

## THE TITANIUM ISOTOPIC COMPOSITIONS OF CHONDRITES AND EARTH

N.D. Greber<sup>1,\*</sup>, N. Dauphas<sup>1</sup>, M.A. Millet<sup>2</sup> and I.S. Puchtel<sup>3</sup>, <sup>1</sup>Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, Chicago, IL 60637, USA; <sup>2</sup>Durham University, Department of Earth Sciences, South Road, Durham DH1 3LE, UK; <sup>3</sup>Department of Geology, University of Maryland, College Park, MD 20742, USA, \*corresponding author, greber@uchicago.edu

**Introduction:** Due to its lithophile and strongly refractory character, Ti is an element of particular interest in planetary sciences as the range of processes susceptible of fractionating its isotopic composition is rather limited and involves primarily magmatic/metamorphic processes. Indeed, Ti is refractory and cannot easily be lost during impact heating, it is lithophile meaning that core partitioning is irrelevant, and it is fluid immobile, meaning that it is immune to parent-body alteration.

Here, we present first Ti isotope data for chondritic meteorites and komatiites and discuss and summarize the current state of knowledge for this promising new isotope system.

**Methods:** Samples analyzed in this study have been digested using the LiBO<sub>2</sub> fusion technique, which, unlike the more conventional acid digestion technique, affords complete dissolution of refractory accessory minerals and it avoids the creation of insoluble Ti-bearing fluoride. As a test, several samples were also digested using the conventional high-temperature acid attack. Chemical purification and Ti isotope measurements using a <sup>47</sup>Ti-<sup>49</sup>Ti double spiking procedure were done following published methodology [1]. This separation guarantees proper removal of Li, which may cause ArLi molecular interferences on masses <sup>46</sup>Ti and <sup>47</sup>Ti.

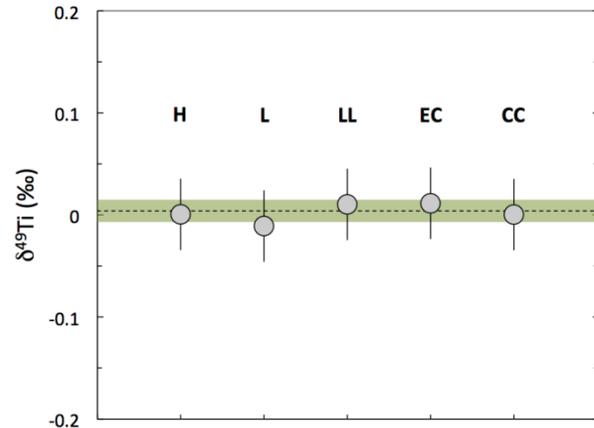
All measurements were corrected for the presence of <sup>47</sup>Ti and <sup>49</sup>Ti isotopic anomalies (<sup>50</sup>Ti is not used for isotope reduction procedure) based on the published values [2]. The Ti isotope composition is expressed in the delta notation (i.e.  $\delta^{49}\text{Ti}$ ) relative to the <sup>49</sup>Ti/<sup>47</sup>Ti isotope ratio. The 2SD uncertainty on the standard measurements during each analytical session was always below  $\pm 0.035\%$ , and this value served as a measure of external precision of the isotopic analysis, unless stated otherwise.

**Samples:** To date, 13 chondritic meteorites have been analyzed for their Ti isotopic composition; these included the CO, CM, EC, LL, L, and H groups of chondrites. In addition, three USGS standard reference materials (SRM) (BHVO-2; BIR-1a, and G3) and Archean komatiites from four different localities were also analyzed for their Ti isotope compositions. This included komatiites from the 3.55 Ga Schapenburg, 3.48 Ga Komati, 3.26 Ga Weltevreden, and 2.72 Ga Alexo komatiite systems. For all four localities, sets of

samples that included both olivine cumulates and spinifex-textured rocks, were analyzed for their  $\delta^{49}\text{Ti}$ .

**Results:** The Ti isotope compositions obtained by both digestion techniques are identical within the respective uncertainties, indicating that the flux fusion technique yields accurate results. The measured Ti isotope composition of the USGS SRM BHVO-2 ( $\delta^{49}\text{Ti} = 0.009 \pm 0.035\%$ ) and BIR-1a ( $\delta^{49}\text{Ti} = -0.062 \pm 0.035\%$ ) are identical to our previous measurements [1]. The  $\delta^{49}\text{Ti}$  of the USGS SRM G3 is  $+0.412 \pm 0.035\%$  and is, thus, significantly heavier than that of the other two SRMs.

The  $\delta^{49}\text{Ti}$  values of all chondrites are indistinguishable within uncertainty, ranging from  $-0.027\%$  (Bald Mountain, L4) to  $+0.027\%$  (Blithfield, EL6) with a mean value of  $0.004 \pm 0.010\%$  (95% c.i, n=13; Fig. 1). The Komati and Schapenburg komatiites have an average  $\delta^{49}\text{Ti}$  that is identical to that of chondrites, while the Weltevreden and Alexo komatiites have slightly lighter Ti isotope compositions (Fig. 2).

