

CHROMIUM AND TITANIUM ISOTOPE SYSTEMATICS OF ALLENDE CAIs. C. M. Mercer¹, A. K. Souders¹, S. J. Romaniello¹, C. D. Williams², G. A. Brennecka³, and M. Wadhwa¹, ¹Center for Meteorite Studies, School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA (camer-on.m.mercer@asu.edu), ²University of California Davis, Davis, CA, USA, ³Institut für Planetologie, Westfälische Wilhelms-Universität, Münster, Germany.

Introduction: As the first-formed solids in the Solar System (SS), calcium-aluminum-rich inclusions (CAIs) can preserve evidence for the original isotopic heterogeneity of the solar nebula ([1] and references therein). Certain isotopic patterns are considered to reflect nucleosynthetic components [2]. In particular, isotopic anomalies in the vicinity of the Fe-peak are potentially highly diagnostic for constraining the nucleosynthetic components produced in an *r*-process environment (e.g., [3]). These anomalies may help elucidate how and when presolar components, and possibly late-injection supernova (SN; plural: SNe) materials, were homogenized in the early SS, providing constraints on SS formation models (e.g., [4, 5]). We report Ti and Cr isotopic data for six Allende CAIs to contribute to a growing, multi-element isotopic dataset that currently includes measurements of Mg, Sr, Zr, Mo, Te, Ba, Nd, Sm, Gd, Dy, and U on the same set of eleven CAIs [6-11].

Titanium has five stable isotopes (⁴⁶Ti, ⁴⁷Ti, ⁴⁸Ti, ⁴⁹Ti and ⁵⁰Ti) while chromium has four stable isotopes (⁵⁰Cr, ⁵²Cr, ⁵³Cr and ⁵⁴Cr) that are synthesized by distinct processes during hydrostatic and explosive nucleosynthesis in stars [12]. Also, ⁵³Cr is produced by radioactive decay of ⁵³Mn (*t*_{1/2} = 3.7 Ma). Here we focus on the neutron-rich isotopes ⁵⁰Ti and ⁵⁴Cr, which are thought to be produced primarily by *r*-process nucleosynthesis in either: (1) Type Ia SNe of white dwarf stars near the Chandrasekhar mass that have neutron-rich, low-entropy conditions (e.g., [12-14]), or (2) Type II SNe (which additionally provide O-rich environments for the condensation of refractory oxides that carry ⁵⁴Cr [14-16]).

Compared to younger SS objects, CAIs have positive *r*-process anomalies in nuclides with *A* < 140 (including ⁵⁴Cr, [17-20]), and negative *r*-process anomalies in nuclides with *A* > 140 [7]. This implies that SS materials incorporated *r*-process nuclides from multiple stellar sources, and that SN material was injected into a reservoir that was unsampled by CAIs [7]. We explore how the Ti and Cr isotopic compositions of Allende CAIs can refine our understanding of nucleosynthetic components in the early SS.

Analytical Methods: Ti was purified by ion-exchange chromatography following [21]. Ti isotopic data were acquired with a Thermo Finnigan *Neptune* MC-ICP-MS operated in high resolution mode (*M*/ Δ *M* > 9000) at Arizona State University (ASU). The sam-

ples were introduced into the mass spectrometer using an Elemental Scientific *Apex-Q* with a 50 μ L/min flow rate. A 2 ppm Ti solution yielded a ⁴⁸Ti signal of ~16 V. We used a dynamic Faraday cup configuration to measure the intensities of ⁴⁴Ca, ⁴⁶Ti, ⁴⁷Ti, ⁴⁸Ti, and ⁴⁹Ti before switching the magnet to measure ⁴⁷Ti, ⁴⁹Ti, ⁵⁰Ti, ⁵¹V, and ⁵²Cr. Signals for ⁴⁴Ca, ⁵¹V, and ⁵²Cr were used to correct for isobaric interferences. Ti isotopic data are reported relative to an in-house SPEX Ti standard after internal normalization to ⁴⁹Ti/⁴⁷Ti (=0.749766 [22]) using an exponential fractionation law.

