

THE ISOTOPIC FRACTIONATION OF TITANIUM IN IGNEOUS SYSTEMS: IMPLICATIONS FOR STUDIES OF EARLY DIFFERENTIATED ASTEROIDS. M. P. Ptáček¹, N. D. Greber¹, T. Pettke², L. Gfeller³, and N. Dauphas¹, ¹Origins Lab, University of Chicago, 5734 S Ellis Ave, Chicago IL 60637-1468, mptacek@uchicago.edu. ²Institut für Geologie, Universität Bern, Baltzerstrasse 1+3, CH-3012 Bern, Switzerland. ³TrES Gruppe, Geographisches Institut, Universität Bern, Hallerstrasse 12, CH-3012 Bern, Switzerland.

Introduction: The existence of highly differentiated asteroids in the early Solar System has long been hypothesised, and many instances of basaltic achondrites have been catalogued. However, the corresponding discovery of andesitic meteorites has taken much longer, and their petrogenetic studies are complicated by alteration and sulphite melt processes [1], which make it difficult to determine exactly how much partial melting a given sample has undergone. Herein we illustrate how the Ti isotope composition can be used to constrain the degree of partial melting, and thus shed some light on early Solar System processes.

The published literature contains very little work on mass-dependent Ti isotope systematics. In addition to being refractory and lithophile, Ti is also highly immobile, and is present (in terrestrial redox conditions) only in the Ti⁴⁺ valence state. Hence, Ti isotopic fractionation should be resistant to alteration, and affected predominantly by magmatic processes.

Significant variation in the Ti isotopic composition ($\delta^{49}\text{Ti}$) of terrestrial rocks has been observed, with values ranging from -0.07 to +0.55 ‰, and a well-defined correlation between $\delta^{49}\text{Ti}$ and the SiO₂ bulk concentration [2]. Calculations have also shown that in intermediate compositions (SiO₂ < 65 wt.%), the positive trend between $\delta^{49}\text{Ti}$ and silica content can be explained via the fractionation of light Ti isotopes into Fe-Ti oxides, which leaves behind a melt enriched in heavy isotopes [2]. However, this simple model begins to diverge from reality when applied to more evolved melts.

We present new Ti isotope measurements of samples from the Kos Plateau Tuff (KPT) in eastern Greece, where Mediterranean seafloor is subducted beneath the Aegean plate. Xenoliths from protracted calc-alkaline magmatic activity can be found among the eruptive products of the KPT [3]. Petrological studies have indicated that this magmatic system evolved predominantly by crystal fractionation with no or only very minor assimilation of sedimentary rocks [4], making it an ideal candidate for studies of Ti isotope fractionation in magmatic systems. Within the course of this study we measured the Ti isotope composition of two rhyolites (SiO₂ > 73 wt.%), two andesites, an olivine basalt, and a hornblende cumulate. The latter is a solid residue from an early-stage basaltic melt, measured in order to verify our hypothesis that as the fractionating melt becomes isotopically heavy, the cumulate should also become correspondingly lighter.

Measurement Methods: The samples were digested using flux fusion carried out in a graphite crucible, with a sample to LiBO₂ ratio of 1:6. A clean fragment of the resultant quenched glass was selected, mixed with a ⁴⁷Ti-⁴⁹Ti double spike, and then digested in 3M HNO₃ acid. Titanium was extracted from the sample through two stages of ion-exchange chromatography, using the TODGA and AG1-X8 resins respectively.

The resulting purified sample was dissolved in 0.3M HNO₃ + 0.005M HF and analysed in a Neptune ICPMS. Results are reported in the δ notation relative to the Origins Lab OL-Ti standard, the isotopic signature of which is within measurement error of the bulk silicate Earth [2]. The 2 σ uncertainty for the KPT samples was calculated as $\pm 0.035\%$ [5].

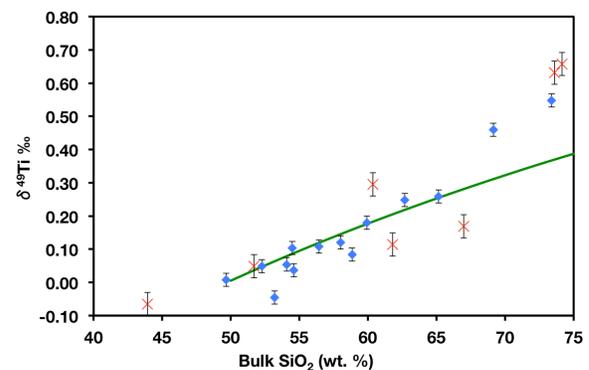


Fig. 1: Bulk rock isotopic fractionation data from Millet & al. (blue diamonds) and new measurements from the Kos Plateau Tuff (red crosses), alongside the best-fitting distillation model (green line). Whilst the fit to intermediate rocks is acceptable, highly evolved samples consistently plot above expected values. The measurement on the far left represents the hornblende cumulate, which is the solid residue of early fractional crystallisation, and shows significant depletion in the heavy Ti isotope. Errors are 95% confidence intervals.

Results: A trend of increasing isotopic fractionation with silicate content has been observed in the KPT samples, ranging from $-0.06 \pm 0.035\%$ in the magmatic hornblende cumulate to $+0.66 \pm 0.035\%$ in the heavily differentiated rhyolites. This trend is in general agreement with previously published terrestrial data [2], as shown in Fig. 1.

