

### A SEARCH FOR TITANIUM STABLE ISOTOPIC VARIATIONS IN METEORITES AND THE EARTH

Z. B. Deng<sup>1,\*</sup>, F. Moynier<sup>1,2</sup>, K. van Zuilen<sup>1</sup>, E. A. Pringle<sup>1</sup>, M. Chaussidon<sup>1</sup>, <sup>1</sup>Institut de Physique du Globe de Paris, Université Paris Diderot, Université Sorbonne Paris Cité, CNRS UMR 7154, Paris, France. <sup>2</sup>Institut Universitaire de France, Paris, France. \*corresponding author, deng@ipgp.fr

Refractory lithophile elements, such as Ca and Ti, have the potential to trace the building blocks of the terrestrial planets because their abundance (and therefore isotopic composition) is not modified during planetary evolution (e.g., volatilization<sup>[1]</sup> or core formation<sup>[2]</sup>). The Ca isotopic compositions of enstatite (EC), ordinary (OC) and CO-type carbonaceous (CC) chondrites are indistinguishable from the Earth<sup>[3]</sup>, while most types of CC (CI, CV and CR) display pronounced enrichments in the lightest Ca isotopes up to ~0.2‰ per atomic mass unit (AMU) compared to the bulk silicate Earth (BSE)<sup>[3,4,5,6]</sup>. In addition, individual CC groups show distinct Ca isotopic compositions with progressive enrichment in the heaviest isotopes in the order CR<CV<CI<CM<CO<sup>[3]</sup>. The heterogeneous calcium isotopic composition of C-chondrites is remarkable and puzzling since among the five most abundant elements present in terrestrial planets only oxygen shows isotopic variability<sup>[7]</sup>. At first order, the origin of these variations may be attributed to incorporation of different amounts of isotopically light refractory condensates in the form of Ca-, Al-rich inclusions (CAIs). To test the origin of the Ca stable isotope variations among meteorites and terrestrial planets, it may be helpful to measure the isotopic composition of Ti. Titanium has a similar 50% condensation temperature as calcium<sup>[8]</sup>, and it is much less insoluble in aqueous fluids. Here we have developed a technique with <sup>47</sup>Ti-<sup>49</sup>Ti double spike to measure high-precision Ti stable isotopic compositions of basalt standards and meteorite samples in order to search for possible Ti isotopic variations between meteorites and thus understand the origin of the Ca isotopic variations in the solar system.

Three different digestion methods have been tested to check the effects of digestion on measured Ti isotopic ratios, including alkali fusion, Parr-bomb digestion and hot-plate HF-HNO<sub>3</sub> digestion. Titanium was purified by ion exchange chromatography, using a combination of anion exchange resin and Eichrom DGA resin. Samples were spiked with a <sup>47</sup>Ti-<sup>49</sup>Ti double spike mixture before column chemistry. The signal intensities of the five Ti isotopes were measured simultaneously on a Thermo Fisher Neptune Plus MC-ICP-MS at IPG-Paris, and the intensity of <sup>44</sup>Ca<sup>+</sup> was monitored for correction of <sup>46</sup>Ca<sup>+</sup> and <sup>48</sup>Ca<sup>+</sup> isobaric interferences on <sup>46</sup>Ti<sup>+</sup> and <sup>48</sup>Ti<sup>+</sup>, respectively. All sample data are reported as δ<sup>49</sup>Ti, which is the per mille deviation of the sample's <sup>49</sup>Ti/<sup>47</sup>Ti ratio from that of our Ti in-house standard. Repeated measurements of basalt and andesite reference materials indicate that Ti stable isotopic compositions of silicate rocks can be reproduced with an intermediate measurement precision of ± 0.03‰ for δ<sup>49</sup>Ti.

We have analyzed the Ti stable isotopic composition of 1 CI, 1 CM, 3 CO, 1 CV, 1 CK, 2 CR, 1 CH, 4 L, 2 LL, 1 EL, 4 angrites, 6 martian meteorites as well as 4 terrestrial igneous rocks (BHVO-2, BCR-2, BIR-1, AGV-1). The isotopic composition of the geological reference materials agrees well with previous measurement<sup>[10]</sup> (δ<sup>49</sup>Ti<sub>BHVO-2</sub> = -0.09 ± 0.03‰, δ<sup>49</sup>Ti<sub>BCR-2</sub> = -0.12 ± 0.03‰, δ<sup>49</sup>Ti<sub>BIR-1</sub> = -0.16 ± 0.03‰ and δ<sup>49</sup>Ti<sub>AGV-1</sub> = -0.03 ± 0.03‰), which confirms the presence of small but resolvable Ti isotopic variations among terrestrial igneous rocks<sup>[10,11]</sup>. On average, all chondrite groups have a homogeneous Ti stable isotopic composition (CC: δ<sup>49</sup>Ti = -0.04 ± 0.08‰, OC: δ<sup>49</sup>Ti = -0.05 ± 0.12‰ and EC: δ<sup>49</sup>Ti = -0.03 ± 0.05‰), which is indistinguishable from the terrestrial basalt BHVO-2 (δ<sup>49</sup>Ti = -0.09 ± 0.03‰) within analytical uncertainty. This is consistent with previous data on CM, CO, EC and OC<sup>[11]</sup>. We also show that the martian meteorites and angrites have a similar average Ti isotopic composition with δ<sup>49</sup>Ti = -0.03 ± 0.11‰ and δ<sup>49</sup>Ti = -0.09 ± 0.05‰, respectively.

The absence of Ti stable isotopic variations between chondrite groups is consistent with the isotopic composition of other major elements such as Mg<sup>[12]</sup> and Fe<sup>[13]</sup>, it is however in contrast with Ca<sup>[3]</sup>. Recent studies showed that Ti isotopes are less fractionated in CAIs than Ca<sup>[6,9]</sup>, and therefore CAI content may not play a major role on the Ti isotopic composition of the chondrites. All together the present data show that Ti stable isotope systematics in bulk chondrites does not follow that of Ca, which may bring new constraints on nebular and planetary processes.

**References:** [1] Paniello R. C. et al. 2012. *Nature* 490:376-379. [2] Savage P. S. et al. 2015. *Geochim. Persp. Lett.* 1: 53-64. [3] Valdes M. C. et al. 2014. *Earth Planet. Sci. Lett.* 394:135-145. [4] Huang S. et al. 2012. *Geochim. Cosmochim. Acta* 77:252-265. [5] Simon J. I. and DePaolo D. J. 2010. *Earth Planet. Sci. Lett.* 289:457-466. [6] Simon J. I. et al. 2016. 47th Lunar and Planetary Science Conference. pp. 1397. [7] Clayton R. N. et al. 1988. *Phil. Trans. R. Soc. Lond.* A325:483-501. [8] Lodders K. 2003. *Astrophys. J.* 591:1220-1247. [9] Davis A. M. et al. 2016. 47th Lunar and Planetary Science Conference. pp. 3023. [10] Millet M. A. and Dauphas N. 2014. *J. Anal. At. Spectrom* 29: 1444-1458. [11] Greber N. D. et al. 2016. 47th Lunar and Planetary Science Conference. pp. 1448. [12] Teng F. Z. et al. 2010. *Geochim. Cosmochim. Acta* 74:4150-4166. [13] Craddock P. R. et al. 2013. *Earth Planet. Sci. Lett.* 365:63-76.