

# LITHIUM ISOTOPIC COMPOSITION OF ECLOGITES: IMPLICATIONS FOR SUBDUCTION ZONE PROCESSES

Roberta L. Rudnick<sup>1</sup>, William F. McDonough<sup>1</sup>, Paul B. Tomascak<sup>1</sup>, Thomas Zack<sup>1\*</sup>

<sup>1</sup>University of Maryland, U.S.A., \*Now at Universität Heidelberg, Germany

## INTRODUCTION

Lithium is a fluid mobile alkali metal that can be used to track fluid processes in the Earth. It is moderately incompatible during partial melting, and is incorporated into mantle minerals at the ppm level, where it is thought to substitute for  $Mg^{2+}$  in octahedral coordination. The large mass difference (~15%) between its two isotopes,  $^6Li$  and  $^7Li$ , produces large isotopic fractionations in near-surface, low temperature environments ( $^7Li$  from -20 to +40‰; Hoeffs and Sywall, 1997; Njo et al., unpublished data, where  $^7Li = [(^7Li/^6Li)_{sample}/(^7Li/^6Li)_{standard}] - 1$ , and the reference standard used is the NIST pure Li solution L-SVEC). Although the temperature-dependence of lithium isotope fractionation has yet to be established, it is known that Li does not fractionate at the high temperatures of basaltic magmatism (1000-1200°C, Tomascak et al., 1999a).

The isotopic fractionation in Li between fluids and rocks is in the opposite sense from oxygen: fluids are isotopically heavier than the minerals with which they equilibrate. This is reflected by the fact that seawater Li is very heavy (+32 ‰) compared to Li in fresh (+2 to +6 ‰) or altered (+6 to +14 ‰) MORB (Chan et al., 1992). This fractionation sense is attributed to the changing coordination number between water and minerals: tetrahedral in water vs. octahedral in most minerals (e.g., clays and ferro-magnesian minerals, where Li substitutes for Mg).

Chan et al. (1992) demonstrated that Li isotopic composition of MORB is positively correlated with the degree of alteration and Li abundance (Fig. 1). This suggests the uptake of heavy oceanic Li during low temperature sea floor alteration. Thus, low temperature alteration makes oceanic crust heavier than the mantle and Li isotopes may therefore provide a sensitive tool for tracing recycled materials in the Earth's mantle.

We have measured the Li isotopic composition of Alpine and xenolithic eclogites, both of which have been suggested to represent or be analogs of subducted oceanic crust (Zack et al., 2001, 2002; Barth et al., 2001, 2002a, 2002b). The aims of this investigation are to determine the utility of Li isotope studies in tracing recycled oceanic crust in the mantle, to understand the processes that affect

Li isotopes during subduction and to gain further insight into the origin of xenolithic eclogites.

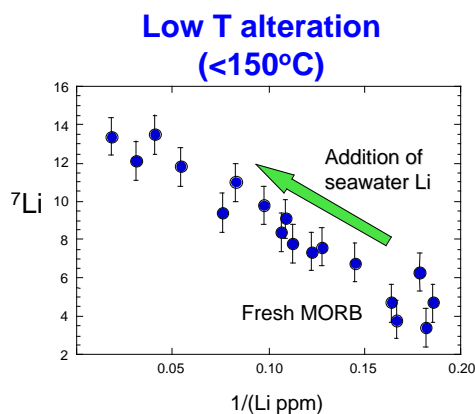


Fig. 1. Correlation of Li isotopic composition and Li concentration in MORB altered at low temperature (from Chan et al., 1992).

## ANALYTICAL METHODS

Whole rock powders for Trescolmen eclogites are from the same samples investigated in companion studies (Zack et al., 2001, 2002) and were produced from cm-sized splits that were individually selected for their low degree of alteration. We also prepared omphacite and phengite separates from the eclogites and surrounding mica schists, respectively. Pure omphacite separates were prepared from xenolithic eclogites from the Koidu kimberlite pipe, Sierra Leone (Hills and Haggerty, 1989; Fung and Haggerty, 1995; Barth et al., 2001, 2002, 2003). Mineral separates (omphacite and phengite) were hand-picked from grain size fractions of 180-300  $\mu m$ . The mineral separates are estimated to be >99% pure for phengite and >99.9% pure for omphacite.

Acid digestion and column chemistry methods employed for the Trescolmen samples follow the procedures described in Tomascak et al. (1999) with some minor modifications outlined in Zack et al. (2003). The four-column Li separation procedure of Moriguti and Nakamura (1999) was employed for the Koidu omphacites.

Prior to analyses, the Na:Li ratio of each solution was measured semi-quantitatively, as ratios greater than ~5 cause unstable instrumental fractionation, thus inhibiting accurate Li isotope determinations (Tomascak et al., 1999). About ~20% of the samples required additional purification.

