

DIFFERENT HETEROGENEOUSLY DISTRIBUTED TITANIUM ISOTOPE COMPONENTS IN SOLAR SYSTEM MATERIALS AND MASS-DEPENDENT TITANIUM ISOTOPE VARIATIONS.

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Introduction: The presence of nucleosynthetic heterogeneities in bulk rock samples from the inner solar system is well documented. These heterogeneities place important constraints on the evolution of the protoplanetary disk and the stellar sources of solar system materials. Several recent studies identified nucleosynthetic Ti isotope anomalies [1-4]. Titanium isotopes analyzed for a suite of solar system materials display correlated variations in the $^{50}\text{Ti}/^{47}\text{Ti}$ and $^{46}\text{Ti}/^{47}\text{Ti}$ ratios. The data were obtained by MC-ICPMS and internally normalized to $^{49}\text{Ti}/^{47}\text{Ti} = 0.749766$ [5] in order to achieve the necessary precision. The latter assumption, however, is not necessarily justified for all solar system materials and this can obscure the true location of the anomalies. The correct isotopic signature of a heterogeneously distributed component is important for the identification of its nucleosynthetic source (e.g. AGB-star environment versus supernova Type Ia or II). In this study, we developed a new ^{47}Ti - ^{49}Ti double spike procedure to determine the absolute Ti isotope compositions of solar system materials to (i) determine the true magnitude and location of the nucleosynthetic variations and (ii) to identify mass-dependent Ti isotope fractionation that may have occurred in the solar nebula or during planetary differentiation.

Analytical techniques: The new procedure involved the set-up and calibration of a ^{47}Ti - ^{49}Ti double spike by MC-ICPMS. The ideal double spike composition ($^{47}\text{Ti}/^{49}\text{Ti} = 0.94$) was determined using error propagation calculations. Titanium isotopes and ^{44}Ca were measured on a Neptune MC-ICPMS simultaneously followed by a second line with ^{50}Ti , ^{51}V and ^{53}Cr to correct for isobaric interferences. The data evaluation adopted the three dimensional procedure of [6] and was crosschecked with the iterative Newton-Raphson procedure [7]. The samples were bracketed with a Ti standard solution that was prepared from a Alfa Aesar wire. The external reproducibility of the method (2sd) is 8 ppm, 15ppm, 15 ppm and 22 ppm for $^{46}\text{Ti}/^{47}\text{Ti}$, $^{48}\text{Ti}/^{47}\text{Ti}$, $^{49}\text{Ti}/^{47}\text{Ti}$ and $^{50}\text{Ti}/^{47}\text{Ti}$, respectively, obtained from standards solutions analyzed over one day. All samples were digested in a Parr Bomb. The separation of Ti from the sample matrix followed the ion exchange procedure for Zr purification [8]. For each sample, a spiked and unspiked aliquot was analyzed to determine the absolute Ti isotope composition, which was then deconvoluted into mass-

dependent and mass-independent (nucleosynthetic) effects.

Results and Discussion: We report new double spike Ti data for the terrestrial basalts BHVO-2 and BCR-2, the andesite AGV-2, calcium-aluminum-rich inclusions (CAI), a chondrule separate from Allende (CV3), various carbonaceous (CI, CR, CM, CV), ordinary and rumuruti chondrites, eucrites, an acapulcoite and an urelite. A subset of the samples was spiked after sample digestion, while the others were spiked after the ion exchange procedure. Nine samples were processed both ways. Comparisons of sample aliquots - spiked before and after column chemistry - reveal that mass-dependent isotope fractionation occurs during the ion exchange procedure. Therefore, the results for samples spiked after the ion exchange procedure can only be used for the determination of the mass-independent effects, because the mass-dependent data reflects a combination of natural and laboratory induced Ti isotope fractionation.

Mass-dependent Ti isotope variations. The andesite AGV-2 exhibits a slightly heavier isotope composition (0.3 ± 0.2 epsilon/amu) than the two basalts. This provides evidence that igneous processes can fractionate Ti isotopes. The data for carbonaceous, ordinary and rumuruti chondrites, the acapulcoite Dhofar 125 and the eucrite Juvinas fall in the same range as the terrestrial samples. They spread over 0.6 epsilon/amu with the eucrite being the lightest (-1.3 epsilon/amu relative to the Ti wire standard) and the carbonaceous chondrite Allende and Murchison being the heaviest (-0.7 epsilon/amu). Only the CAI NV1 displays a distinctly lighter Ti composition with a value of -1.5 epsilon/amu. This more extreme fractionation in CAIs compared to other samples is in line with results reported for isotopes of other elements (e.g. Mg [9]). Overall, based on the samples analyzed so far, there is no evidence for significant stable isotope fractionation during planet formation for the refractory element Ti.

Mass-independent Ti isotope variations. The internally normalized data obtained from the unspiked sample aliquots agree well with previously published data [1-4]. The exception is Allende, where our data is consistent with [3,4], but not [1]. This is most likely the result of incomplete dissolution of refractory pre-solar phases or sample heterogeneities. Our data also confirms the correlated $^{50}\text{Ti}/^{47}\text{Ti}$ - $^{46}\text{Ti}/^{47}\text{Ti}$ variations when normalizing relative to $^{49}\text{Ti}/^{47}\text{Ti} = 0.749766$ [5].

