

Titanium Isotope Fractionation in Kilauea Iki Lava Lake is Driven by the Crystallization of Oxides

ALEISHA C. JOHNSON^[1], SARAH AARONS^[2,3], NICOLAS DAUPHAS^[2], NICOLE XIKE NIE^[2], HAO ZENG^[2], FANG-ZHEN TENG^[4], ROSALIND HELZ^[5], GIULIA GALLI^[6,7], STEPHEN J. ROMANIELLO^[1], ARIEL D. ANBAR^[1]

¹School of Earth and Space Exploration, Arizona State University, Tempe AZ 85287

²Department of Geophysical Sciences, University of Chicago, Chicago IL 60637

³Scripps Institution of Oceanography, University of California-San Diego, San Diego CA 92093

⁴Department of Earth and Space Sciences, University of Washington, Seattle WA 98195

⁵United States Geophysical Survey, MS 926A, Reston VA 20192

⁶Institute for Molecular Engineering, University of Chicago, Chicago IL 60637

⁷Department of Chemistry, University of Chicago, Chicago IL 60637

Recent work has demonstrated that stable titanium (Ti) isotopes are fractionated during magmatic differentiation, leaving evolved silicic melts enriched in heavy Ti isotopes. Accurate calibration of Ti isotope fractionation to magmatic silica content has the potential to trace the evolution of the continental crust, but has been hindered by a lack of mechanistic studies. To this end, we present Ti isotope measurements of Fe-Ti oxide mineral separates of Kilauea Iki Lava Lake basalts. We find the Fe-Ti oxides are isotopically light and the residual melt and minerals are isotopically heavy. This result is consistent with the fact that Ti in oxides is primarily in 6-fold coordination whereas Ti in silicate melts is in 5- or 4-fold coordination. We also present density functional theory (DFT) calculations supporting this conclusion. These calculations demonstrate that pseudobrookite, K-titanate, and Ba-titanate show a progressive heavy isotope enrichment for Ti in 6-fold, 5-fold, and 4-fold coordination, respectively. Accounting for potential variations in equilibrium vs. kinetic fractionation, we calculate the following temperature-dependence for this fractionation factor: $\Delta^{49}\text{Ti}_{\text{silicate-oxide}} = (0.75 \pm 0.04) \times 10^6/T^2$. We use this fractionation factor in Rhyolite MELTs to model the $\delta^{49}\text{Ti}$ evolution of plume lavas and find it to accurately predict the fractionations observed in Kilauea Iki, as well as the fractionations observed in volcanics from Hekla, Iceland and Afar, East Africa reported in previous studies.