RENEWED SEARCH FOR FUN BASED ON Al-Mg SYSTEMATICS IN CAIs WITH LA-MC-ICP-MS: J. B Wimpenny[1], Q.-Z. Yin[1], J. Zipfel[2] G. MacPherson[3], D. S. Ebel[4], and P. R. Heck[5], [1]Department of Earth and Planetary Sciences, University of California, One Shields Avenue, Davis, CA 95616 (jbwimpenny@ucdavis.edu) [2]Senkenberg Museum, 60325 Frankfurt, Germany, [3]Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, Washington, DC 20560. [4]Dept. of Earth and Planetary Sciences, American Museum of Natural History, New York, NY 10024, [5]Robert A. Pritzker Center for Meteoritics and Polar Studies, Field Museum of Natural History, Chicago, IL 60605.

Introduction: Calcium-, aluminum-rich inclusions (CAIs) provide a unique record of the earliest processes and conditions in the solar system [e.g. 1, 2]. A small number of CAIs contain fractionated and unidentified nuclear anomalies (FUN); these FUN CAIs have mostly been found in CV chondrites [e.g. 3, 4]. Nuclear anomalies have been observed in many elements including Ti, Ca, and Sr [5-8], while large mass dependent fractionations have been observed in the isotopic composition of O, Si and Mg [4, 9]. These FUN CAIs were once thought to show little evidence for the former presence of ^{26}Al [e.g. 6, 10], suggesting that they either formed prior to the injection of ^{26}Al into the protoplanetary disc or that the ^{26}Al had not yet been homogenised. However, a wide range of initial ^{26}Al levels discovered in FUN CAIs now challenges this notion of formation prior to injection of ^{26}Al [11]. Further study of these rare objects would provide important new constraints regarding the age of the solar system, while also potentially providing new information about the timing of injection and distribution of short lived radioisotopes in the early solar system.

The limiting factor in further studies of FUN CAIs is sample size. Many of the first found FUN CAIs were consumed during analyses by TIMS, and little or nothing of these original samples remain. Recently, two new FUN CAIs have been found; STP-1 [10] and CMS-1 [12, 13], both in Allende (CV3). Both have been subject to isotopic analyses (e.g. O, Al-Mg, Hf-W [10, 12]), but neither have been dated by U-Pb for absolute ages. Clearly we require more FUN CAIs to be found in order to build a more representative sample population so that a wider range of analyses can be performed.

To this end we have undertaken a systematic search for FUN CAIs, building on previous work [14] and utilizing the Mg isotope system as a way to quickly and efficiently identify highly fractionated objects by LA-MC-ICP-MS. Modern analytical methods allow acquisition of Mg isotope data by laser ablation with precision on δ^{25}Mg ranging from 0.05-0.3‰, depending on the signal intensity. While this level of uncertainty is an order of magnitude greater than what would be expected for solution analysis it is still far smaller than the observed fractionation effects for FUN CAIs (>20‰ per a.m.u.). In this study we present the results of a new search for FUN CAIs, including CAIs which might have highly positive or highly negative mass dependent Mg isotope fractionations.

Methods: Mg isotopes and Al/Mg ratios were collected using a Thermo Fisher Scientific *Neptune Plus* MC-ICP-MS connected to a PhotonMachines *Analyte* 193 nm excimer laser ablation system. Collectors are aligned to allow for simultaneous acquisition of all isotopes in static multi-collection mode using 10^{11} Ω resistors: ^{24}Mg (L4), ^{25}Mg (L1), ^{26}Mg (H1), and ^{27}Al (H4) without dispersion or magnet jumps. A laser spot size of 20-40 μm was used for all analyses. The 6 Hz laser was operated at 5 mJ energy and a fluence of 1.2 J cm^{-2}. Data were collected in medium resolution (mass resolving power ~4000) to avoid the small (< 5 mV) ^{12}C^{14}N interference on the side of the ^{26}Mg peak. Data were corrected for mass bias and instrument drift by standard-sample bracketing with San Carlos olivine, assuming linear drift between successive analyses. The data are presented in delta notation:

$$\delta^{x}\text{Mg} = [(^{x}\text{Mg}/^{24}\text{Mg})_{smpl}/(^{x}\text{Mg}/^{24}\text{Mg})_{SC\text{-}Ol} - 1] \times 1000,$$

where ^{x}Mg is either ^{25}Mg or ^{26}Mg. Excess ^{26}Mg (^{26}Mg*) due to ^{26}Al decay is calculated using:

$$\delta^{26}\text{Mg}^{*} = [(1+\delta^{26}\text{Mg}/10^{3})/(1+\delta^{25}\text{Mg}/10^{3})^{(1/0.511)} - 1] \times 10^{3}$$