Our new double spike data corroborates that the largest nucleosynthetic effects are indeed in ^{50}Ti correlated with smaller anomalies in ^{46}Ti . The data, however, also reveal small nucleosynthetic variations in ^{47}Ti , which will affect the internally normalized data through the normalization scheme. In contrast, ^{48}Ti and ^{49}Ti are distributed homogeneously within our solar system. This is surprising to some extent, because larger variations in ^{49}Ti are known from presolar grain work [10]. The nucleosynthetic origin of the ^{47}Ti variations requires further investigations. For most samples, the nucleosynthetic variations in $^{46,47,50}\text{Ti}$ are correlated. As previously stated by [1], these isotopes are produced in different stellar sources and this implies that the solar nebula was generally well mixed at one stage and that an additional process such as selective thermal destruction of presolar phases or grain sorting may have led to the isotopic heterogeneity. This is also supported by studies using Zr isotopes [11].

However, there are a few exceptions to the overall $^{46,47,50}\text{Ti}$ correlation (Fig.1). Some Allende CAIs, the Allende chondrule separate and the carbonaceous chondrites Murchison and Allende fall off the general trend. They point toward an additional nucleosynthetic component, which is enriched in ^{50}Ti , but depleted in ^{47}Ti , while ^{46}Ti is not affected.

Based on Ti isotopes, two analyzed CAIs (CAI NV1 and NV2) are influenced by this exotic $^{47-50}\text{Ti}$ component, while CAI NV3 falls on the high end of the general solar system trend. The three CAIs were also analyzed for Zr and Hf isotopes. Previous studies showed that normal CAIs can be divided into two groups [12, 13], depending on whether they show moderate or large ^{96}Zr excesses. CAI NV1 and NV2 belong to the more common normal CAIs with relatively large ^{96}Zr , ^{62}Ni , ^{50}Ti excesses and deficits in r-process Hf isotopes. Our new Ti double spike data demonstrates that these CAI have also sampled an exotic $^{47-50}\text{Ti}$ component. The same component was also included into Allende chondrules (offset from the general solar system trend, Fig. 1) and is reflected in the bulk rock composition of Allende and Murchison. However, the exotic $^{47-50}\text{Ti}$ component is not apparent in bulk rock samples of CR and potentially CI chondrites. This indicates that CAI-poor carbonaceous (and ordinary) chondrite groups have not sampled variable amounts of the exotic $^{47-50}\text{Ti}$ component.

In contrast to the other CAIs, CAI NV3 shows smaller excesses in ^{96}Zr and ^{50}Ti , excesses in r-process Hf (= depletion in s-process isotopes) and no exotic $^{47-50}\text{Ti}$ component. These types of CAIs are less abundant. Based on these results, it is evident that normal CAIs did not form from a single homogeneous reservoir.

Conclusions: Our new double spike data yield absolute Ti isotope compositions of solar system materials. The data demonstrates the presence of correlated nucleosynthetic $^{46,47,50}\text{Ti}$ variations. Some samples (CV and CM chondrites, a subset of Allende CAIs and Allende chondrules) show correlated variation in ^{47}Ti and ^{50}Ti offset from the general trend (Fig.1). This indicates the presence of a third component, whose nucleosynthetic origin needs further investigation.

Limited variations in the mass-dependent Ti isotope composition were identified. They imply limited, but resolvable mass-dependent isotope fractionation that occurred during igneous processes. However, no evidence for larger stable isotope fractionation during planetary accretion and differentiation was identified.

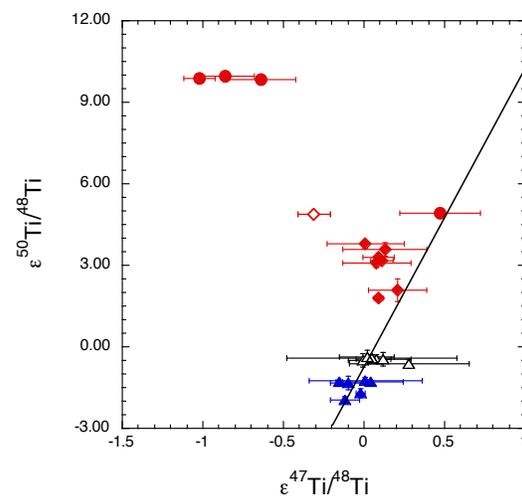


Figure 1: Titanium isotope compositions corrected for mass-dependent isotope fractionation. Red circles: CAI, red closed diamonds: carbonaceous chondrites, red open diamond: Allende chondrules, Black open triangles: rumuruti and ordinary chondrites, blue triangles: achondrites, black line: best-fit line through achondrites, ordinary, rumuruti, CI and CR chondrites and CAI NV3. The composition of the Earth is zero by definition.

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