

TITANIUM ISOTOPIC COMPOSITIONS OF SOLAR SYSTEM OBJECTS. I. Leya^{1,2}, M. Schönbachler^{3,2}, U. Wiechert² and A.N. Halliday^{4,2}, ¹Physikalisches Institut, Universität Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland, ²Institute for Isotope Geology, ETH Zürich, Switzerland, ³Carnegie Institution of Washington, Washington DC, USA, ⁴Department of Earth Sciences, University of Oxford, Oxford, UK. Email: Ingo.Leya@phim.unibe.ch.

Introduction: Isotopic anomalies in solar system objects provide powerful constraints on the origin and evolution of the early solar system. To a large degree, the solar system is surprisingly homogeneous isotopically, indicating very efficient mixing of the material that formed the solar system out of the molecular cloud. Exceptions are isotopic anomalies due to *in situ* effects such as radioactive decay and particle irradiation. Therefore, isotopic anomalies indicating incomplete homogenization are of great importance for understanding the processes and their timing in the early solar system. Isotopic anomalies have been known for many years for, *e.g.*, noble gases, O, Ti, Cr, Zr, Sm, Nd and Ba.

Virtually every Ca-Al-rich refractory inclusion (CAI) from the Allende meteorite carries Ti isotopic anomalies, *e.g.* [1,2,3,4]. Titanium isotopic anomalies were also detected in whole rock samples and chondrules of some carbonaceous chondrites [5,6]. Besides being of a general interest, Ti isotopes may also serve as an indicator of possible irradiation processes in the early solar system, *e.g.* [7]. For example, assuming that some of the short-lived radionuclides alive in the early solar system have been produced by particle irradiation [7], a collateral shift in $^{48}\text{Ti}/^{47}\text{Ti}$ of a few epsilon would be expected, where 1 epsilon is the deviation in parts/ 10^4 from the standard.

Our primary purpose of this work is two-fold: 1) to determine the Ti isotopic composition in various solar system objects and search for $^{48}\text{Ti}/^{47}\text{Ti}$ anomalies in early refractory condensates to prove or reject the hypothesis that some of the short lived radionuclides have been produced by particle irradiation. 2) to add Ti to the list of elements measured via high resolution MC-ICPMS, which is an experimental challenge due to various plasma specific interferences.

Experimental: The sample preparation and chemical separation of the samples is described in [8]. Briefly, the samples (after crushing and mineral separation) were digested using a mixture of concentrated HF and HNO₃. Subsequently, the samples were dried down and re-dissolved in HCl with traces of HF. For Ti (as for Zr) a two-stage anion exchange chromatography was used for sample purification. In the first step the matrix was eluted with HF, while Zr, Hf, Ti, Mo, Te and W remained on the column. Titanium, together with Zr and Hf, was stripped from the column with a mixture of HF-HCl. The second separation step

isolated Ti from Zr and V. The aliquots containing Zr were measured earlier by Schönbachler et al., *e.g.*, [9,10]. The values presented here are from the same samples as the data given in [9,10], only different fractions of the chemical separation procedure were used.

Mass spectrometry: All Ti isotopic measurements were performed on the high sensitive high resolution MC-ICPMS at the ETH Zürich (NU1700). Since peak jumping is not feasible at high resolution, all samples were measured with two different data collection protocols. The first comprises the measurements of the masses from 44 to 49 and the second the masses from 47 to 53. The mass resolution was always about 2000 to resolve interferences on mass 50 from, *e.g.*, $^{14}\text{N}^{36}\text{Ar}$. The interferences of doubly charged Zr and Mo cannot be resolved. Traces of these elements, which always occur in the Ti fraction, can significantly compromise precise measurements, when present in higher amounts. To monitor such possible effects, all samples were measured for their Zr/Ti and Mo/Ti ratios using a low resolution quadrupole mass spectrometer.