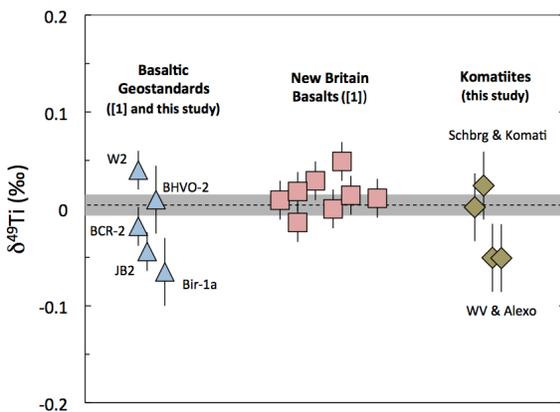


**Figure 1:** Ti isotope composition of the different chondrite groups analyzed. All  $\delta^{49}\text{Ti}$  are identical within the uncertainty, averaging at  $+0.004 \pm 0.010\%$  (95% c.i.) relative to Chicago-Ti standard. CC includes CM and CO chondrite groups.

**Discussion:** The similarity in the Ti isotope composition among all investigated chondrite groups indicates the absence of Ti isotope fractionation during accretion on a bulk planetary scale, at least for the samples investigated. In addition, the average chondritic  $\delta^{49}\text{Ti}$  is identical to the recent estimate of the bulk silicate Earth [1]. Due to the lithophile character

of Ti, these results show that the bulk silicate Earth has a chondritic mass-dependent Ti isotope composition.

Calcium is an element with a similar refractory and lithophile character as Ti and recently published data revealed that the Ca isotope compositions of most carbonaceous chondrites (except CO) are lighter than that of the bulk silicate Earth, ordinary and enstatite chondrites [3]. Our preliminary measurements of CM chondrites indicate that they have Ti isotope composition similar to the bulk Earth and all the enstatite and ordinary chondrites. Further work is needed to test whether other carbonaceous chondrites also have indistinguishable Ti isotopic composition as Earth. A possible reason why carbonaceous chondrites have light Ca isotopic composition is that they incorporated a greater proportion of refractory dust, which carries a very light Ca isotopic signature, reaching -5 ‰ [4]. Such a signature was found in the abundance of the REEs in the form of a Tm excess in carbonaceous chondrites relative to other meteorite groups, Earth, Mars, and Vesta [5,6]. CAIs also have fractionated  $\delta^{49}\text{Ti}$  [7] but the fractionations are on both sides of the terrestrial composition and have on average a  $\delta^{49}\text{Ti}$  isotopic value (around 0.22 ‰) that is not very different from the terrestrial value. Thus, while the greater incorporation of refractory dust in carbonaceous chondrites may have affected their Ca isotopic composition and REE pattern, such an effect is not necessarily expected for Ti isotopes.



**Figure 2:** Ti isotope composition of basalts and komatiites. Most samples have Ti isotope compositions that are identical, within uncertainties, to the chondritic  $\delta^{49}\text{Ti}$  (grey bar with dotted line). Schbrg, Schapenburg; WV, Weltevreden

As mentioned earlier, the bulk silicate Earth [1] and chondritic Ti isotope compositions are identical within the uncertainties. However, small deviations from the chondritic  $\delta^{49}\text{Ti}$  towards lighter and heavier Ti isotope compositions are observed for the Alexo and the

Weltevreden komatiites, as well as for some of the Cenozoic basalts (Fig. 2). This implies that some sort of  $\delta^{49}\text{Ti}$  heterogeneity exists in the terrestrial mantle. The solubility of Ti in different mantle minerals changes with pressure [8] and thus, Ti is an element affected by metamorphic reactions occurring in the Earth mantle. The inter-mineral Ti exchange that takes place during such reactions might fractionate Ti isotopes and thus produces variable  $\delta^{49}\text{Ti}$  between different mantle phases. Fractional melting or melting of refractory mantle residues could then lead to the observed  $\delta^{49}\text{Ti}$  variations found in mafic rocks.

While the  $\delta^{49}\text{Ti}$  differences in mafic and ultramafic rocks are rather small, the only granitic rock measured exhibits a pronounced heavier Ti isotope composition. Thus, processes involved in the production of continental crust might favor heavy Ti isotopes [9].

**Summary:** Ordinary, enstatite and carbonaceous chondrites have uniform mass dependent Ti isotope compositions. The chondritic average is within error identical to the recent estimate for the Ti isotopic composition of the bulk silicate Earth. This indicates insignificant Ti isotope fractionation during accretion processes of planets.

Significant variation in the Ti isotope composition is found among igneous terrestrial rocks. The only granitic sample measured has a pronounced heavier Ti isotope composition than the bulk Earth and chondrites, indicating preferential incorporation of heavy isotopes into Earth's crust.

**Acknowledgments:** This work was supported by the Swiss National Science Foundation, grant P2BEP2\_158983 to NDG.

**References:** [1] Millet and Dauphas (2014) JAAS 29, 8, 1444. [2] Zhang et al., (2012) Nat. Geosci. 5, (4), 251–255. [3] Valdes et al., (2014) Earth Planet. Sci. Lett. 394, (C), 135–145. [4] Huang et al., (2012), GCA 77, 252–265 [5] Dauphas and Pourmand (2015) Geochim. Cosmochim. Acta 163, 234–261 [6] Barrat et al., (2016) Geochim. Cosmochim. Acta, 176, 1–17 [7] Zhang (2012) Phd Thesis, University of Chicago [8] Zhang et al., (2003) Earth Planet. Sci. Lett. 216, (4), 591–601. [9] Millet et al. (in review) Earth Planet. Sci. Lett.