

THE MEASUREMENT OF TITANIUM ISOTOPIC COMPOSITIONS OF ALLENDE REFRACTORY INCLUSIONS BY LA-MC-ICPMS. C. D. Williams¹, M. Wadhwa¹, P. E. Janney¹, R. R. Hines¹, E. S. Bullock², and G. J. MacPherson². ¹School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287-1404, USA, curtis.williams@asu.edu. ²Smithsonian Institution, Washington D.C. 20560, USA.

Introduction: Titanium has five stable isotopes. Their relative ratios, as measured in primitive chondritic meteorite components, preserve information regarding nucleosynthetic sources of materials input into the solar nebula, nebular processes and degree of isotopic heterogeneity in the early Solar System. Early studies [1-4] noted resolvable titanium isotopic anomalies (particularly associated with ⁵⁰Ti), mainly in calcium-aluminum-rich inclusions (CAIs) in chondritic meteorites but also in some bulk chondrites. Subsequent studies have documented the presence of Ti isotopic anomalies in a wider range of meteoritic materials, but the largest observed effects remain those in CAIs [5-17].

CAIs are the oldest Solar System materials dated by absolute radiogenic methods [18-23], and preserve the largest isotopic anomalies for a range of elements. Previous titanium isotopic studies focused primarily on Type A and Type B CAIs from CV chondrites [1-8,10,16], as well as hibonite-bearing inclusions from CV and CM chondrites [9,11-15]. Hibonite-bearing inclusions and isolated hibonite grains exhibit the largest anomalies and the widest range in Ti isotope compositions, with excesses in ⁵⁰Ti up to 104‰ [14] and deficits as low as -68‰ [12] (after normalization to the ⁴⁶Ti/⁴⁸Ti ratio). These large variations are likely a “chemical memory” of nucleosynthetic anomalies originally hosted in presolar dust. On the other hand, the majority of Type A and Type B inclusions (“normal” CAIs) display relatively small, but resolvable, excesses in ⁵⁰Ti [1-8,10,16]. Two notable exceptions included CAIs EK-1-4-1 and C-1 [2,4]. The ⁵⁰Ti composition of EK-1-4-1 shows an excess of ~15ε, while C-1 exhibits a deficit of ~38ε (when reported Ti isotope compositions are normalized to the ⁴⁹Ti/⁴⁷Ti ratio). EK-1-4-1 and C-1, as well as four additional inclusions analyzed by [10], also show large mass-dependent O and Mg isotope fractionations along with unresolvable excesses in ²⁶Mg*, and are termed FUN CAIs (i.e. having Fractionated and Unidentified Nuclear effects).

Based on their isotopic characteristics, it has been suggested that either FUN inclusions formed in a distinct isotopic reservoir or they pre-date “normal” CAIs (review in [24]). However, no absolute ages have been determined for any FUN CAIs, and little material remains from previously studied ones for such investigations. Therefore, it is important to locate new FUN inclusions so that their unique isotopic signatures can be placed in temporal context of the evolving solar

Table 1. Compositions of synthetic glass standards measured by electron microprobe.

	MgO wt.%	Al ₂ O ₃ wt.%	CaO wt.%	TiO ₂ wt.%	SiO ₂ wt.%	V ₂ O ₅ ppm	Cr ₂ O ₃ ppm	Total wt.%
Brack.Std.	7.7	18.9	25.9	7.2	39.6	50	30	99.9
Glass #1	7.6	18.8	25.9	7.2	39.5	0	1300	99.7
Glass #2	7.4	18.5	25.5	7.0	38.8	3760	1250	99.3
Glass #3	7.6	18.8	26.6	7.1	39.3	80	80	99.7
Glass #4	7.4	18.3	27.3	6.9	38.3	530	390	99.4
Glass #5	7.4	18.4	25.2	6.9	38.7	7700	1100	99.2

Total values include minor and trace amounts of Na₂O, K₂O and FeO. Brack.Std. = Synthetic glass used as the bracketing standard when making LA-MC-ICPMS measurements of other synthetic glasses and CAIs.

nebula. To this end, we have developed a method to determine the titanium isotopic composition of CAIs by laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICPMS). This technique offers a precise and efficient means of determining the titanium isotopic compositions of a large suite of inclusions, which will allow the identification of potential FUN CAIs while still preserving the bulk of the material for additional geochemical and isotopic investigations. Here, we report on the *in situ* measurement of titanium isotope ratios by LA-MC-ICPMS in nine Allende CAIs. Matrix-matched glass standards were synthesized and used for the correction of matrix-effects and isobaric interferences during these isotopic analyses.

