ZIRCONIUM AND CHROMIUM ISOTOPIC SYSTEMATICS OF NON-ALLENDE CAIs. P. Mane[1], Z.A. Torrano[1], S.J. Romaniello[1], G.A. Brennecka[2], Q.R. Shollenberger[2], L. Borg[3] and M. Wadhwa[1], [1]Center for Meteorite Studies, School of Earth and Space Exploration, Arizona State University, Tempe, AZ, USA (ztorrano@asu.edu), [2]Institut für Planetologie, Westfälische Wilhelms-Universität, Münster, Germany, [3]Lawrence Livermore National Lab, Livermore, CA, USA.

Introduction: Calcium-aluminum-rich inclusions (CAIs) in chondrites preserve a record of the earliest Solar System processes [1]. They show anomalies in a variety of isotope systems when compared to the bulk chondritic composition [2]. These anomalies have been attributed largely to incomplete homogenization of distinct nucleosynthetic components in the nebular reservoir sampled by CAIs. In recent years, we have reported the isotopic compositions of an unprecedented number of elements from a single suite of Allende CAIs [3-6]. This work has shown that these Allende CAIs have uniform isotopic compositions in the mass range of ~46 to ~164 amu that are still distinct from terrestrial or bulk chondritic values, suggesting that they originated from an isotopically homogeneous nebular reservoir. However, it is important to determine the isotope compositions of CAIs from other primitive chondritic meteorites to ascertain the degree of isotopic heterogeneity in the broader CAI-forming region in the early Solar System. Recently, [7] reported the Sr, Ba, Nd, and Sm isotope compositions of four CAIs from four different desert chondrites (two CV3, one CK3, and one CK5 meteorite). These authors attributed the slight variations in isotopic composition that they observed in this sample set to varying contributions from terrestrial weathering. The goal of this investigation was to determine the isotope compositions of several other key elements (specifically Zr, Cr, and Ti) in these CAIs that are less likely to be affected by terrestrial weathering and that considerably expand the mass range being investigated for these samples.

Samples and Analytical Methods: We analyzed Zr and Cr isotope compositions of the same set of four CAIs that were previously studied by [7]. We additionally plan to measure their Ti isotope compositions in the near future. As described by [7], "Marge" and "Lisa" are from two different CV3 carbonaceous chondrites; "Bart" is from the CK5 chondrite, while "Homer" is from a CK3 chondrite. Bart, Lisa, and Marge show flat Group III REE patterns whereas Homer shows a modified Group II REE pattern. Since we had previously only reported the Zr isotope compositions of a subset of our original suite of Allende CAIs [4], we also measured the Zr isotope compositions of the remaining CAIs from this suite (166, 167, 170, and 175) for the sake of completeness. CAIs 166, 167, and 175 are fine grained inclusions that show Group II Rare Earth Element (REE) patterns [8], suggesting

formation from a fractionated reservoir in the nebula [9]; CAI 170 is a coarse-grained CAI that has a flat Group III REE pattern [8] that can be explained by condensation from a solar nebula of CI composition.

The CAIs were separated from their respective meteorites and a small fragment was mounted in a polished section for petrographic analyses. The major fraction of each CAI was digested in a Parr bomb, followed by multiple treatments with aqua regia. Chemical separation for a suite of elements was done following the methods outlined in [3]. The CAIs, as well as BCR-2 and Allende whole rock samples (used as internal laboratory standards), were chemically processed to separate Zr from the rest of the matrix using protocols adapted from those described in [9]. Subsequently, Cr purification was accomplished using the procedure modified from [10].

