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Empirical and Experimental Constraints on Fe-Ti Oxide-Melt Titanium Isotope Fractionation Factors

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Recent studies [1-3] have demonstrated the potency of titanium (Ti) isotopes as a tracer of Fe-Ti oxide-melt equilibria. Titanium primarily occupies a 5-fold coordination in silicate melts and 6-fold coordination in Fe-Ti oxides. This coordination contrast serves as the main mechanism driving Ti isotope fractionation, which results in a progressive enrichment in heavy Ti isotopes (expressed as high $\delta^{49/47}$Ti) during magmatic differentiation. Additionally, the magnitude of Ti isotope fractionation observed during magmatic differentiation is controlled by melt TiO_2 content and redox conditions, both of which influence the timing of Fe-Ti oxide crystallisation and the composition of Fe-Ti oxides [3].

Analyses of Fe-Ti oxide mineral separates (titanomagnetite+ilmenite) [2] and ab-initio studies [4,5] have confirmed oxides are isotopically light compared to silicate melts or minerals. However, there is currently no data for individual oxide-melt Ti isotope fractionation factors.

We present Ti isotope fractionation factors for titanomagnetite, ilmenite and rutile, which have been derived from crystal-groundmass pairs in lavas from Santorini (calc-alkaline) and Heard Island (intraplate), and from rutile-melt experiments [6]. Selected oxides and groundmass/glass were extracted via micro-mill for MC-ICP-MS analysis. Our results show that titanomagnetites display the largest mineral/melt $\Delta^{49/47}$Ti fractionation factors, followed by ilmenite, then rutile. This is consistent with stable isotope theory which dictates that lighter isotopes prefer longer bonds, with Ti-O bond length decreasing from magnetite to ilmenite and rutile. The titanomagnetite-melt fractionation factor also increases as a function of titanomagnetite TiO_2 content, with magnetite from Heard Island (>20 wt% TiO_2) consistently displaying a greater fractionation factor in comparison to Santorini (≤15 wt% TiO_2). Our data enables the calculation of oxide-melt fractionation factors as a function of temperature, and TiO_2 content in the case of titanomagnetite. We apply these fractionation factors to successfully reproduce the $\delta^{49/47}$Ti evolution of a series of differentiation suites [4] using Rayleigh modelling and constraints from mineral compositions and modal proportions in lavas from the aforementioned differentiation suites.

[1] Millet et al. (2016), *EPSL*. [2] Johnson et al. (2019), *GCA*. [3] Hoare et al. (2020), *GCA*. [4] Leitzke et al. (2018), *CMP*. [5] Wang et al. (2020), *GCA*. [6] Klemme et al. (2005), *GCA*.