

Li Isotopes of Hawaiian Lavas: Kea vs Loa Source Variation

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Hawaiian volcanism delineates into two distinctive geographical series, the Kea and the Loa trends, identified by their unique geochemical and isotopic characteristics. Traditionally, these trends have been attributed to mixing of different components in the source of the Hawaiian mantle plume, mainly an enriched end-member (Ko'olau) characterized by the presence of recycled oceanic crust \pm sediment, a more depleted end-member (Kea) with high ϵ_{Nd} , ϵ_{Hf} , and $^{206}Pb/^{204}Pb$, and a more primitive component defined by high $^3He/^4He$ (Lo'ihi). Because of the sizeable fractionation of lithium isotopes in low temperature environments, lithium serves as a powerful tracer for the presence of altered oceanic crust and sediments in the sources of oceanic island basalts. Lithium can thus be used to help distinguish the source components of Hawaiian lavas, most importantly for post-shield and rejuvenated lavas, where depleted/recycled components are thought to play a larger role.

This study analyzed fifty-six samples of Hawaiian shield (13), post-shield (36) and rejuvenated lavas (7) for lithium isotopes. Post-shield volcanics exhibit the lightest δ^7Li values, ranging from $0.75 \pm 0.33\%$ to $5.20 \pm 0.20\%$, while rejuvenated lavas from Kaua'i, Ka'ula, and West Ka'ena Ridge are intermediate with an average of 3.72% . Finally, shield basalts exhibit the highest δ^7Li , ranging from $3.03 \pm 0.27\%$ to $5.19 \pm 1.07\%$. For both post-shield and shield lavas, δ^7Li is able to delineate between Kea and Loa trends (e.g., post-shield Kea average: 3.67% and post-shield Loa average: 2.48%). Lithium isotopes correlate positively with Pb and Nd isotopes, indicating that Li isotopic signatures survive residence time in the mantle and are suitable tracers of source components [1], in this case ancient subducted oceanic crust and/or sediments, in Hawaiian volcanism. In $^{206}Pb/^{204}Pb$ and ϵ_{Nd} vs δ^7Li diagrams, Loa shield lavas plot along the extension of Kea shield lavas with lower δ^7Li , ϵ_{Nd} and $^{206}Pb/^{204}Pb$. Enriched Loa shield lavas from West Ka'ena Ridge, the Mile High Section of Mauna Loa, and subaerial Ko'olau show higher δ^7Li , but with their lower ϵ_{Nd} and $^{206}Pb/^{204}Pb$, these lavas define a sub-parallel trend that indicates there are at least two enriched end-members in the Loa source, one in Ko'olau [2] and one in Loa trend lavas [3]. Finally, Hualalai post-shield volcanics show the lowest δ^7Li values, ranging from $0.75 \pm 0.33\%$ to $3.53 \pm 0.53\%$, which might reflect the presence of recycled oceanic crust.

In this study, lithium isotopes not only suggest the presence of a recycled component in post-shield, rejuvenated, and Loa shield lavas, they also help distinguish Loa enriched source components. Further characterization of the trends in lithium isotopes may unearth some additional insights into the source of Loa-type volcanism [4].

[1] Vlastélic *et al* (2009) *Earth and Planetary Science Letters* **286**, 456-466. [2] Tanaka *et al.* (2007) *Earth and Planetary Science Letters* **265**, 450-465. [3] Weis *et al.* (2011) *Nature Geosciences* **4**, 831-838. [4] Hanano *et al* (2010) *G3* **11**, doi:10.1029/2009GC002782

Incorporation of Perrhenate into Nitrate Sodalite

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Technetium-99 (Tc), a long-lived radionuclide, is one of the most widespread contaminants within the Hanford subsurface with an estimated inventory of 5.31×10^3 curies. For example, Tc contamination has been found in the sediments beneath the C, S, SX, T, and TX Tank Farms as a result of high-level waste (HLW) solutions that have leaked or spilled from Hanford Tanks. The HLW solutions are characterized as highly alkaline (hydroxide ion concentration > 8.5 M) and high ionic strength solutions (up to saturation with respect to $NaNO_3$). Previous research focused on Sr-90 and Cs-137 has demonstrated that these elements are incorporated into feldspathoid minerals, such as nitrate sodalite [$Na_8(Al_6Si_6O_{24})(NO_3)_2$], that formed as a result of the contact between Hanford sediments and the HLW solutions (Chorover *et al.*, 2008; Deng *et al.* 2006). The desire to immobilize Tc in aluminosilicate minerals through the application of subsurface amendments for contaminated sediments as well as the production of mineralized wasteforms further emphasizes the need to understand the long-term stability and release of Tc from aluminosilicate minerals, specifically the feldspathoid mineral sodalite.

Nonradioactive perrhenate (ReO_4^-) was used as a surrogate for TcO_4^- due to its similar ionic potential. Sodalite was synthesized over 24 h at 80C from 1.76 M solutions of $NO_3^- + ReO_4^-$, with ReO_4^- concentrations of 0, 0.18, 0.35, 0.71, 0.88, and 1.76 M with NaOH and 4A zeolite added as sources of Na, OH, Al, and Si. Perrhenate concentrations in the sodalite ranged from 0 to 13 mmol kg^{-1} in the 0 – 0.88 M ReO_4^- samples. The 1.76 M sample, without NO_3^- , contained 760 mmol kg^{-1} . Using the 211 x-ray diffraction peak to determine alteration of crystal structure, no significant shifts occurred, except in the NO_3^- -free sample where the 211 d-spacing increased by 0.01 nm. Increased reaction time from 1 to 7 d narrowed the peak widths, implying more crystallinity, but ReO_4^- incorporation did not change in a consistent manner. We conclude that the larger ReO_4^- ion ($r = 260$ pm) does not form as stable a sodalite structure as the NO_3^- ($r = 190$ pm). Further experiments will determine the role of ion size in the formation of sodalite in the presence of more than one species.

[1] Chorover, J., Choi, S., Rotenberg, P., Serne, R.J., Rivera, N., Strepka, C., Thompson, A., Mueller, K.T., O'Day, P.A., 2008, *Geochimica et Cosmochimica Acta* **72**, 2024-2047.

[2] Deng, Y., Harsh, J.B., Flury, M., Young, J.S., and Boyle, J.S. 2006, *Applied Geochemistry*, **21**, 1392-1409.