



Variation of lithium isotope geochemistry during basalt weathering and secondary mineral transformations in Hawaii

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Abstract

Lithium isotopes are a potential tracer of silicate weathering but the relationship between lithium isotope compositions and weathering state still need to be established with precision. Here, we report Li concentrations and Li isotope compositions of soils developed along a 4 million year humid-environment chronosequence in the Hawaiian Islands. Li concentrations are variable with depth and age, ranging from 0.24 to 21.3 ppm, and significant Li depletions (up to 92%) relative to parent basalts are systematically enhanced towards the surface. Our calculations show that the relative contribution from atmospheric deposits to the Li soil budget remains small, with a maximum contribution from dust Li of 20% at the oldest site. This is explained by the capacity of the weathering products to retain, within the profiles, the Li coming from basalt alteration, and allows us to explore more specifically the role of alteration processes on soil Li isotope signatures. The $\delta^7\text{Li}$ values display a large range between -2.5‰ and $+13.9\text{‰}$. The youngest soils (0.3 ka) display the same $\delta^7\text{Li}$ value as fresh basalt, regardless of depth, despite $\sim 30\%$ Li loss by leaching, indicating that there is little Li isotope fractionation during the incipient stage of weathering. $\delta^7\text{Li}$ values for the older soils (≥ 20 ka) vary non-linearly as a function of time and can be explained by progressive mineral transformations starting with the synthesis of metastable short-range order (nano-crystalline) minerals and followed by their transformation into relatively inert secondary minerals. Results highlight significant Li isotope fractionation during secondary mineral formation and in particular during Li uptake by kaolinite. Finally, we suggest that the non-monotonous evolution of the regolith $\delta^7\text{Li}$ value over the last 4 Ma is consistent with climatic variations, where congruent release of Li isotopes occurs during warmer periods.

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1. INTRODUCTION

Chemical weathering of silicate rocks is an important regulator of the long-term global carbon cycle and there-

fore climate history (Walker et al., 1981; Dessert et al., 2001; Berner, 2004). In particular, basalt weathering accounts for about 35% of the global CO_2 sink associated with silicate weathering (Dessert et al., 2003), even though it covers a relatively small portion of Earth's surface. However, the key parameters and controlling factors of basalt weathering in nature are still debated (e.g., Gislason and Eugster, 1987; Gislason and Hans, 1987; Brady and Gislason, 1997; Dessert et al., 2001, 2003).

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In this context, lithium isotopes of large rivers and oceans have potential as a proxy for tracing the type and intensity of silicate weathering (Huh et al., 1998, 2001; Vigier et al., 2009; Pogge von Strandmann et al., 2010; Misra and Froelich, 2012). Nevertheless, more work is required to provide clear linkages between fractionation processes occurring at the weathering profile scale with those inferred to be operating based on aqueous samples from large rivers. Experimental investigations have shown that basalt dissolution is not associated with significant isotope fractionation (Pistiner and Henderson, 2003; Wimpenny et al., 2010a; Verney-Carron et al., 2011) and that the formation of secondary phases, such as smectite and Fe oxides, leads to preferential enrichment of ^6Li into the weathering solids (Williams and Hervig, 2005; Vigier et al., 2008; Wimpenny et al., 2010b). The few existing studies of basaltic soils show that lithium isotopes hold great promise for tracing terrestrial weathering processes, but that the soil isotope signatures can be rapidly buffered by atmospheric deposits such as dust, rain or marine aerosols (Pistiner and Henderson, 2003; Huh et al., 2004; Kisakürek et al., 2004; Pogge von Strandmann et al., 2012; Liu et al., 2013). Here, we examine the processes responsible for changes in the Li isotope composition during progressive weathering and development of basaltic soils along a humid-environment chronosequence in the Hawaiian Islands. The exceptionally clear variations in lava flow ages and relatively stable variations in climate in Hawaii (Hotchkiss et al., 2000; Vitousek, 2004) provide a useful natural laboratory to evaluate non-traditional isotope systems as tracers of basalt weathering and/or vegetation recycling (e.g., Kennedy et al., 1998; Stewart et al., 2001; Pistiner and Henderson, 2003; Huh et al., 2004; Wiegand et al., 2005; Ziegler et al., 2005; Bern et al., 2010). This study focuses on the behavior of lithium isotopes during the initial stages of basalt weathering, and leaching through the slow accumulation of metastable secondary minerals and their reorganization into relatively inert secondary crystalline phases. We assess ways in which these various factors fractionate lithium isotopes into soil solids and the implications for isotopic signatures in streams fed by waters passing through the weathering profiles. Furthermore, we assess the role of atmospheric deposition and recent climate variations that could modify the soil isotopic signals.

