

COMBINED INVESTIGATION OF CHROMIUM, TITANIUM, AND MAGNESIUM ISOTOPE COMPOSITIONS OF REFRACTORY INCLUSIONS FROM A VARIETY OF CARBONACEOUS CHONDRITES. Z. A. Torrano¹, V. K. Rai¹, and M. Wadhwa¹, ¹Center for Meteorite Studies, School of Earth and Space Exploration, Arizona State University, Tempe, AZ, USA (ztorrano@asu.edu)

Introduction: As the first solids to form in the early Solar System, calcium-aluminum-rich inclusions (CAIs) in chondrites preserve a record of the earliest processes and conditions in the solar nebula [1]. Mass-independent anomalies in a variety of isotope systems have been found in CAIs, and these anomalies have been attributed largely to incomplete homogenization of distinct nucleosynthetic components in the nebular reservoirs sampled by these objects [2]. Recent work on the isotopic compositions of a variety of elements in a suite of CAIs from Allende and a few other chondrites has shown that these CAIs have relatively uniform isotopic compositions (within the analytical precision) for elements ranging from Sr to Dy that are nevertheless distinct from terrestrial or bulk chondritic compositions [3-5]. This suggests that, at least for these elements, these CAIs formed from a homogeneous nebular reservoir which was distinct from the one from which the remainder of chondritic components originated. However, our recent work on Cr and Ti isotopes in these same CAIs found resolvable heterogeneity in their isotopic compositions, suggesting that the CAI-forming region in the solar nebula was isotopically heterogeneous for these elements [6-9]. This is consistent with another recent study of Ti isotopes in a large group of Allende CAIs that also found resolvable Ti isotopic heterogeneity [10].

This work is part of an ongoing project, the goal of which is to constrain the degree of isotopic heterogeneity recorded in CAIs from primitive chondrites other than Allende in order to more rigorously assess the degree of isotopic heterogeneity in the broader CAI-forming region in the early Solar System. Specifically, the suite of CAIs from chondrites other than Allende studied thus far include the following 12 inclusions: “Bart” from CK3 Northwest Africa (NWA) 4964; “Homer” from CK3 NWA 6254; “Marge” from CV3 NWA 6619; ZT1 and ZT2 from CV3 Leoville; “Lisa” and ZT3 from CV3 NWA 6991; ZT4 and ZT5 from CV3 NWA 7891; and ZT7, ZT8, and ZT9 from CV3 NWA 3118. Each CAI was carefully extracted from the meteorite slab using clean stainless steel dental tools. A small fraction of each CAI was also mounted and characterized using the JEOL JXA-8520F electron microprobe in the LeRoy Eyring Center for Solid State Science at Arizona State University (ASU). We previously presented Ti isotope compositions for all of these samples [8,9] and Cr data for five of these (i.e., CAIs

Bart, Lisa, Homer, Marge, and ZT9) [7,8]. Here we report the Cr isotope compositions for six more of these samples (i.e., ZT1, ZT2, ZT3, ZT5, ZT7 and ZT8). Moreover, we also report Al-Mg isotope systematics in five of these CAIs (ZT1, ZT2, ZT3, ZT5, and ZT7).

Samples and Methods: All sample handling and chemical processing was conducted in the Isotope Cosmochemistry and Geochronology Laboratory (ICGL) at ASU. Extracted fractions were digested in Parr bombs, followed by multiple treatments with aqua regia. Subsequently, a ~5% aliquot of each was reserved for elemental analyses, and the remainder of the solutions were processed for the separation of elements of interest. Concentrations of a variety of elements, including rare earth elements (REE), Al, and Mg, were determined in the 5% aliquot reserved for this purpose using the iCAP-Q quadrupole ICPMS in the Keck Laboratory at ASU.

Chromium was purified using procedures adapted from [11]. Purified Cr samples and standards were analyzed on the Thermo Neptune Multicollector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS) in the ICGL using methods similar to those described previously [6-8]. Samples and standards (800 ppb concentration) were introduced using an Aridus II desolvating nebulizer with a 50 $\mu\text{L}/\text{min}$ flow rate. Measurements were done in high resolution mode to avoid polyatomic interferences [12]. The intensities of ^{50}Cr , ^{52}Cr , ^{53}Cr , and ^{54}Cr were measured, along with ^{49}Ti , ^{51}V , and ^{56}Fe to monitor and correct for isobaric interferences. The Cr isotopic data are reported relative to the NBS 979 standard after internal normalization to $^{50}\text{Cr}/^{52}\text{Cr}$ (=0.051859; [13]).