^{27}Al/^{24}Mg ratios were corrected for instrumental mass bias and laser-induced elemental fractionation by standard-sample bracketing to MPI-DING GOR128 (assuming ^{27}Al/^{24}Mg = 0.381; [15]). Typical internal errors were 0.17‰ for δ^{25}Mg, and 0.20‰ for δ^{26}Mg*.

Results: Over a one month period a total of 365 Al-Mg analyses were made of CAIs in slabs of the CV chondrite Allende that were borrowed from the American Museum of Natural History (AMNH), the Smithsonian National Museum of Natural History and the Senkenberg Museum in Frankfurt. The majority, 316 analyses, had δ^{25}Mg values between -3 and 3‰. The remaining 49 analyses spanned a range in δ^{25}Mg from -11.51 to 17.64‰, that is approximately 28‰ per a.m.u.

If the radiogenic δ^{26}Mg* value is plotted vs. the ^{27}Al/^{24}Mg ratio the data lie on an array corresponding to an initial ^{26}Al/^{27}Al ratio of (5.85 ± 0.26) × 10^{-5} (Fig 1). This is similar to, though slightly higher than, the canonical ratio of 5.23 × 10^{-5} [1, 2, 16], but consistent with the results of previous studies of CAIs in CV chondrites by laser ablation [14, 17].

Discussion and Conclusions: The traditional view of a FUN CAI is that it has a highly fractionated Mg isotopic composition (>20 ‰ per amu) and no radiogenic excess in ^{26}Mg (i.e., ^{26}Al/^{27}Al of $<5\times10^{-6}$). By this definition most of the CAIs in our study so far are not FUN as the CAIs with large isotopic fractionations also have resolvable excesses in ^{26}Mg (Fig 2). However, the traditional (old) definition of FUN CAIs may be obsolete. Recent Mg isotope analyses in distinct phases from FUN CAIs by ion microprobe show a range of mass dependent fractionation (f_{Mg}) from 4 to 40‰ per a.m.u., and a range of initial ^{26}Al/^{27}Al ratios from $\sim3\times10^{-6}$ to within error of canonical [11]. The most fractionated objects in our study have Al-Mg systematics that are consistent with these FUN CAIs. Three CAIs from Smithsonian slabs 24, 25 and 27 have f_{Mg} values of 17.6, 15.6 and 13.9‰ per a.m.u. respectively and so based on the data of [11] require further study. In particular it will be important to search for a nuclear anomaly in the isotopic composition of elements such as Ti and Si. These measurements can be performed in situ by LA-MC-ICP-MS, as used in the identification of CMS-1 [12].

As well as considering the magnitude of f_{Mg} it is interesting to compare the range of f_{Mg} values within single CAIs. In most previously studied CAIs this range is narrow, for example in Allende CAIs Egg-3 and A43 the range is less than 0.5‰ per a.m.u. [1, 2]. We see similar results, for example multiple analyses of CAI #14 from AMNH 4884 give a limited range of f_{Mg} values from 11.5 to 12.6‰ per a.m.u. In contrast, a small number of recent studies have observed a large range of f_{Mg} values (~11-14‰) within single CAIs [11, 18]. Park et al. [11] observe this in 2 FUN inclusions that have initial ^{26}Al/^{27}Al ratios of $\sim3\times10^{-6}$, Sapah et al. [18] observe this in a CAI from NWA 4502 with a canonical ^{26}Al/^{27}Al ratio. In our study, CAI #93 from Smithsonian slab 27 contains f_{Mg} values between 0.7-13.9‰ per a.m.u. This CAI also contains an excess in ^{26}Mg that roughly corresponds to increasing Al/Mg ratio, with an initial ^{26}Al/^{27}Al ratio of approximately 2-5 × 10^{-5}. The diverse range of f_{Mg} within single CAIs and the diversity in initial ^{26}Al/^{27}Al ratios offers a unique opportunity to study the results of isotopic fractionation associated with evaporation.