Zirconium and chromium isotopes were measured on the Neptune Multicollector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS) at Arizona State University (ASU) using methods similar to those described previously [4,6]. Purified zirconium samples and standards were analyzed at a concentration of 100 ppb and data were internally normalized to ^{94}Zr/^{90}Zr (= 0.33381; [11]) to correct for mass dependent fractionation. The external reproducibilities (2SD) based on repeat analyses of the NIST 3169 isotopic standard over the course of this study for ε^{91}Zr, ε^{92}Zr and ε^{96}Zr are ±0.14, ±0.14, and ±0.31, respectively. Each sample was analyzed 3 to 5 times during an analytical session. The errors reported here are either the 2SD of multiple analyses or the external reproducibility (2SD) of NIST 3169 standard (the larger of the two). Purified chromium samples and standards were analyzed at a concentration of 800 ppb. 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}Cr/^{52}Cr (=0.051859; [13]). Our external reproducibility is ±0.04 and ±0.08 (2SD) for ε^{53}Cr and ε^{54}Cr, respectively, based on repeat measurements of terrestrial rock standards over the course of this study. The Nb/Zr and Mn/Cr ratios were measured using a Thermo quadrupole ICPMS at Lawrence Livermore National Laboratory (LLNL).

Results and Discussion: The Zr isotopic composition of the CAIs analyzed here is shown in Fig. 1. No mass independent anomalies in ε^{91}Zr are resolvable. However, all analyzed CAIs except Homer show excesses in ε^{96}Zr that are identical within the analytical errors, with an average value of 2.05 ± 0.38 (2SD); this is indistinguishable from the average value based on our 8 previously analysed Allende CAIs [4]. Homer shows a slightly, but resolvably, lower ε^{96}Zr of 0.99 ± 0.40. The average ε^{96}Zr value reported here for CAIs (with the possible exception of Homer) is consistent with the most recent reports from other laboratories [14, 15]. Our complete Zr data set [4; this study] suggests that the CAI-forming region was mostly homogenous with respect to Zr isotopes. The enrichment in the r-process isotope ^{96}Zr is consistent with the model proposed by [3, 16] to explain the systematic r-process enrichments and depletions observed in the isotopes of Sr, Mo, Ba, Nd, Sm, Gd, and Dy in the same set of Allende CAIs studied here.
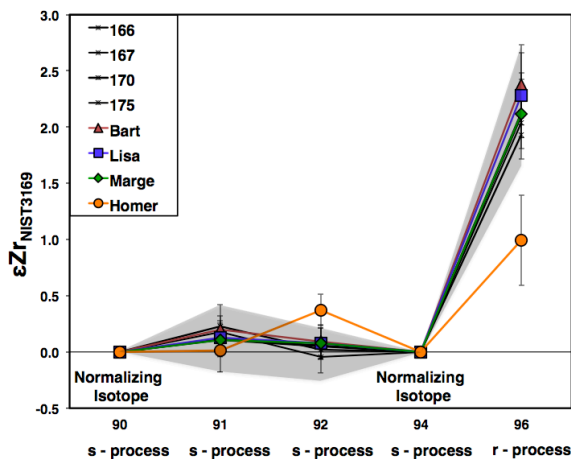

Figure 1: Mass independent Zr isotopic composition of the CAIs analyzed here. The grey region shows the range of Zr isotopic composition previously reported for 8 Allende CAIs [4].

As evident in Fig. 1, Homer shows a resolvable excess in ε^{92}Zr; it also has a higher higher Nb/Zr ratio compared to the other CAIs analyzed here. Taken together, the four non-Allende CAIs define a slope in a ^{92}Nb-^{92}Zr isochron plot that corresponds to an initial ^{92}Nb/^{93}Nb ratio of (1.31 ± 0.72) × 10^{-5}. This value is consistent with the Solar System initial ^{92}Nb/^{93}Nb ratio defined by an equilibrated ordinary chondrite and a eucrite clast [17], but does not agree with the higher initial ^{92}Nb/^{93}Nb ratio of ~10^{-3} suggested by earlier studies [18, 19].

