

IRON ISOTOPE SYSTEMATICS OF REFRACTORY INCLUSIONS AND THE SEARCH FOR THE SOURCE OF NUCLEOSYNTHETIC ANOMALIES. Q.R. Shollenberger^{1*}, G.A. Brennecka¹, S. Schuth², and S. Weyer². ¹Institut für Planetologie, University of Münster, Wilhelm-Klemm-Strasse 10, 48149 Münster, Germany (*shollenberger@wwu.de), ²Institut für Mineralogie, Leibniz Universität Hannover, Hannover, Germany.

Introduction: Information about the earliest reservoirs in our Solar System is contained in the oldest condensates of our Solar System, calcium-aluminum-rich inclusions (CAIs). Previous work has shown for a variety of elements that isotopic differences exist between normal (non-FUN) CAIs and terrestrial rock standards [e.g., 1-6]. Depending on the element, these differences can be attributed to mass dependent isotope fractionation such as condensation or evaporation processes, nucleosynthetic differences, or both [e.g., 1-10]. Previous work focusing on the Fe-peak elements like Ti, Ca, Cr, and Ni have reported both mass dependent variations along with nucleosynthetic variations in CAIs [e.g., 4, 6-8], although Fe has largely been ignored because of its susceptibility for contamination in CAIs from secondary processes.

This study seeks to examine the Fe isotopic composition of bulk CAIs along with three mineral separates from the Allende CAI Egg-2. Since Sr and Ti are typically thought to be contained in primary minerals in CAIs, the Sr and Ti isotopic compositions of the mineral separates could assist in distinguishing primary Fe from secondary Fe in CAIs and their components. We present the Fe data in combination with Sr and Ti in order to better understand the isotopic material present in the earliest reservoir(s) of our Solar System and how this material evolved over time.

Samples and Methods: Aliquots of terrestrial rock standards, bulk Allende, and a variety of CAIs previously shown to have isotopic anomalies in other elemental systems were selected for Fe isotopic study. This sample set includes CAIs from Allende, other CV3 meteorites [1-2], as well as CAIs removed from CK meteorites [3]. Aliquots of three mineral fractions separated by magnetic susceptibility from the Allende CAI Egg-2 were obtained from [11] and represent high-Fe pyroxene, high-Mg pyroxene, and plagioclase-rich separates. Following the procedure from [12], Fe was separated from all samples using AG1-X8 (100-200 mesh) anion exchange resin. For the mineral separates only, Sr was isolated from the matrix following the procedures from [2] using AG50W-X8 (200-400 mesh) resin followed by Sr-spec resin. Titanium was separated from the matrix washes of the mineral separates using the procedure from [13].

Isotopic measurements: The Fe isotopic compositions of the samples and standards were measured on a Thermo-Scientific Neptune Plus MC-ICP-MS at the University of Hannover, Germany. The isolated Fe

solutions were subsequently doped with Cu to monitor instrumental mass bias during the run, enabling simultaneous mass dependent and internally normalized data collection [12]. Instrumental mass bias was corrected using both external and internal normalization ($^{63}\text{Cu}/^{65}\text{Cu} = 2.24359$ [14] and $^{57}\text{Fe}/^{54}\text{Fe} = 0.36255$ [15]). The Sr isotopic compositions of the mineral separates were measured on a Triton Plus TIMS at the University of Münster (Germany) and the data were internally normalized using $^{86}\text{Sr}/^{88}\text{Sr}=0.1194$. The Ti isotopic composition of the mineral separates was measured at the University of Münster using a Neptune Plus MC-ICP-MS modifying the method from [13] and the data were internally normalized to $^{49}\text{Ti}/^{47}\text{Ti} = 0.74977$.

Results and Discussion: The Fe, Sr, and Ti data are presented and discussed below. Mass dependent variations are presented in δ -notation (parts per thousand) and nucleosynthetic variations are shown in ϵ -notation (parts per ten thousand). The uncertainties shown represent the 2SD of replicate sample analyses or the 2SD of the long-term reproducibility of the terrestrial standard during the measurement campaign, whichever was larger.