In summary, our study, together with other recent work, shows that Al-Mg systematics in CAIs and FUN CAIs are widely variable. This is true both in their initial ^{26}Al/^{27}Al ratios and in the extent of f_{Mg}, which varies even in FUN CAIs. Furthermore it is clear that some CAIs have large internal variations in f_{Mg}. Identifying more FUN CAIs will be an important step both in shedding light on the behavior of the Al-Mg system, but also lending crucial insights to our understanding of early solar system processes and chronology, and the precursor materials to emerging planets.

References: [1] Jacobsen et al. 2008, *EPSL*, *272*, 353-374. [2] Wasserburg et al. 2012, *MAPS*, *47*, 1980-1997. [3] Wasserburg et al. 1977, *GRL*, *4*, 299-302. [4] Clayton et al. 1984, *GCA*, 535-545. [5] Lee et al. 1978, *ApJ*, *220*, 21-25. [6] Lee et al. 1979, *ApJ*, *228*, 93-98. [7] Niederer et al. 1981, *GCA*, 45, 1017-1031. [8] Papanastassiou & Wasserburg, 1978, *GRL*, *5*, 595-598. [9] Clayton et al. 1987, 18th LPSC, 185. [10] Holst et al. 2013, *PNAS*, *110*, 8819-8823. [11] Park et al. 2013, *75th MetSoc.* #5085. [12] Williams et al. 2012, 75th MetSoc. #5102, [13] Williams et al. 2013, 44th LPSC, #2435. [14] Tollstrup et al. 2011, 42nd LPSC, # 2216. [15] Jochum et al. 2006, *G3*, 7, 2, doi:10.1029/ 2005GC001060. [16] Larsen et al. 2011, *ApJ*, 735, L37. [17] Young et al. 2005, *Science*, 308, 223-227. [18] Sapah et al. 2013, 76th MetSoc. #5156.

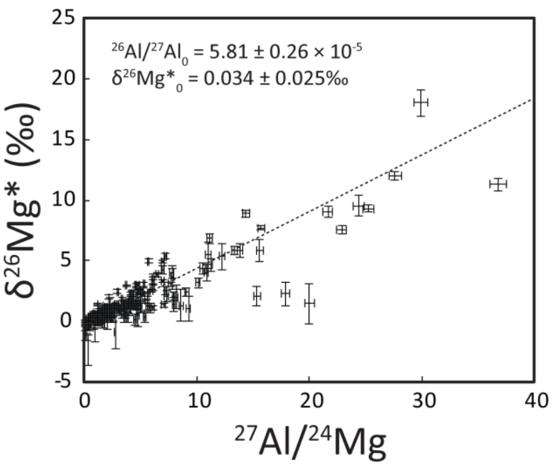

Fig. 1 – Plot of Al-Mg systematics for CAIs in rock slabs from the CV chondrite Allende. Each datum is shown as a 2σ error cross in all figures.

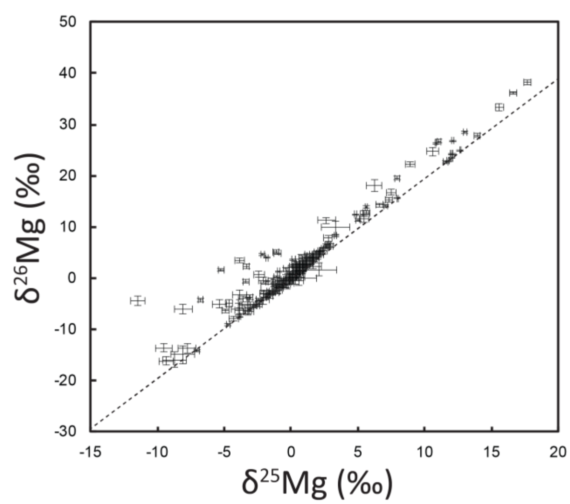

Fig. 2 – Stable Mg isotope data for CAIs in rock slabs from the CV chondrite Allende.