2. STUDY AREA

The Hawaiian Islands are an ideal place to study the complex patterns of soil and ecosystem development imposed by variations in climate and lava-flow age (Porder and Chadwick, 2009; Porder et al., 2007; Vitousek and Chadwick, 2013). The Hawaiian chronosequence considered here varies in age from 0.3 to 4100 ka and has been referred to as the “Long-Substrate Age Gradient (LSAG)”. Detailed descriptions of the LSAG are given in previous studies (e.g., Crews et al., 1995; Vitousek, 2004; Vitousek et al., 1997). All sites are near 1200 m elevation, receive 2500 mm annual rainfall, and have a mean annual temperature of 15 °C. The two youngest sites (0.3 ka; Thurston (Th) and Ola’a (Ol)) are in

Keanakakoi tephra derived from phreatomagmatic eruptions of tholeiitic composition at the summit of Kilauea (McPhie et al., 1990; Fiske et al., 2009), while the older sites (≥ 20 ka) are composed of alkali basalt, such as hawaiite, mugearite, and their associated tephra (MacDonald et al., 1983; Wright and Heltz, 1986; Wolfe and Morris, 1996). The soils exhibit a general trend of increasing crystallinity of secondary minerals with age (Chorover et al., 1999, 2004). In detail, the two youngest soils (0.3 ka) are Andisols composed primarily of glass, olivine, clinopyroxene, feldspar and magnetite-ilmenite. The three intermediate-aged soils (20, 150, and 1400 ka) are progressively more weathered Andisols with high concentrations of short-range-order materials, such as allophane, imogolite and ferrihydrite, whereas the oldest soil (4100 ka) is an Oxisol dominated by refractory secondary minerals, such as goethite, gibbsite, and kaolinite.

All soils are located on primary shield volcano surfaces, where physical erosion and groundwater influences are minimal. Erosion itself is nearly non-existent on Kilauea and Mauna Kea because the highly permeable lava flows have not yet been extensively capped by clay-rich soils that dramatically slow downward water flux and re-route it laterally (Lohse and Dietrich, 2005). On the older mountains, sampling sites are on constructional surfaces that are isolated on interfluvial surfaces far from stream channels. None of the core sites has been cleared or systematically altered by direct human action. A fundamental assumption associated with this work is that the soil age approximates the age of the underlying lava flow. Although there is no definitive test of the assumption, research performed over the past two decades suggests it to be tractable. However it is reasonable to assume that there is a greater divergence between lava flow age and soil residence time as volcano age increases (for further discussions of this point see Vitousek et al., 1997; Hotchkiss et al., 2000; Kurtz et al., 2001; Vitousek, 2004).

3. MATERIALS AND METHODS

3.1. Sample preparation and chemical analysis

Soils were collected from hand-dug pits to about 1 m depth except for the youngest soil; Thurston (Th) is about 40 cm deep and overlies unweathered pahoehoe lava, and Ola’a (Ol) is about 70 cm deep and overlies a buried soil on the ~1000 year old Kulanaokuaiki tephra (Fiske et al., 2009; Fig. 1). All samples were air dried, passed through a 2-mm sieve, and then crushed in a shatter box equipped with a tungsten carbide grinding container. About 0.1 g of each sample was completely digested using concentrated, ultrapure HCl, HClO₄, HF, and HNO₃. The samples were dried, refluxed several times in 6.0 M HCl to remove fluorides, and re-dissolved in 5% HNO₃. Cation and trace element concentrations were measured using a Perkin Elmer Optima 4300DU ICP-AES and a Thermo Elemental X-7 ICP-MS, respectively at the Korea Basic Science Institute (KBSI). Accurate quantification was achieved by external calibration of the data relative to three USGS basalt standard powders (BCR-2, BHVO-2, and BIR-1).

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