Iron isotopes: Relative to terrestrial standards, no variations are observed outside analytical uncertainty for $\epsilon^{56}\text{Fe}$ or $\epsilon^{58}\text{Fe}$ in the bulk CAIs. However, the bulk CAIs show variation in their $\delta^{56}\text{Fe}$ ranging from ~ -1.5 to 1.0 for $\delta^{56}\text{Fe}$, spanning a larger range but still in agreement with [16]. Interestingly, the observed $\delta^{56}\text{Fe}$ in the mineral separates (~ 4.0 to ~ 9.5 for $\delta^{56}\text{Fe}$) span a range that is both considerably larger and isotopically heavier than the bulk CAIs (see Fig. 1). The heavy $\delta^{56}\text{Fe}$ of the mineral separates is most easily explained by initial condensation of isotopically light Fe from a nebular gas followed by extensive evaporation of Fe, driving it isotopically heavy. No variations for the mineral separates are observed outside analytical uncertainty for $\epsilon^{58}\text{Fe}$. Previous work on bulk CAI Egg-2 reported an $\epsilon^{58}\text{Fe}$ of ~ 30 [9]; however, none of the mineral separates from our study reproduce that anomaly regardless of the internal normalization ratio. However, the mineral separates display varying excesses in their $\epsilon^{56}\text{Fe}$ composition that correlate with $\delta^{56}\text{Fe}$ (Fig. 1).

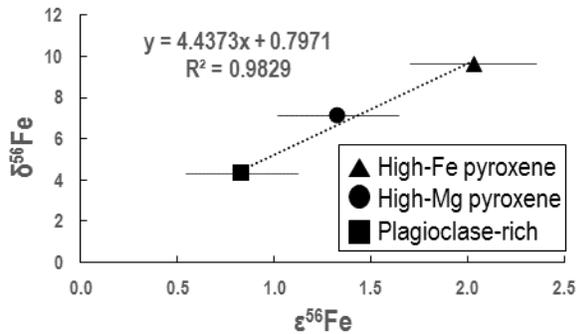


Fig. 1 – The Fe isotopic composition of the Egg-2 mineral separates. The y-axis shows the mass dependent variation ($\delta^{56}\text{Fe}$), or deviation from the terrestrial standard (IRMM-014) in parts per thousand. The nucleosynthetic variations ($\epsilon^{56}\text{Fe}$) are displayed on the x-axis in ϵ -notation, or parts per ten thousand.

Since the mineral separation was done by magnetic susceptibility, the high-Fe pyroxene is more likely to contain the most original Fe while Fe from secondary processes is more likely to be incorporated into less magnetic phases such as the plagioclase-rich fraction. The linear correlation observed in Fig. 1 most likely represents mixing between the original condensed Fe indigenous to the CAI (most closely represented by the high-Fe pyroxene phases) and later condensed secondary Fe (represented by terrestrial values which plot at zero).

Strontium and Titanium isotopes: Relative to the terrestrial standards, the mineral separates all have an ^{84}Sr excess spanning a range of $1.1\text{--}1.6 \pm 0.5 \epsilon^{84}\text{Sr}$. These values agree within analytical uncertainty to each other and also to most bulk CAI Sr data [e.g., 2-3]. Interestingly, the mineral separates have varying $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (most likely due to the decay of ^{87}Rb to ^{87}Sr) that are shown in Fig. 2. However, the mineral separates also display varying excesses in $\epsilon^{50}\text{Ti}$ (Fig. 2). Most bulk CAIs typically show $\epsilon^{50}\text{Ti} \sim 9.4$ [e.g., 6], while the mineral separates range from $7.2\text{--}10.5 \epsilon^{50}\text{Ti}$.

