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The lithium isotopic composition of orogenic eclogites and deep subducted slabs

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Abstract

We have modelled the Li budget of subducting oceanic crust during dehydration, using recently established input parameters. The results show that the entire prograde metamorphic process, up to anhydrous eclogite, can account for a decrease in δ^7Li of only ≤3‰. Given that altered, oceanic crust entering the subduction zone should have Li isotopic compositions between −3 and +14‰, dehydration cannot account for markedly light Li isotopic compositions (δ7Li<0 to −10‰) previously measured in some high-pressure metamorphic (HPM) rocks. We have analysed another 41 orogenic HPM rocks from 11 different localities. These samples show a wide range in Li abundances from 1 to 77 µg/g. Li isotopic compositions of the rocks display both very heavy (δ^7Li>+6‰) and very light (δ^7Li<0‰) compositions, as low as −21.9‰. Notably some of the samples with highest Li concentrations are also isotopically light, which would not be predicted by isotopic fractionation as a consequence of Li loss during dehydration. Li abundances in excess of 30 µg/g in orogenic HPM rocks of basaltic composition (eclogites) are higher than any value of altered MORB and presumably result from addition of Li after the onset of subduction, most probably during eclogitisation or exhumation. Hence we propose that light-δ^7Li values are generated by kinetic fractionation of the Li isotopes during diffusive influx of Li from the country rocks into the exhuming eclogite bodies. Our conclusions are in stark contrast to the previously accepted model, as we predict the deeply subducted eclogites to have a Li isotopic signature heavier than the mantle.

Keywords: lithium isotopes; eclogite; high-pressure; modelling; subduction zone

1. Introduction

The light alkali metal lithium with its two stable isotopes, ^{6}Li and ^{7}Li, has gained significant attention among geochemists during the last decade. Moderate incompatibility during mantle melting, high mobility in hydrous fluids and a strong isotopic fractionation at low temperatures make this trace element a potentially powerful tracer for recycled material in the Earth's mantle (Zack et al., 2003; Tomascak, 2004; Elliott et al., 2004, 2006). Lithium is enriched in low-temperature oceanic crust with an increase of ^{7}Li/^{6}Li ratios (noted as δ^7Li, the deviation from the L-SVEC standard in permil) due to the interaction with the heavy-Li seawater (Donnelly et al., 1980; Ryan and Langmuir, 1987; Chan and Edmond,

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1988; Chan et al., 1992, 2002a; Moriguti and Nakamura, 1998; Tomascak et al., 2000). Rocks entering subduction zones, therefore, have heavy Li isotopic signatures relative to fresh MORB. Hence, fluids released from subducting slabs, infiltrating the overlying mantle, should also contain heavy Li. The relatively low temperatures at which subduction zone dehydration occurs, allow for stable isotope fractionation between metamorphosed rocks and released fluids. This process makes the slab-derived fluids yet heavier, as ^{7}Li is preferentially partitioned into the hydrous fluids. Tomascak et al. (2000) emphasised that the fractionation processes taking place in subducting slabs are important for understanding the Li isotopic compositions of island arc volcanic rocks, but the quantification of the element and isotope budgets of deeply subducted slabs are also essential for a prediction on the impact of subduction on the generation of mantle heterogeneities and global recycling.

Zack et al. (2003) presented a pioneering study on the alpine eclogites from Trescolmen (Switzerland) that provided the first Li isotope data on high-pressure metamorphic rocks. These authors reported extremely light δ^7Li-values in these rocks that were interpreted as the high-pressure equivalents of low-temperature altered basalts. Zack et al. argued that these low δ^7Li-values were the result of Li isotope fractionation during subduction dehydration. These findings have been a key in developing current models of geochemical cycling of Li in the mantle and the interpretation of δ^7Li signatures in mantle-derived magmatic rocks. However, no further investigation of Li isotopes in such rocks has so far been conducted.

Zack et al. (2003) presented their subducted light-Li hypothesis with clearly articulated caveats: (i) the Rayleigh dehydration modelling was completed on the basis of poorly-known parameters, i.e. Li partition coefficients and Li isotope fractionation between solids and fluids, and (ii) the samples came from a single locality and it is questioned how representative the Trescolmen eclogites are of subducting oceanic crust in general. Recently, Wunder et al. (2006, 2007) have completed a series of experimental studies on Li isotope fractionation between different silicates and hydrous fluids of variable composition at a wide range of temperatures. Marschall et al. (2007) have modelled the release of Li from dehydrating subducting crust based on mineral–mineral and mineral–fluid partition coefficients from earlier studies, in combination with petrologic modelling of the metamorphic phase transitions and the resulting fluid loss. With the parameters from these studies it is now possible to put the Li isotope fractionation model of dehydrating slabs on a sounder basis. Additionally, we analysed the Li isotope ratios of a large number of different high-pressure metamorphic rocks from a variety of localities and compared these results to the now larger set of data on altered oceanic crust, sediments and serpentinites. By including the new experimental data into modelling, we demonstrate that Li isotope ratios in subducting crust cannot be shifted significantly by dehydration. Hence, the extremely light Li observed in orogenic eclogites is not a result of prograde dehydration of altered oceanic crust. We argue that Li is mobilised and redistributed among different lithologies at depth and isotopically fractionated due to kinetic effects. Li isotope fractionation during diffusion has been shown to produce extremely light Li on various scales (Richter et al., 2003; Lundstrom et al., 2005; Teng et al., 2006; Jeffcoate et al., 2007; Parkinson et al., 2007) and may well have also operated in orogenic eclogite bodies.

2. Analytical methods

Li isotope analyses were made in both Bristol and Frankfurt and although similar approaches were used, details of the different procedures are given separately below.

2.1. Frankfurt

Samples were dissolved in several steps using HF-HNO_3 and HCl, and finally dissolved in 5N HNO_3-methanol mixture (1:4 by volume). For column separation we followed the procedure of Seitz et al. (2004). Samples were finally taken up in 2% HNO_3 (10 ng/g solution) for measurement by the ThermoElectron®-Neptune multi-collector (MC) ICP-MS at the Institut für Mineralogie, Universität Frankfurt. Analyses corrected for total analytical blanks agreed with the uncorrected analyses within ±0.6‰, 2σ. Analyses were carried out sequentially by "bracketing" the sample with the L-SVEC standard solution (10 ng/g), followed by a blank-measurement. The internal precision and long term external reproducibility is ~1.2‰. Repeat measurements of JB-2 yielded values of 5.2±1.2‰. Li isotopic compositions are given in delta values relative to the NIST L-SVEC standard (Flesch et al., 1973).

2.2. Bristol 1

Initially, samples at Bristol were analysed following the method of Jeffcoate et al. (2004), which is similar to the Frankfurt procedure. In brief, samples were dissolved using several steps of HF-HNO_3–$HClO_4$ and HCl. Li was separated from 10–25 mg aliquots of powder using a two step, dilute HNO_3-methanol/dilute