To our knowledge, the $\delta^{49}\text{Ti}$ signatures of the two rhyolites are the heaviest igneous Ti isotope compositions recorded to date. The measurement of the cumulate is consistent with our earlier prediction. Further-

more, the new data also confirm that at high values of SiO_2 , we observe isotopic values in excess of what was expected from an extrapolation of earlier data.

Fractionation Model: We have chosen to model isotopic fractionation through a simple Rayleigh distillation equation [5], of the form:

$$\delta_l = \delta_0 + 1000(\alpha - 1) \cdot \left(\ln \frac{c_l}{c_0} + \ln F \right)$$

where δ_l and c_l represent the isotopic composition & Ti concentration of a partially-fractionated liquid, δ_0 and c_0 the original values of the bulk liquid, α the isotopic fractionation factor, and F the remaining melt fraction. This model requires the knowledge of the Ti concentration in the melt as a function of F . We have chosen to parameterise this via a second distillation equation, of the form:

$$c_l = c_0 \cdot F^{(K_d-1)}$$

where K_d is the bulk solid-melt partition coefficient for Ti. Although the values generated by this model can be used to create a good fit to the isotopic data, the model cannot fully reproduce the measured TiO_2 concentrations of the data set, especially in the case of the non-intermediate samples (c.f. Fig. 2).

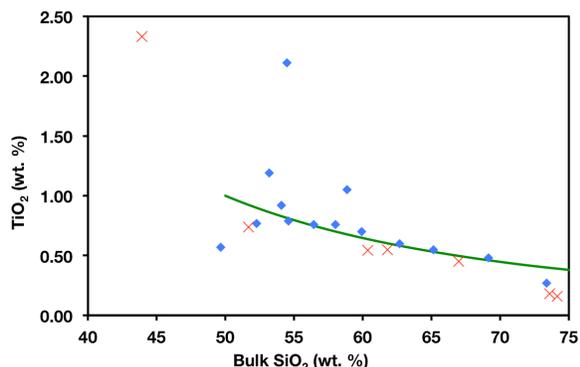


Fig. 2: Results from the first-order distillation model show a rough fit with Ti concentration outside intermediate SiO_2 compositions, suggesting a more complex chemical model might be necessary. Point on far left is the hornblende cumulate, which is not part of the fractionation trend. See Fig. 1 for legend.

Discussion: We observe there exists no single value for the isotopic fractionation factor that can adequately fit data from both intermediate and evolved samples, especially in the case of the new KPT data. This suggests the underlying mechanisms are more complex than assumed by our model.

One possibility is to consider other magma chamber processes besides from pure fractional crystallisation. For instance, petrological studies show that an evolved melt crystallising in a magma chamber often mixes with a freshly injected basaltic melt [6], and exactly such an event is thought to have triggered the

KPT eruption [4]. Since highly evolved melts have lower Ti concentrations than basaltic melts (Fig. 2), even a minimal amount of mixing could significantly alter their isotopic composition. However, since the isotopic trend caused by the mixing of basaltic and silicic endmembers should be very different from the fractionation trend, $\delta^{49}\text{Ti}$ could also provide insights into the mixing history of a given sample, in addition to its fractionation history. To disentangle the effects of mixing & fractionation with greater reliability, the amount of mixing could also be independently constrained with another geochemical system, for instance one of the high field strength elements.

Furthermore, as fractionation progresses, the liquid will be precipitating different mineral phases, each of which could have a different isotopic fractionation factor. For instance, evolved calc-alkaline systems have been known to precipitate biotite containing up to 5.8 wt.% TiO_2 [7]. In this case, our model will have to incorporate several mineral-specific fractionation factors, instead of a single bulk value. Should mineralogy prove significant, it will also be important to better identify when particular Ti-bearing phases stabilise during fractional crystallisation, and to fully integrate these results with the isotopic model.

Further Work: Mineral separates from the Kos Plateau Tuff will be analysed to determine whether the isotopic partition coefficient varies significantly across mineralogies. Furthermore, the rhyoliteMELTS software package will be used to constrain the evolution of the TiO_2 content and mineralogy better than a simple one-parameter distillation model.

Summary: Due to the immobility of Ti in the presence of fluids, the Ti isotopic system should prove a superior approach for investigating the fractional crystallisation history of heavily altered rocks and meteorites, compared to more traditional geochemical inversion methods. This technique has numerous applications – for instance, an isotopic study of the Graves Nunataks (GRA) 06128 and GRA 06129 differentiated meteorites, alongside brachinite samples, could help to confirm or reject the hypothesis that the latter represent the melt residues of the former [8][9].

References: [1] Day J. M. D. et al. (2009) *Nature*, 457, 179–182. [2] Millet M.-A. et al. (2016) *EPSL*, 449, 197–205. [3] Bachmann O. et al. (2012) *Contrib. Mineral. Petrol.*, 163, 151-166. [4] Bachmann O. (2010), *Cent. Eur. J. Geosci.*, 2, 270-305. [5] Greber N. D. et al., under review, *GCA*. [6] Cassidy et al. (2015) *J. Petrology*, 56, 325-346. [7] Yavuz F. et al. (2002) *Geochem. J.*, 36, 563-580. [8] Day J. M. D. et al (2012) *GCA*, 81, 94-128. [9] Usui T. et al. (2015) *Meteorit. Planet. Sci.*, 50, 759-781.