Data processing and interference corrections: Mass dependent fractionation (*mdf*) effects introduced by the mass spectrometer and/or the chemical separation is internally corrected via $^{49}\text{Ti}/^{47}\text{Ti} = 0.749766$ [2] using the exponential law (see also below). Interferences on ^{50}Ti by $^{14}\text{N}^{36}\text{Ar}$ can be resolved on the Nu1700. Interferences on ^{50}Ti by ^{50}V and ^{50}Cr and on ^{46}Ti by ^{46}Ca are corrected via ^{51}V , ^{53}Cr and ^{44}Ca signals measured in the same run, respectively. The interference corrections were checked to be reliable up to a few hundred epsilon. Interferences by doubly charged Zr and Mo were corrected via the Zr/Ti and Mo/Ti ratios measured in the samples and experimentally determined $\text{Zr}^{2+}/\text{Ti}^+$ and $\text{Mo}^{2+}/\text{Ti}^+$ ratios. The corrections were checked to be reliable up to a few tens of epsilon.

The Ti isotopic composition of our standards: Different Ti standard solutions were analysed. All solutions yield $^{50}\text{Ti}/^{47}\text{Ti}$ ratios about 12 ϵ -units higher than the reference value of 0.729175 [2]. The grand average for all measured standard solutions is $\epsilon(^{50}\text{Ti}/^{47}\text{Ti}) = 12.63 \pm 0.09$. The grand average for $^{48}\text{Ti}/^{47}\text{Ti}$ and $^{46}\text{Ti}/^{47}\text{Ti}$ is 0.47 ± 1.18 and 2.31 ± 1.01 ϵ -units relative to the values given in [2]. The given uncertainty is the 1σ external reproducibility. Remember that all ratios are measured relative to $^{49}\text{Ti}/^{47}\text{Ti} = 0.749766$.

The offset of the $^{50}\text{Ti}/^{47}\text{Ti}$ ratio of about 12ε does not depend on the Ti concentration of the analysed solutions. We also checked whether the $^{50}\text{Ti}/^{47}\text{Ti}$ ratio is affected by the cup configuration used for measurement, *i.e.* if the apparently too high ratio is caused by an offset or gain error of the faraday cup used. However, changing the cup configuration had no influence on the offset. Furthermore, various dilution series with variable Ti, Cr, V, Ca, Zr and Mo concentrations all display $\varepsilon(^{50}\text{Ti}/^{47}\text{Ti}) \sim 12$.

From our data alone we cannot propose that the terrestrial $^{50}\text{Ti}/^{47}\text{Ti}$ ratio used so far is off by about 12ε units but the excess we observe is most probably not due to an experimental artifact. Strong support for the integrity of our measurements is gained from the fact that we measured $\varepsilon(^{50}\text{Ti}/^{47}\text{Ti}) \sim 22$ for a CAI from Allende (preliminary, not corrected for Zr^{2+} and Mo^{2+}), again apparently too high by $\sim 12\varepsilon$. However, normalizing the data to our (too high) standard $^{50}\text{Ti}/^{47}\text{Ti}$ yields an excess of $\sim 10\varepsilon$ for the CAI, in good agreement with [1,2,3,4]. We conclude that the observed offset is not due to an experimental artifact and therefore normalized the $^{50}\text{Ti}/^{47}\text{Ti}$, $^{48}\text{Ti}/^{47}\text{Ti}$ and $^{46}\text{Ti}/^{47}\text{Ti}$ ratios measured for the samples and corrected for *mdf* via $^{49}\text{Ti}/^{47}\text{Ti} = 0.749766$ relative to the ratios obtained for the standard solutions on the same day (also corrected for *mdf* via $^{49}\text{Ti}/^{47}\text{Ti} = 0.749766$).