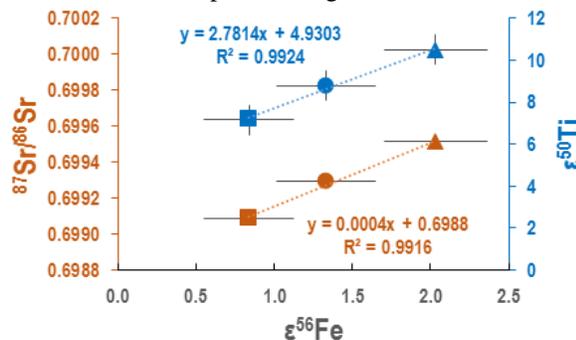


Fig. 2 – The $^{87}\text{Sr}/^{86}\text{Sr}$ plotted against $\epsilon^{56}\text{Fe}$ (shown in orange) along with the $\epsilon^{50}\text{Ti}$ plotted against $\epsilon^{56}\text{Fe}$ (shown in blue). Symbols are consistent with Fig. 1.

The correlated $^{87}\text{Sr}/^{86}\text{Sr}$ and $\epsilon^{56}\text{Fe}$ suggests that the high-Fe pyroxene incorporated the most Rb compared to the other mineral separates. A strong correlation is also observed between $\epsilon^{50}\text{Ti}$ and $\epsilon^{56}\text{Fe}$. All of these above-mentioned correlations are likely representative of a two-component mix between 1) high values of $\delta^{56}\text{Fe}$, $\epsilon^{56}\text{Fe}$, Rb ($^{87}\text{Sr}/^{86}\text{Sr}$), and $\epsilon^{50}\text{Ti}$ with 2) lower values that are closer to and/or resemble terrestrial compositions. On the contrary, these separates still contain indistinguishable nucleosynthetic $\epsilon^{84}\text{Sr}$ anomalies similar to the measured U isotopic composition in the mineral separates that showed no variation outside analytical uncertainty [11]. However, it is possible that nucleosynthetic variations exist in $\epsilon^{84}\text{Sr}$ but are not observed at the current level of precision. The combined Sr, Ti, and Fe isotopic compositions of the mineral separates suggests some mixing in components of CAIs, although how and what these components mixed with remains unclear. One possible scenario is that original components in CAIs mixed with objects that have isotopic compositions similar to or resembling terrestrial values.

Conclusions: Bulk CAIs show no Fe nucleosynthetic variations but have varying mass dependent ($\delta^{56}\text{Fe}$) compositions that likely stem from fractionation during condensation and subsequent evaporation. However, three mineral separates from the Allende CAI Egg-2 show both $\epsilon^{56}\text{Fe}$ and $\delta^{56}\text{Fe}$ variations along with variability in their $\epsilon^{50}\text{Ti}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. A strong correlation between the $\delta^{56}\text{Fe}$, $\epsilon^{56}\text{Fe}$, Rb ($^{87}\text{Sr}/^{86}\text{Sr}$), and $\epsilon^{50}\text{Ti}$ suggests mixing between an early formed (possibly original) component of a CAI and a later formed solid, potentially of average Solar System composition.

References: [1] Burkhardt et al. (2011) *EPSL*, 312, 390. [2] Brennecka et al. (2013) *PNAS*, 110, 17241. [3] Shollenberger et al. (2015) *LPSC*, 46, #2593. [4] Mercer et al. (2015) *LPSC*, 46, #2920. [5] Mane et al. (2014) *LPSC*, 45, #1685. [6] Trinquier et al. (2009) *Science*, 324, 374. [7] Simon et al. (2016) *LPSC*, 47, #1397. [8] Birck & Lugmair (1988) *EPSL*, 90, 131. [9] Völkening & Papanastassiou (1989) *ApJ*, 347, L43. [10] Dauphas & Schauble (2016) *Annu. Rev. Earth Planet. Sci.*, 44, 709. [11] Brennecka & Wadhwa (2011) *MetSoc 2011*, #5030. [12] Schuth et al. (2015) *Chem. Geol.*, 392, 74. [13] Zhang et al. (2011) *JAAS*, 26, 2197. [14] Berglund & Wieser (2011) *Pure Appl. Chem.*, 83, 397. [15] Dauphas et al. (2004) *Anal. Chem.*, 76, 5855. [16] Hezel et al. (2008) *LPSC*, 39, #1603.