The Cr isotopic compositions determined here for the four non-Allende CAIs are shown in Fig. 2; the ε^{53}Cr show a significant range from -0.60ε to -0.01ε, and the ε^{54}Cr values show a smaller range from 3.7ε to

4.7ε. Some of the variation in ε^{53}Cr is due to the presence of radiogenic ^{53}Cr from the decay of ^{53}Mn. As such, we have subtracted a radiogenic ^{53}Cr component that was estimated using the initial Solar System ^{53}Mn/^{55}Mn value of (6.28 ± 0.66) × 10^{-6} [20] and the Mn/Cr ratios measured in these samples (corrected data are shown as red symbols in Fig. 2). As suggested for the Allende CAIs [6], it is possible that the observed large variation in ε^{53}Cr is the result of addition of Cr to the CAIs from their host matrix. If true, the implication then would be that the Cr isotopic composition of the CAI-forming reservoir in the nebula is homogenous as well. Titanium isotopic measurements of these non-Allende CAIs will be performed and will be used to assess this possibility further.
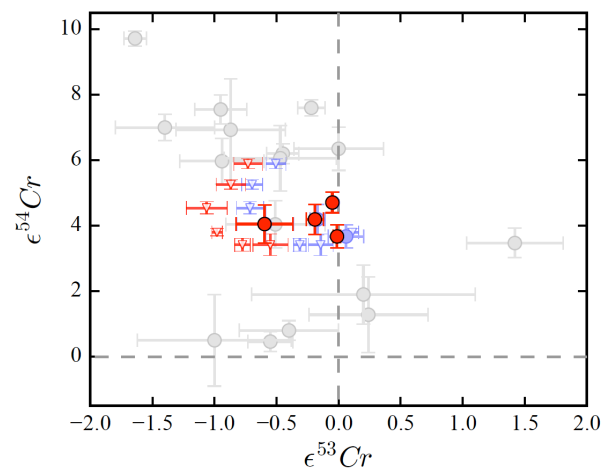

Figure 2: Chromium isotopic compositions of the 4 non-Allende CAIs studied here (solid colored circles) and of the Allende CAIs analyzed by [6] (open colored symbols); blue symbols are measured values, while red data indicate ε^{53}Cr values that have been corrected for radiogenic ^{53}Cr from decay of ^{53}Mn. For comparison, previously published data for CAIs from Vigarano and Allende (grey circles, not corrected for radiogenic ^{53}Cr) [20-24].

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 2014,* #5403. [5] Williams et al. (2014) *Goldschmidt 2014,* #2712. [6] Mercer et al. (2015) *LPSC 46,* #2920. [7] Shollenberger et al. (2015) *LPSC 46,* #2593. [8] Brennecka et al. (2010) *Science, 327,* 449-451. [9] Zhang et al. (2011) *J. Anal. Atom. Spect.,* 26, p. 2197. [10] Yamakawa et al. (2009) *Anal. Chem,* 81, p. 9787. [11] Nomura et al. (1983) *Int. J Mass. Spectrom. Ion Phys.* 50: 219-227 [12] Schoenberg et al. (2008) *Chem. Geol.,* 249, p. 294. [13] Shields et al. (1966) *J. Res. Nat. Bur. Stand,* 70A, p. 193. [14] Schönbächler et al. 2003. *EPSL* 216: 467-481 [15] Akram et al. 2013. *ApJ* 777: 169-181. [16] Brennecka et al. (2014) *LPSC 45,* #2280. [17] Schönbächler et al. (2002) *Science, 295,* 1705-1708. [18] Sanloup et al. (2000) *EPSL,* 184.1: 75-81. [19] Münker et al. (2000), *Science, 289,* 1538-1542. [20] Trinquier et al. (2008) *GCA,* 72, p. 5146. [21] Birck and Allègre (1984) *GRL,* 11, p. 943. [22] Birck and Allègre (1985) *GRL,* 12, p. 745. [23] Birck and Lugmair (1988) *EPSL,* 90, p. 131. [24] Loss et al. (1994) *Astrophys. J,* 436, L193.