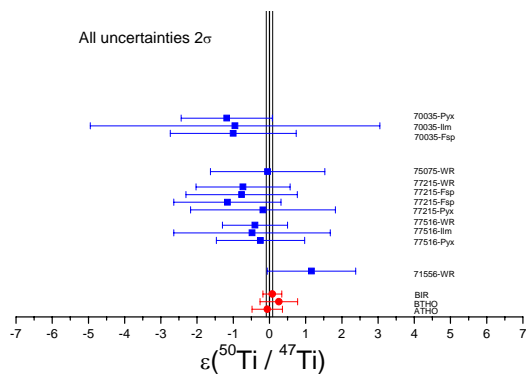


Figure 1. The $\varepsilon(^{50}\text{Ti}/^{47}\text{Ti})$ values for lunar whole rock samples and mineral separates and for terrestrial basalts.

Reproducibility and accuracy: The external reproducibility is estimated from the Ti standard measurements performed during the last two years. The reproducibility (1σ) for $^{50}\text{Ti}/^{47}\text{Ti}$, $^{48}\text{Ti}/^{47}\text{Ti}$ and $^{46}\text{Ti}/^{47}\text{Ti}$ is 0.09ε , 1.18ε and 1.01ε , respectively. Note that these values are slightly too low because the standard solutions typically do not match exactly the samples. Currently we determine the external reproducibility by repeated measurements of the carbonaceous chondrite Allende.

Results: The experimental results for $\varepsilon(^{50}\text{Ti}/^{47}\text{Ti})$ and $\varepsilon(^{46}\text{Ti}/^{47}\text{Ti})$ for lunar whole rock samples and mineral separates and for terrestrial basalts (ATHO, BTHO, BIR) are shown in Fig. 1 and 2, respectively. The uncertainty of the standard is the 1σ external reproducibility. For the individual samples either the external or the internal uncertainties are plotted (2σ), whichever is bigger.

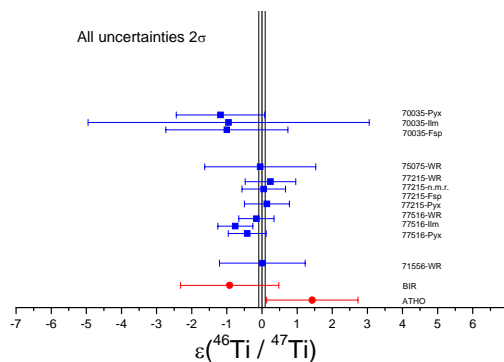


Figure 2. The $\varepsilon(^{46}\text{Ti}/^{47}\text{Ti})$ values for lunar whole rock samples and mineral separates and for terrestrial basalts.

Discussion: Figure 1 and 2 demonstrate that the Ti isotopic composition in the samples measured so far is strikingly uniform. Neither lunar whole rock samples nor any of the mineral separates show any deviation from terrestrial. For lunar samples this is of no surprise because no anomaly is expected. Turning the argument around, the uniformity of the Ti isotopic composition clearly demonstrates that we are well able to accurately determine Ti isotopic data in samples having variable matrix compositions and a wide range of Ti concentrations. The data therefore indicate that the chemical separation procedure, the mass spectrometric measurements as well as the data processing procedures are reliable and accurate. Currently we are determining the Ti isotopic data for “more interesting” samples, *i.e.* CAIs, mineral separates from Vaca Muerta, Juvinas and Estacado as well as leachates from Allende and Murchison.

References: [1] Niederer F.R. et al. (1980) *ApJ*, 240, L73-L77. [2] Niederer F.R. et al. (1981) *GCA*, 49, 835-851. [3] Niemeyer S. and Lugmair G.W. (1981) *EPSL*, 53, 211-225. [4] Niemeyer S. and Lugmair G.W. (1984) *GCA*, 48, 1401-1416. [5] Niemeyer S. (1985) *JGR*, 12, 733-736. [6] Niemeyer S. (1988) *GCA*, 52, 309-318. [7] Leya I. et al. *ApJ*, 594, 605-616. [8] Schönbachler M. et al. (2004) *Analyst*, 129, 32-37. [9] Schönbachler et al. (2002) *Science*, 295, 1705-1708. [10] Schönbachler M., PhD. Thesis, ETH Zürich (2004).