Magnesium was purified using ion chromatography adapted from [14]. Purified Mg samples and standards were analyzed on the Thermo Neptune MC-ICPMS in the ICGL using methods described previously [14,15]. Samples and standards (250 ppb concentration) were introduced using an Elemental Scientific Apex-Q desolvating nebulizer with a 50 $\mu\text{L}/\text{min}$ flow rate. The non-mass dependent effects on $^{26}\text{Mg}/^{24}\text{Mg}$ were calculated relative to DSM-3 Mg standard after internal normalization to $^{25}\text{Mg}/^{24}\text{Mg}$ (=0.12663; [16]) using an exponential fractionation law.

Samples of homogenized Allende powder and the BCR-2 terrestrial rock standard were chemically processed and analyzed alongside the samples to assess the accuracy and precision of our analyses.

Results and Discussion: The 12 CAIs in the suite considered here (from chondrites other than Allende) represent a diversity of petrologic and geochemical types. In particular, the rare earth element compositions of these CAIs indicate that they include ones that have both fractionated Group II patterns (Homer, ZT2, ZT3, ZT5, ZT9) and relatively unfractionated REE patterns (Bart, Lisa, Marge, ZT1, ZT4, ZT7, ZT8).

Cr and Ti Isotopic Systematics. The Cr isotopic compositions of these CAIs show a range of $\epsilon^{53}\text{Cr}$ from -1.16 ± 0.06 to -0.02 ± 0.12 and $\epsilon^{54}\text{Cr}$ from 3.16 ± 0.30 to 7.28 ± 0.28 . Some of the measured variation in $\epsilon^{53}\text{Cr}$ is likely due to the presence of radiogenic ^{53}Cr from the decay of ^{53}Mn . As such, we can subtract a radiogenic ^{53}Cr component that can be estimated using the initial Solar System $^{53}\text{Mn}/^{55}\text{Mn}$ value of $(6.28 \pm 0.66) \times 10^{-6}$ [17] and the Mn/Cr ratios measured in these samples. With this subtraction, the $\epsilon^{53}\text{Cr}$ values show a range from -1.42 ± 0.31 to -0.05 ± 0.06 . Thus, we find that there is resolvable variation in the $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ values in this suite of CAIs from chondrites other than Allende (this study; [7,8]). However, there is no correlation between the $\epsilon^{53}\text{Cr}$ or $\epsilon^{54}\text{Cr}$ anomalies, nor is there a correlation between these Cr isotope anomalies and the REE patterns in these CAIs. These variations in the Cr isotopic compositions, in combination with the previously reported Ti isotopic compositions of these same samples [8,9], indicate significant isotopic heterogeneity in the CAI-forming region in the protoplanetary disk.

Figure 1 shows the $\epsilon^{50}\text{Ti}$ versus $\epsilon^{54}\text{Cr}$ values in the CAI suite considered here (see caption for details). It is possible that some of the variation in the Cr isotope compositions of these CAIs is the result of the addition of Cr to the CAIs from the host chondrite matrix, either on the parent body or in the laboratory during sample extraction. Nevertheless, even if such an addition took place, it cannot account for the full range of $\epsilon^{50}\text{Ti}$ and $\epsilon^{54}\text{Cr}$ values in these CAIs (since the end-member CAI compositions would need to define a range, shown as the gray oval, along the solid black line in Fig. 1).

Al-Mg Systematics. The CAIs ZT1, ZT2, ZT3, ZT5, and ZT7 have a range of $^{27}\text{Al}/^{24}\text{Mg}$ from 1.16 ± 0.06 to 4.59 ± 0.23 . The “bulk CAI” isochron (Fig. 2) yields an initial $^{26}\text{Al}/^{27}\text{Al}$ ratio of $(4.90 \pm 0.33) \times 10^{-5}$ and a $(\delta^{26}\text{Mg}^*)_0$ of $0.00 \pm 0.05\%$. This is consistent with the canonical CAI $^{26}\text{Al}/^{27}\text{Al}$ value of $\sim 5.2 \times 10^{-5}$ (e.g., [18-20]). These preliminary results are consistent with a homogeneous distribution of ^{26}Al in the early Solar System.

