Lithium isotope compositions measured by multi-collector ICP-MS and the question of light isotope fractionation at high temperatures

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We report on initial efforts to measure the isotopic composition of lithium using a VG Plasma 54-30 multi-collector magnetic sector ICP-MS. Precision of multiple replicate and duplicate measurements for a variety of sample types ranges from ±0.98‰ to ±2.1‰ (2σ population) level, with a mean uncertainty of ±1.6‰. The method allows for the rapid (*c.* 9 min/sample) analysis of small samples (*c.* 40 ng Li). The technique has been applied to a suite of basalts from the Kilauea Iki lava lake, Hawaii. The samples, which range from olivine-rich, high-Mg lava to highly differentiated liquids, have δ^6Li (^{6}Li/^{7}Li relative to the L-SVEC standard) of −4.6 to −3.0‰. The data indicate, given our current capacity to resolve differences in δ^6Li, a lack of Li isotope fractionation concomitant with crystal-liquid fractionation at temperatures greater than 1000°C. This conclusion has been tacitly assumed but never demonstrated, and is important to the interpretation of Li isotope results from such geochemically complex situations as island arcs.

The analytical method

After standard acid digestion, rock samples are loaded on cation exchange columns in a mixture of dilute HNO_3 and methanol. Lithium is eluted completely in the 30-150 ml fraction of 1.0 M HNO_3 in 80% methanol. As shown by Strelow *et al.* (1974), this medium produces large contrast in the equilibrium resin-solvent distribution of Li and Na, the next most chemically similar element. Solutions dry to small droplets and are subsequently diluted in 1 M HNO_3 to approximately 100 ppb Li. Standard materials exposed to ion exchange separation as samples show no offset in ^{6}Li/^{7}Li, as would be the

TABLE 1. Lithium isotope results for multiply duplicated and replicated samples

		δ^6Li (‰)
Seawater	duplicates (n = 5):	(2/24) −29.6; (2/27) −31.3, −32.3, −30.4; (3/2) −30.1
	replicate (n = 2):	(3/26) −30.2, −30.0
	average (±2σ):	−30.7±1.8
Groundwater #1	duplicates (n = 5):	(3/2) −12.8, −13.6, −13.8; (3/3) −15.6; (3/6) −14.8
	replicate (n = 1):	(3/26) −14.8
	average (±2σ):	−14.2±2.0
Groundwater #2	duplicates (n = 5):	(3/3) −12.5, −12.5, −12.1; (3/4) −11.2; (3/6) −12.9
	replicate (n = 1):	(3/26) −12.4
	average (±2σ):	−12.3±1.2
Kilauea basalt 67−2−85.7	duplicates (n =5):	(3/4) −4.5, −3.9; (3/6) −4.0, −3.3; (3/26) −3.8
	replicate (n = 1):	(3/26) −3.2
	average (±2σ):	−3.8±0.98
Kilauea basalt 79−1R1−167	duplicates (n = 5):	(3/4) −3.1, −4.1; (3/6) −5.5, −4.5; (3/26) −5.6
	average (±2σ):	−4.6±2.1

case if Li was not extracted quantitatively from the resin.

Solutions are aspirated into the Ar plasma through a CETAC MCN-6000 desolvating nebulizer. This allows for very slow sample uptake yet elevated ion intensity relative to conventional nebulizers. The ratio ^{6}Li/^{7}Li is measured without peak-jumping, owing to the employment of a high-mass faraday cup. A 100 ppb solution analyzed with the MCN-6000 yields a ^{7}Li ion current of *c.* 4.0×10^{-12} A. Samples of diverse matrices (e.g., saline groundwaters, seawater, rocks of variable bulk composition) and those of different specific dilutions (for between 50 and 500 ppb) demonstrate analytical performance equivalent to one another and to the pure standard solution.

Sample analyses are bracketed by analyses of an L-SVEC standard solution in order to achieve normalized ^{6}Li/^{7}Li, expressed as δ^6Li. Under identical instrument conditions the measured ^{6}Li/^{7}Li of the standard is seen to drift systematically over time (up to 3% over 8 hr). Isotope ratios of unknowns normalized to the mean value of temporally adjacent standards exhibit reproducibility of $\leqslant \pm 2.1‰$ (2σ population) when duplicated hours or days later (Table 1). Replicate preparations of individual samples show similar reproducibility. The measured δ^6Li of seawater from the central Pacific Ocean ($-30.7‰$) is within analytical uncertainty of the values measured by You and Chan (1996) and Hoefs and Sywall (1997) (Table 1). Although our present analytical precision is not equal to that achieved by most TIMS workers (*c.* $\pm 1‰$; You and Chan, 1996; Tomascak and Tera, 1997), the multi-collector ICP-MS technique has several notable advantages. Even when nebulizer rinsing and standard measurements are taken into account sample throughput is much more expedient than with TIMS. Individual analyses require only 40 ng Li, nearly a factor of 100 less than required by some TIMS methods. Also, the delicacy required in TIMS filament loading is avoided using ICP.

Kilauea Iki lava lake

The Kilauea Iki lava lake lies near the summit of Kilauea volcano, just to the east of its main caldera. The lava lake formed when the 1959 eruption of Kilauea filled a previously existing crater. A stable crust formed within a few weeks of the end of the eruption, and the lake has cooled and crystallized as a closed system ever since. The lava lake has been monitored and periodically drilled over the period 1960-1988. As a result of this intensive monitoring, the crystallization history of the picritic magma in the lake is exceedingly well understood. The lake drill cores contain both residual, olivine-rich zones and highly differentiated secondary liquids. The bulk of the chemical differentiation of the lava took place between 1200 and 1100°C, and internal fractionation was complete by the time the liquids reached 1060°C (Helz *et al.*, 1989). Hence, samples of the lake represent an unparalleled opportunity to examine if high temperature liquid-crystal fractionation affects isotope distribution of a very light element, such as lithium.

Five Kilauea Iki samples have been analyzed for their lithium isotope compositions. The total range in δ^6Li is -4.6 to $-3.0‰$. These values are within the expected range for MORB (Chan *et al.*, 1992). The samples include an olivine-rich eruption sample (δ^6Li = $-3.1‰$) and two highly differentiated liquids (δ^6Li = -4.6 and $-3.8‰$). The results for all of the lake samples are within analytical uncertainty, indicating that no appreciable Li isotope fractionation took place during high temperature differentiation. This conclusion is essential to the interpretation Li isotope data from geologically and geochemically complex areas, such as island arcs, in order to constrain the processes in nature by which Li isotopes will fractionate.

References

Chan, L.H., Edmond, J.M, Thompson, G. and Gillis, K. (1992) *Earth Planet. Sci. Lett.*, **108**, 151–60.

Helz, R.T., Kirschenbaum, H. and Marinenko, J.W. (1989) *Geol. Soc. Amer. Bull.*, **101**, 578–94.

Hoefs, J. and Sywall, M. (1997) *Geochim. Cosmochim. Acta*, **61**, 2679–90.

Strelow, F.W.E., Weinert, C.H.S.W. and Van der Walt, T.N. (1974) *An. Chim. Acta*, **123**, 123–32.

Tomascak, P.B. and Tera, F. (1997) *EOS Trans. Amer. Geophys. Union* (abstr.)

You, C.F. and Chan, L.H. (1996) *Geochim. Cosmochim. Acta*, **60**, 909–15.