Lithium isotopic measurements were performed on a Nu Plasma MC-ICP-MS at the University of Maryland Geochemistry Laboratory by simultaneous collection of  $^6\text{Li}^+$  and  $^7\text{Li}^+$  beams in Faraday cups. Samples were introduced to the plasma using a desolvating nebulizer (Cetac Technologies Aridus®) employing a PFA nebulizer (Elemental Scientific Inc.). Uptake rate varied depending on the individual nebulizer employed but ranged between 30 to 60  $\mu\text{l}/\text{min}$ . Sensitivity was on the order of 1.5 to 2 V  $^7\text{Li}^+$  ( $10^{11}$  ohm resistor) for a 50 ppb solution aspirated at 35  $\mu\text{l}/\text{min}$ .

Isotopic analysis of each unknown was bracketed by measurement of the L-SVEC standard and  $^7\text{Li}$  values were calculated directly from the comparison of the unknown to average standard analysis (as described in Tomascak et al., 1999). Several standards (the in-house Li-UMD-1 [a purified Li solution from Alfa Aesar®] and IRMM-016, and international standard reference material) were routinely run during the course of sample analyses. Reproducibility for these materials was  $\pm 1.0\text{‰}$  (2 sigma) over the course of the analyses performed here. Accuracy, assessed on the basis of measurement of international rock (BHVO-2 and JB-2) and pure Li standards (IRMM-016) is better than  $\pm 1.0\text{‰}$  (2 sigma).

## ALPINE ECLOGITES, TRESCOLMEN, SWITZERLAND

Alpine eclogites from Trescolmen, Switzerland, derive from MORB-like rocks that experienced variable degrees of low-T seafloor alteration prior to high-pressure metamorphism (Zack et al., 2001, 2002).  $^7\text{Li}$  of the whole rock eclogites (-11 to +0.3‰) are generally within error of those of the omphacite separates (Fig. 2). When exceptions occur, the whole rocks are generally heavier than the omphacites, which may reflect some minor retrograde overprinting (Zack et al., 2003). The omphacites are considered to be the most reliable indicator of the  $^7\text{Li}$  during high P metamorphism.

The Li isotopic compositions of Trescolmen eclogites range to dramatically lighter values than are observed in fresh or altered MORB (+4.5 to +14‰ for low T (Chan et al., 1992) and -2 to +8‰ for high T altered MORB (Chan et al., 2002)). These light values cannot be explained by fluid interaction with surrounding garnet mica schist, which is generally isotopically heavier ( $^7\text{Li}$  of +2.4 to

+3.8‰) (Fig. 3). The light  $^7\text{Li}$  values were likely produced by isotope fractionation through Rayleigh distillation during dehydration of clays and/or chlorite at early stages of subduction (Zack et al., 2003). These data are consistent with isotopically heavy Li being released into the forearc mantle wedge in subduction zones (Benton et al., 1999; Chan and Kastner, 2000). The data also suggest that an isotopically light component is subducted deeply, which may form a distinct mantle reservoir that could be sampled by plume-related magmas.

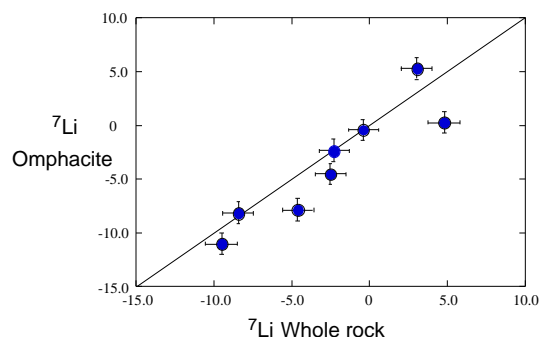


Figure 2. Comparison of  $^7\text{Li}$  in whole rocks and corresponding omphacites from Trescolmen eclogites (from Zack et al., 2003). Error bars are 2 sigma.

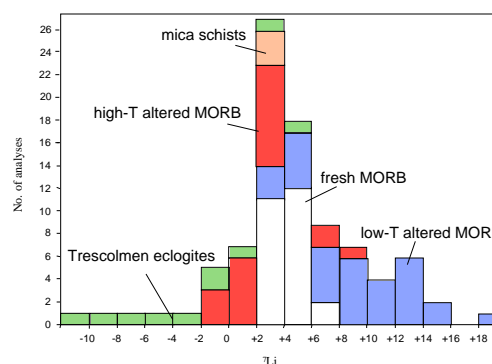


Figure 3. Histogram of Li isotopic compositions for Trescolmen eclogites compared to possible protolith compositions (fresh and altered MORB).

