1.9$‰ (1σ, $n = 33$) (Fig. 1b). High temperature hydrothermal fluids are therefore isotopically fractionated relative to source rocks, especially to fresh MORB ($\delta^7\mathrm{Li}_{\mathrm{MORB}} = +3.7 \pm 1.0$‰ ($1\sigma$, $n = 53$), Tomascak et al., 2008). However, the processes responsible for these elevated and rather homogeneous signatures are not well known yet. Chan et al. (2002) suggested that Li isotope signatures of hydrothermal fluids reflect an average isotope equilibrium with the dyke section (1000–2200 m).

Experimental studies from Pistiner and Henderson (2003), Wimpenny et al. (2010) and Verney-Carron et al. (2011) indicate no preferential release of ^{7}Li during basalt dissolution. Verney-Carron et al. (2011) have highlighted transient ^{6}Li enrichment in solution caused by diffusion. This kinetic effect could be significant in the range of temperatures seen in hydrothermal fluids (200–350 °C), but the high rates of dissolution under high temperature conditions rapidly masks the non-stoichiometric release of Li caused by diffusion.

In the literature, high temperature water–rock Li isotope fractionation factor estimates come either from experimental studies (James et al., 2003; Pistiner and Henderson, 2003; Williams and Hervig, 2005; Vigier et al., 2008) or from natural hydrothermal fluid data, by assuming that the solid phase isotope signature is similar to fresh MORBs (Chan et al., 1993; Millot et al., 2010). There are only few data for natural solids altered at high temperatures (Chan et al., 1994; Gao et al., 2012). In this study, we focus on an accessible, well constrained geothermal system in order to explore Li isotope behavior at high temperatures in a natural basaltic system. Even if differences exist between subaerial and submarine hydrothermal systems in terms of mineralogy and structure (permeability, W/R ratio) (Chan et al., 2002; Alt et al., 2010; Gao et al., 2012; Brant et al., 2012) and in terms of circulating fluids (derived from meteoritic water or seawater) (Alt et al., 2010), the published Li isotope signatures of subaerial and submarine fluids are indistinguishable (Fig. 1b), suggesting that a geothermal system located on a subaerial ridge can be used – as a first approximation – as an appropriate analogue of a submarine hydrothermal system in terms of Li and Li isotopes.

2. Hydrothermal setting

Iceland is a subaerial section of the Mid-Atlantic Ridge at the diverging plate boundary between the North American and Eurasian plates. Active tectonic and volcanic zones cross the island from southwest to northeast. In South Iceland, rifting is divided into two parallel branches whereas in the North, it is confined to a single branch (e.g. Hardarson et al., 1997). The axial rift zone is under tensional stress parallel to the spreading direction. Consequently, regional heat flow is high (Pálmason, 1973) and hydrothermal activity is widespread in the country (Bödvarsson, 1961) with high temperature manifestations (>200 °C) confined to the active zones of rifting and volcanism (Pálmason and Sæmundsson, 1974).

The Hengill area, located 25 km east of Reykjavík, sits between the Reykjanes Peninsula rift zone, the Western Volcanic Zone and the South Iceland Seismic Zone. This is one of the most extensive geothermal areas in Iceland (host to two geothermal power plants: Nesjavellir and Hellisheidi) that has been extensively studied as a resource for electrical and heating needs. Permeability in the reservoir is believed to relate largely to intrusions and major faults. The sampling site for this study is located in the Hellisheidi geothermal field located in the southern part of the Hengill volcanic system (Fig. A.1 in Supplementary Materials) in the Western Rift Zone. The local geology consists of volcanic rocks of late Quaternary and Holocene age (Árnason et al., 1969), notably subaerial basaltic lavas (erupted in interglacial periods) and hyaloclastites (formed during the glacial periods). All the basaltic rocks have olivine tholeiite or tholeiite compositions (e.g. Sæmundsson, 1995; Tareke, 2002). The hyaloclastites are divided into hyaloclastite tuffs (with predominant volcanic glass) and hyaloclastite breccias (with glass and partially crystallized basalt) (Fig. 2). The basaltic lavas are either medium-coarse grained or fine-medium grained. The lavas covering the central part of Hellisheidi are postglacial and erupted between 5000 and 2000 years ago (Sæmundsson, 1995; Tareke, 2002). The geothermal fluids are likely low in salinity due to their meteoric origin (Larsson et al., 2002).

The studied samples come from drill cuttings retrieved during the drilling of well HE-50 in 2008. Hyaloclastites were collected at various depths: 350, 500, 650, 850, 900, 1000, 1100, and 1400 m (Fig. 2). The corresponding temperatures of alteration (170 to 300 °C) were determined by temperature logs (Fig. 2). Fluid generally circulates upwards in this zone (Franzson et al., 2010).

3. Analytical methods

3.1. Mineralogy of the samples

The mineralogy of the hyaloclastites was determined by XRD on non-oriented powders at the LEM (Nancy, France). XRD data were collected by using a D8 Bruker diffractometer with Co $K\alpha_1$ radiation ($\lambda = 1.79026$ Å). The operating conditions were 35 kV accelerating voltage and 45 mA intensity. The step scanning was 0.035° (2θ), the counting time was 3 s and the range of measurements was 3–64° (2θ).