

Si isotope systematics of acidic alteration of fresh Kilauean basalts

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Silicon isotopes are fractionated by low-temperature aqueous processes, making them potentially useful as a weathering proxy. Previous authors have reported that secondary minerals like clays and opal are lower in $^{30}\text{Si}/^{28}\text{Si}$ than the dissolved reservoirs from which they precipitated [1-2]. Young basalts from Kilauea, on the big island of Hawai'i, frequently feature opaque amorphous silica coatings, 2-80 μm thick, that form *in situ*, apparently by acidic surface leaching [3]. Here we show that, in contrast to secondary minerals in other settings, these coatings have higher $\delta^{30}\text{Si}$ than their basaltic substrate (which is presumed to be the source of Si in the surficial solutions from which the coatings precipitate).

Silica coated basalt samples were collected from 1974 and 1998 flows along Kilauea's East and Southwest Rift Zones. We removed the coating material by scraping and then dissolved it in dilute HF and HNO_3 [4]. The resulting solutions were purified by ion-exchange chromatography and analyzed by MC-ICP-MS. Basalt glasses had $\delta^{30}\text{Si} = -0.10$ to -0.24‰ ; silica coatings had $\delta^{30}\text{Si} = +0.92$ to 1.36‰ . These isotopic compositions are difficult to reconcile with previously reported fractionation factors (i.e. $\Delta^{30}\text{Si}_{\text{solid-aqueous}} < 0\text{‰}$). We hypothesize that the atypical direction of fractionation is a result of unusual aqueous Si speciation (e.g. fluoride, chloride and/or sulfate complexation).

Batch experiments in which fresh glassy basalt gravel was reacted in HCl or HF (0.1 or 1 M) at 60° C replicated Hawaiian amorphous silica layer morphology. The fluids preferentially mobilized Al, Mg, Fe, Na, and Ca, leaving behind amorphous silica residues up to 100 μm thick. In HCl-bearing experiments, reacted fluids were ^{30}Si -enriched (up to $\delta^{30}\text{Si} = 2.29\text{‰}$). HF-bearing experiments produced ^{28}Si -enriched fluids, suggesting preferential incorporation of ^{30}Si into precipitated silica or volatilization of ^{30}Si . These results indicate that fluid chemistry influences the direction and magnitude of Si isotope fractionation during weathering.

[1] Georg *et al.* (2007), *EPSL* **261**, 476-490. [2] Milligan *et al.* (2004) *Limnol. Oceanogr.* **49**, 322-329. [3] Chemtob *et al.* (2010), *JGR* **115**, 2009JE003473. [4] Ziegler *et al.* (2010) *EPSL* **295**, 487-496.