Acknowledgments: This work was supported by a NASA Emerging Worlds grant (NNX15AH41G) to MW. We thank R. Hines and S. Romaniello for their invaluable assistance in the ICGL at ASU.

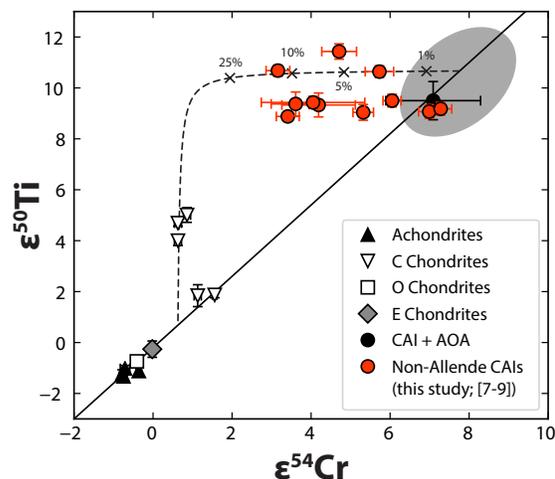


Figure 1. $\epsilon^{50}\text{Ti}$ versus $\epsilon^{54}\text{Cr}$ for a suite of CAIs from chondrites other than Allende (red symbols); Ti isotope compositions are from [8,9], while Cr isotope data are from this study and [7,8]. Also shown are data for several achondrites, chondrites, and CAIs (grayscale symbols) reported by [21]. Black solid line represents correlation line defined by these objects; black dashed line represents an example of a model [21] estimating the effect of mixing Ti and Cr between CAIs and matrix (labels indicate the percentage of matrix in the mixture). Gray oval indicates the range of CAI end-member compositions required to account for the measured range of $\epsilon^{50}\text{Ti}$ and $\epsilon^{54}\text{Cr}$ values even if matrix addition contributed to this variation.

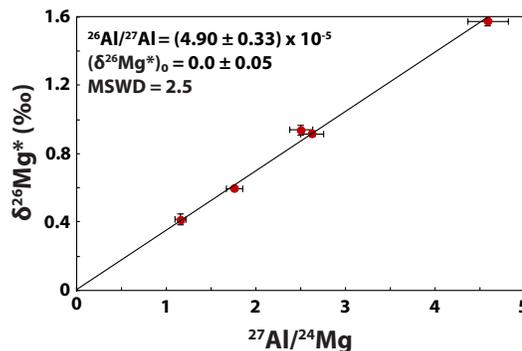


Figure 2. ^{26}Al - ^{26}Mg isochron diagram for bulk CAIs studied here.

References: [1] MacPherson (2014), *Treatise on Geochemistry* (2 Ed.), p. 139. [2] Meyer and Zinner in *Meteorites and the Early Solar System II*, (U. Arizona Press, 2006). [3] Brennecka et al. (2013) *PNAS*, 110, 17241. [4] Mane et al. (2014) *MetSoc* 77, #5403. [5] Shollenberger et al. (2015) *LPSC* 46, #2593. [6] Mercer et al. (2015) *LPSC* 46, #2920. [7] Mane et al. (2016) *LPSC* 47, #2778. [8] Torrano et al. (2017) *LPSC* 48, #3045. [9] Torrano et al. (2017) *MetSoc* 80, #6318. [10] Davis et al. (2018) *GCA*, 221, 275-295. [11] Yamakawa et al. (2009) *Anal. Chem.*, 81, p. 9787. [12] Schoenberg et al. (2008) *Chem. Geol.*, 249, p. 294. [13] Shields et al. (1966) *J. Res. Nat. Bur. Stand.*, 70A, p. 193. [14] Spivak-Birndorf et al. (2009) *GCA*, 73, 5202-5211. [15] Bouvier et al. (2011) *GCA*, 75, 5310-5323. [16] Catanazaro et al. (1966) *J. Res. Natl. Bur. Stand.*, 70A, p. 453. [17] Trinquier et al. (2008) *GCA*, 72, p. 5146. [18] MacPherson et al. (1995) *Meteoritics*, 30, 365-386. [19] Jacobsen et al. (2008) *EPSL*, 272, 353-364. [20] Kita et al. (2013) *MAPS*, 48, 1383-400. [21] Trinquier et al. (2009) *Science*, 324, p. 374.