## XENOLITHIC ECLOGITES, KOIDU, SIERRA LEONE

Xenolithic eclogites from the Koidu kimberlites, Sierra Leone, fall into two groups. Eclogites of the high MgO suite are bi-mineralic (Hills and Haggerty, 1989; Fung and Haggerty, 1995), generally LREE enriched, have

oxygen isotope values that fall completely within the mantle range (Fig. 4; Barth et al., 2002b), and are of uncertain age (Barth et al., 2002a). Barth et al. (2002b) interpreted the high MgO suite to represent low pressure cumulates from basaltic to picritic magmas that have been variably overprinted by LREE-enrich fluids or melts.

In contrast, eclogites of the low MgO suite are mineralogically diverse (Hills and Haggerty, 1989; Fung and Haggerty, 1995), LREE depleted and have oxygen isotope values that range beyond the mantle value (Fig. 4; Barth et al., 2001). Based on Re-Os systematics, these rocks appear to have formed in the Archean (Barth et al., 2002a). Altered oceanic crust shows variable oxygen isotopic compositions, which correlate with the temperature of alteration (Gregory and Taylor, 1981; Muehlenbachs, 1986). Oceanic crust altered near the sea water-basalt interface at low temperatures has heavy oxygen values, whereas  $^{18}\text{O}$  in crust altered at high temperatures may be similar to unaltered MORB, or isotopically light. Accordingly, Barth et al. (2001, 2002a) interpreted the low MgO eclogites as representing subducted oceanic crust that stalled within the lithosphere of the west African craton. We have therefore focused our initial Li isotope investigations on the low MgO eclogites.

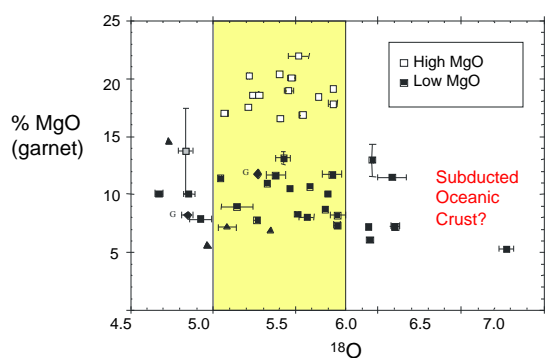


Figure 4. Oxygen isotopic compositions of garnets from the Koidu eclogites (from Barth et al., 2001, 2002b). Horizontal error bars show average reproducibility (one half of the difference between two separate measurements); vertical error bars indicate mineral zoning.

In contrast to the highly variably and very light lithium isotopic composition of the Alpine eclogites,  $^7\text{Li}$  of omphacites from the Koidu eclogites show a more restricted range, from light values of  $-2.3\text{‰}$  up to heavy values of  $+8\text{‰}$  (Fig. 5), with several samples having mantle-like values of  $+4$  to  $+5\text{‰}$ . Interestingly, there is an apparent relationship between  $^7\text{Li}$  and  $^{18}\text{O}$ : samples with the heaviest oxygen isotopes show the greatest

variation in lithium isotopes, whereas those with light oxygen have  $^7\text{Li}$  strictly within the mantle range (Fig. 5). Heavy oxygen occurs in oceanic crust altered under low temperature conditions. Thus the variable Li in the eclogites with heavy oxygen may reflect variable degrees of low temperature dehydration of an altered oceanic protolith having an initially heavy Li isotopic composition (Chan et al., 1992, 2002).

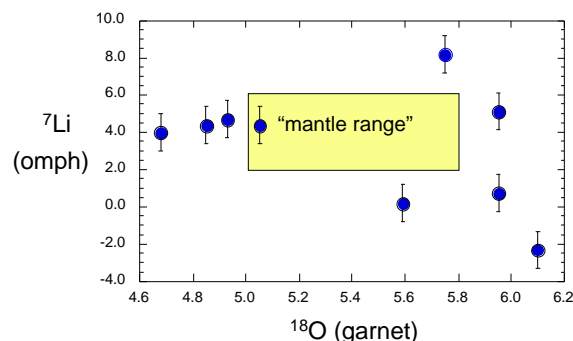


Figure 5. Oxygen isotopic compositions of garnets and Li isotopic compositions in coexisting omphacites from the Koidu low MgO eclogites. Vertical error bars represent 2 sigma uncertainty.

Likewise, light oxygen occurs in the deeper regions of oceanic crust altered under high T conditions. The Li in such crust ranges from “normal” mantle values to light values (down to  $-2\text{‰}$ , Chan et al., 2002). The mantle-like Li isotopic composition of the Koidu eclogites having “light” oxygen is thus consistent with observations from present day oceanic crust.

We conclude that the new Li data for the Koidu eclogites is consistent with their origin from oceanic crust that was altered at both high and low temperatures and then dehydrated during subduction.