Analytical Technique: Matrix effects and isobaric interferences can cause analytical biases in the measured isotopic ratios during *in situ* analyses by LA-MC-ICPMS. Therefore, well-characterized, isotopically homogeneous standards with elemental compositions similar to those of the samples are essential for accurate isotopic measurements. Synthetic glasses were prepared using Ca-Mg-Al-Si (CMAS) oxides that approximate the composition of Ti-Al-rich pyroxene (fassaite) commonly found in CAIs. Pure oxide powders were placed in a Pt-capsule, heated to high temperatures (>1500°C) and then quenched. This glass was powdered, re-melted and quenched several more times to ensure homogeneity. Five fractions of this homogeneous glass were powdered and additionally doped with varying amounts of pure oxide powders of interfering species expected to be present during LA-MC-ICPMS analyses of refractory inclusions (i.e., Ca, Cr, V). These powders were then finally re-melted and quenched to produce glasses (Glass #1-5 in Table 1). These glasses were mounted in an epoxy disk, which

was then polished. One fraction of the undoped homogeneous glass was also mounted with the five doped glasses and was used as the bracketing standard ("Brack. Std." in Table 1) for measuring the isotopic compositions of the synthetic doped glasses and natural samples. Major and minor element compositions of each of these glasses were measured on the CAMECA SX 100 at the University of Arizona; the homogeneity of these glasses was verified by multiple spot analyses on each glass. The compositions of these synthetic glasses are reported in Table 1.

Titanium isotope ratios were measured with the ThermoFinnigan Neptune MC-ICPMS at ASU. A Jet sample cone was inserted in place of the standard sample cone, resulting in a five-fold increase in Ti sensitivity. A standard H-type skimmer cone was used. Ultrapure water was aspirated through an APEX-Q sample introduction system to provide a small amount of water vapor that stabilized the ion beam signal. The isotope ratios were measured on Faraday cups in two peak jumping steps: ^{44}Ca , ^{46}Ti , ^{47}Ti , ^{48}Ti , ^{49}Ti , ^{50}Ti (step 1) and ^{49}Ti , ^{51}V , ^{53}Cr (step 2). All analyses were made in medium resolution with integration times of 8.4 s in step 1 and 4.2 s in step 2. Each run consisted of 20 integrations, resulting in a ~5 minute analysis time. Gas blanks were measured immediately proceeding each sample exchange.

In situ analyses of titanium-rich phases in polished sections of Allende CAIs were made using a Photon Machines Analyte 193 excimer laser ablation system connected to the MC-ICPMS using He as carrier gas. Typical laser operating conditions consisted of a 69 μm spot size and 4 Hz repeat rate with 7 mJ/pulse. Instrumental mass bias was corrected using the sample-standard bracketing technique and internal normalization to a $^{49}\text{Ti}/^{47}\text{Ti}$ ratio of 0.749766 [2]. Typical ^{48}Ti intensity during analyses on the standards and samples was $5\text{-}10 \times 10^{-11}$ A.

Results and Discussion: The Ti isotopic compositions measured in this study (normalized to the $^{49}\text{Ti}/^{47}\text{Ti}$ ratio) are reported in the ϵ notation, or:

$$\epsilon^x\text{Ti} = \left[\left(\frac{^x\text{Ti}}{^{47}\text{Ti}} \right)_{\text{unknown}} / \left(\frac{^x\text{Ti}}{^{47}\text{Ti}} \right)_{\text{standard}} - 1 \right] \times 10^4$$

where x = 46, 48 and 50.

Based on the analyses of the synthetic CMAS glasses doped with varying amounts of Ca, Cr and V, an empirical scheme for correction of potential isobaric interferences and matrix effects was developed. Using this scheme, the external reproducibilities (2 SD) for $\epsilon^{46}\text{Ti}$, $\epsilon^{48}\text{Ti}$, and $\epsilon^{50}\text{Ti}$, based on repeated analyses of the synthetic glasses, are ± 0.6 , ± 0.4 , and ± 1.9 , respectively. This precision is an order of magnitude better than that obtained by previous SIMS investigations [9,11-15], but is comparable to (or slightly better than)

that reported by another recent LA-MC-ICPMS study [5] and previous TIMS studies [1-4,10,16,17].

We measured the titanium isotopic compositions of five compact Type A and four Type B Allende CAIs. The compositions of both Type A and Type B Allende inclusions analyzed here are similar within the uncertainties and have clearly resolved excesses in ^{50}Ti relative to the terrestrial standard composition (Fig. 1). Furthermore, these compositions are in agreement with those previously reported for "normal" Type A and Type B inclusions from Allende (which, considering the uncertainties, define a narrow compositional range). These findings suggest that normal Type A and Type B CAIs from CV chondrites formed from a relatively uniform isotopic reservoir in the solar nebula. However, this reservoir was spatially or temporally distinct from that in which FUN CAIs originated.

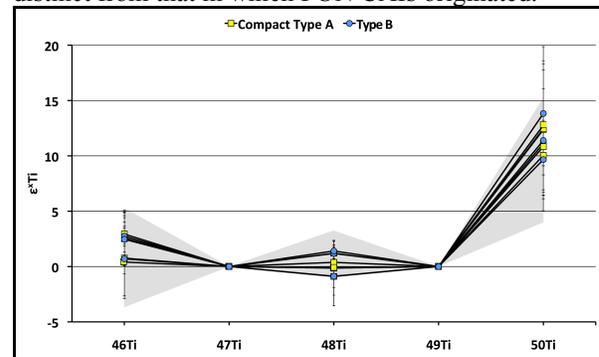


Figure 1 Titanium isotopic compositions of Type A and Type B Allende inclusions. Shaded region shows the range of titanium isotopic compositions (represented by twice the standard deviation of the calculated average) in "normal" Allende inclusions [2,4,16].

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