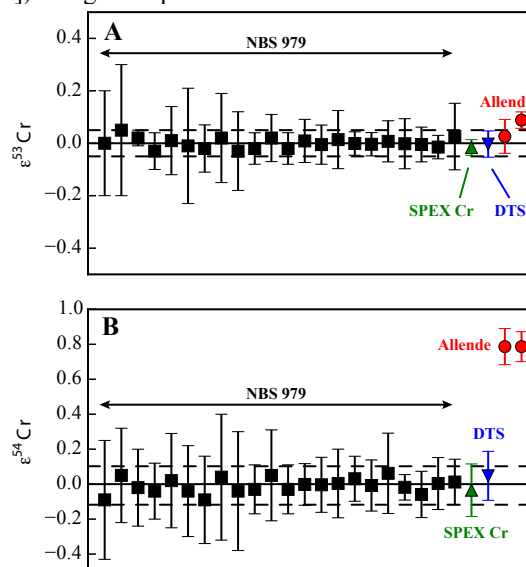


Fig. 1. Long-term reproducibility of non-mass dependent effects (in ϵ units) in (A) $^{53}\text{Cr}/^{52}\text{Cr}$ and (B) $^{54}\text{Cr}/^{52}\text{Cr}$ for NBS 979, SPEX Cr, DTS rock standard, and Allende whole-rock. Each data point represents the average ($\pm 2\text{SE}$) of 3-6 repeat measurements that utilized a total of ~ 1 μg Cr. All unknown analyses are conducted similarly ($n = 3-6$, total Cr consumed ~ 1 μg). The dashed lines bound the 2SD envelope for the average value of terrestrial synthetic Cr and rock standards.

Cr was purified by an ion-exchange chromatography procedure modified from [23]. Cr isotopic data were acquired with the *Neptune* at ASU using an *Apex-Q* and 50 μ L/min nebulizer. An 800 ppb Cr solution resulted in a ⁵²Cr signal of ~30 V. Measurements were done in high resolution mode to avoid polyatomic interferences [24]. The intensities of ⁵⁰Cr, ⁵²Cr, ⁵³Cr, and ⁵⁴Cr were measured, along with ⁴⁹Ti, ⁵¹V, and ⁵⁶Fe to monitor and correct for isobaric interferences. Cr isotopic data are reported relative to the NBS 979 standard after internal normalization to ⁵⁰Cr/⁵²Cr (=0.051859 [25]) using an exponential fractionation

law. Our empirical external reproducibility is ± 0.04 (2SD) for $\epsilon^{53}\text{Cr}$ and ± 0.08 (2SD) for $\epsilon^{54}\text{Cr}$ from measurements of terrestrial synthetic Cr and whole-rock standards (Fig. 1), similar to theoretical limits of ± 0.05 and ± 0.10 , respectively.

Initial Results: We have measured the Ti and Cr isotopic compositions of 6 of the 11 Allende CAIs studied by [6-11], including CAIs 165, 166, 167, 168, 173, and 175. Values for $\epsilon^{53}\text{Cr}$ range from -0.71 to 0.11, and $\epsilon^{54}\text{Cr}$ ranges from 3.42 to 5.89 (blue symbols in Fig. 2). Some of the variation in $\epsilon^{53}\text{Cr}$ is due to the presence of radiogenic ^{53}Cr from the decay of ^{53}Mn , so we have subtracted an estimated radiogenic ^{53}Cr component using the initial SS $^{53}\text{Mn}/^{55}\text{Mn}$ value of $(6.28 \pm 0.66) \times 10^{-6}$ [26] and the $^{55}\text{Mn}/^{52}\text{Cr}$ ratios measured in these samples (red symbols in Fig. 2). Values for $\epsilon^{50}\text{Ti}$ range from 8.55 to 9.59 (Fig. 3).

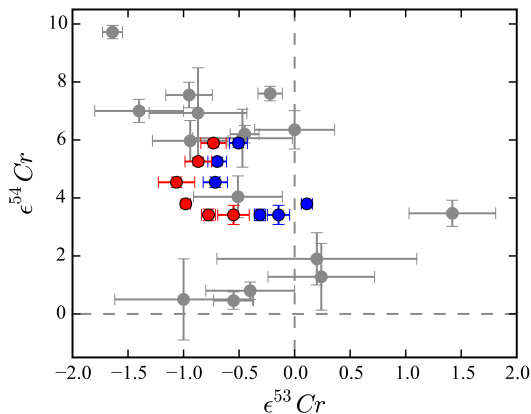


Fig. 2. Chromium isotopic compositions of Allende CAIs from this work before (blue circles) and after (red circles) correction for the presence of radiogenic ^{53}Cr from decay of ^{53}Mn ; errors are either the 2SD external reproducibility (Fig. 1) based on terrestrial standards or the 2SE internal errors based on 3-6 repeats of sample analyses, whichever is larger. Previous literature data for CAIs from Vigarano and Allende are shown for reference (grey circles, not corrected for radiogenic ^{53}Cr) [17-20, 26].