## REFERENCES

- Barth, M.G., Rudnick, R.L., Horn, I., McDonough, W.F., Spicuzza, M.J., Valley, J.W., Haggerty, S.E. (2001) Geochemistry of xenolithic eclogites from West Africa, Part I: a link between low MgO eclogites and Archean Crust Formation, *Geochim. Cosmochim. Acta* 65: 1499-1527.
- Barth, M.G., Rudnick, R.L., Carlson, R.W., Horn, I., McDonough, W.F. (2002a) Re-Os and U-Pb geochronological constraints on the eclogite-tonalite connection in the Archean Man Shield, West Africa, *Precam. Res.* 118, 267-283.

- Barth, M.G., Rudnick, R.L., Horn, I., McDonough, W.F., Spicuzza, M.J., Valley, J.W., Haggerty, S.E. (2002b) Geochemistry of xenolithic eclogites from West Africa, Part II: origins of the high MgO eclogites, *Geochim. Cosmochim. Acta* 66: 4325-4346.
- Benton, L.D., Savoy, I and Ryan, J.G. (1999) Recycling of subducted lithium in forearcs: Insights from a serpentine seamount, *EOS* 80, S349.
- Chan, L.H. and Kastner, M. (2000) Lithium isotopic compositions of pore fluids and sediments in the Costa Rica subduction zone: implications for fluid processes and sediment contribution to the arc volcanoes, *Earth Planetary Sci. Lett.* 183: 275-290.
- Chan, L.H., Alt, J.C. and Teagle, A.H. (2002) Lithium and lithium isotope profiles through the upper oceanic crust: A study of seawater-basalt exchange at ODP Sites 504B and 896A, *Earth Planet. Sci. Lett.* 201: 187-201.
- Chan, L.H., Edmond, J.J., Thompson, G. and Gillis, K (1992) Lithium isotopic composition of submarine basalts – Implications for the lithium cycle in the oceans, *Earth Planet. Sci. Lett.* 108: 151-160.
- Fung, A.T. and Haggerty, S.E. (1995) Petrography and mineral compositions of eclogites from the Koidu Kimberlite Complex, Sierra Leone, *J. Geophys. Res.* 100: 21,451-20,473.
- Gregory, R.T. and Taylor, H.P. (1981) An oxygen isotope profile in a section of Cretaceous oceanic crust, Samail ophiolite, Oman: evidence for  $^{18}\text{O}$  buffering of the oceans by deep (>5 km) seawater hydrothermal circulation at mid-ocean ridges, *J. Geophys. Res.* 86: 2737-2755.
- Hills, D.V. and Haggerty, S.E. (1989) Petrochemistry of eclogites from the Koidu kimberlite complex, Sierra Leone, *Contrib. Mineral. Petrol.* 103: 397-422.
- Hoefts, J. and Sywall, M. (1997) Lithium isotope composition of Quaternary and Tertiary biogenic carbonates and a global lithium isotope balance, *Geochim. Cosmochim. Acta* 61: 2679-2690.
- Moriguti, T. and Nakamura, E. (1999) High-yield lithium separation and precise isotopic analysis for natural rock and aqueous samples, *Chem. Geol.* 145, 91-104.
- Muehlenbachs, K. (1986) Alteration of the oceanic crust and the  $^{18}\text{O}$  history of seawater. In (J.W. Valley, H.P.J. Taylor and J.R. O'Neil, eds.) Stable Isotopes in High Temperature Geological Processes, Mineralogical Society of America, Reviews in Mineralogy, pp. 425-444.
- Tomascak, P. B., Tera, F., Helz, R. T. and Walker, R. J. (1999a) The absence of lithium isotope fractionation during basalt differentiation: New measurements by multicollector sector ICP- MS, *Geochim. et Cosmochim. Acta* 63: 907-910.
- Tomascak, P.B., Carlson, R.W. and Shirey, S.B. (1999b) Accurate and precise determination of Li isotopic compositions by Multi-Collector Sector ICP-MS, *Chem. Geol.* 158, 145-154.
- Zack, T., Rivers, T. and Foley, S.F. (2001) Cs-Rb-Ba systematics in phengite and amphibole: An assessment of fluid mobility at 2.0 GPa in eclogites from Trescolmen, Central Alps, *Contrib. Mineral. Petrol.* 140: 651-669.
- Zack, T., Foley, S.F. and Rivers, T. (2002) Equilibrium and disequilibrium trace element partitioning in hydrous eclogites (Trescolmen, Central Alps), *J. Petrol.* 43, 1947-1974.
- Zack, T., Tomascak, P.B., Rudnick, R.L., Dalpé, C. and McDonough, W.F. (2003) Extremely light Li in orogenic eclogites: The role of isotope fractionation during dehydration in subducted oceanic crust, *Earth Planet. Sci. Lett.* (in press).

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Contact: R.L. Rudnick, Geochemistry Laboratory, Department of Geology, University of Maryland, College Park, MD 20742, U.S.A., E-mail: rudnick@geol.umd.edu