Discussion: The Cr isotopic data presented here and reported previously for Allende CAIs [17-19, 26], demonstrate variations in $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ that significantly exceed the precision of the measurements, while $\epsilon^{50}\text{Ti}$ values show a much more restricted range (Figs. 2 and 3). While it is possible that the observed variation in $\epsilon^{54}\text{Cr}$ reflects CAI formation in an inhomogeneous reservoir, we cannot rule out other potential causes (especially since $\epsilon^{50}\text{Ti}$ does not vary significantly). Interestingly, other stable isotope systems measured for this sample set (Sr, Zr, Mo, Ba, Nd, Sm, Gd, Dy) indicate the CAI reservoir was nearly homogeneous (within the precision of the analyses) [6-11]. Note that the concentration ratio $[\text{Cr}]_{\text{matrix}}/[\text{Cr}]_{\text{CAI}}$ is ~ 10 (using CI chondrites as a proxy for CAI-free matrix, [5]) for

these samples, while other elements (e.g., Ti, Sr, Mo, Nd, Sm, Gd, Dy) tend to have much smaller matrix/CAI concentration ratios (e.g., 0.6–1). It is plausible that the variation that we observe in $\epsilon^{54}\text{Cr}$ could be due to addition of Cr to the CAIs from their host matrix (either by diffusion exchange with, or physical addition of, the matrix). A simple two-component mixture model of these two materials (Fig. 3) is consistent with this possibility, and implies that up to $\sim 10\%$ of the Cr in our samples could have originated from the meteorite matrix. If this is the case, then the highest $\epsilon^{54}\text{Cr}$ values in CAIs may only constrain the minimum $\epsilon^{54}\text{Cr}$ composition of the reservoir from which CAIs formed. This possibility should be considered when relating $\epsilon^{54}\text{Cr}$ excesses to potential nucleosynthetic components in the SS.

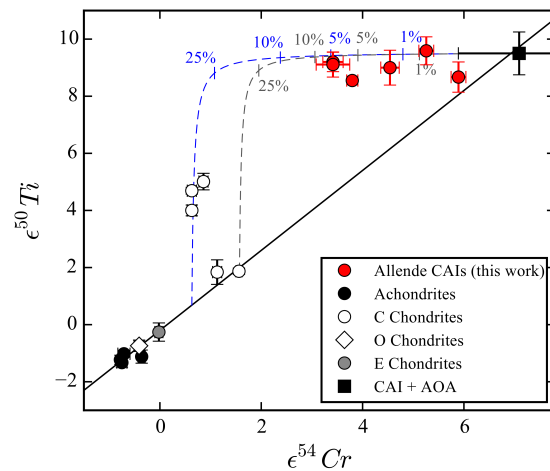


Fig. 3. Plot of $\epsilon^{50}\text{Ti}$ vs. $\epsilon^{54}\text{Cr}$ for several achondrites, chondrites, and CAIs reported by [5], along with our data shown in red. Grey and blue dashed lines represent mixtures of Ti and Cr between CAIs (5400 ppm Ti, 200 ppm Cr; $\epsilon^{50}\text{Ti} = 9.5$, $\epsilon^{54}\text{Cr} = 7$) and CAI-free matrix material (2646 ppm Ti, 458 ppm Cr; grey: $\epsilon^{50}\text{Ti} = 1.87$, $\epsilon^{54}\text{Cr} = 1.57$; blue: $\epsilon^{50}\text{Ti} = 0.68$, $\epsilon^{54}\text{Cr} = 0.63$), with labels indicating the percentage of matrix in the mixture. Figure and model parameters after [5].

References: [1] MacPherson (2014), *Treatise in Geochemistry* (2nd Ed.), p. 139. [2] Meyer and Zimmer in *Meteorites and the Early Solar System II*, (UofA Press, 2006). [3] Jungck et al. (1984) *GCA*, 48, p. 2651. [4] Rotaru et al. (1992) *Nature*, 358, 465. [5] Trinquier et al. (2009) *Science*, 324, p. 374. [6] Brennecka et al. (2010) *Science*, 327, p. 449. [7] Brennecka et al. (2013) *PNAS*, 110, 17241. [8] Mane et al. (2014) *LPSC 45*, #1685. [9] Mane et al. (2014) *MetSoc*, #5403. [10] Brennecka et al. (2014) *LPSC 45*, #2280. [11] Brennecka et al. (*this meeting*). [12] Clayton (Cambridge U Press, 2003), p. 218. [13] Woosley and Heger (2002) *Rev. Mod. Phys.*, 74, p. 1015. [14] Wang et al. (2011) *Astrophys J*, 739, L58. [15] Dauphas et al. (2010) *Astrophys J*, 720, p. 1577. [16] Qin et al. (2011) *GCA*, 75, p. 629. [17] Birk and Allègre (1984) *GRL*, 11, p. 943. [18] Birk and Allègre (1985) *GRL*, 12, p. 745. [19] Birk and Lugmair (1988) *EPSL*, 90, p. 131. [20] Loss et al. (1994) *Astrophys J*, 436, L193. [21] Zhang et al. (2011) *J. Anal. Atom. Spect.*, 26, p. 2197. [22] Niederer et al. (1981) *GCA*, 45, p. 1017. [23] Yamakawa et al. (2009) *Anal. Chem.*, 81, p. 9787. [24] Schoenberg et al. (2008) *Chem. Geol.*, 249, p. 294. [25] Shields et al. (1966) *J. Res. Nat. Bur. Stand.*, 70A, p. 193. [26] Trinquier et al. (2008) *GCA*, 72, p. 5146.