Mg ISOTOPES IN MELILITE, FASSAITE AND SPINELS IN CAIs: EVIDENCE FOR EVAPORATION, EQUILIBRATION AND LATE STAGE ALTERATION.

R.D. Ash[1,2,3], S.S. Russell[2], N.C. Belshaw[3], E.D. Young[1], M. Gounelle[2] and. 1. IGPP, UCLA Los Angeles, California 90095-1567, USA. 2. Department of Mineralogy, The Natural History Museum, Cromwell Rd, London, SW7 5BD, UK. 3. Department of Earth Sciences, University of Oxford, Parks Rd, Oxford OX1 3PR, UK. (rash@ess.ucla.edu)

Introduction: Calcium- Aluminium-rich Inclusions (CAI) are the earliest solids formed in the solar system. They probably formed and evolved by condensation, melting and evaporation [1], with modification by nebular and/or parent body processes. Aspects of each of these processes may be addressed by the study of Mg isotopes, through isotope fractionation processes and the decay of ^{26}Al to ^{26}Mg. Due to technical limitations of the ion microprobe technique there are limited data available for the degree of Mg isotope fractionation, and reported values are generally confined to TIMS analyses, hence are bulk values and yield no information on internal isotope distribution within the CAI. However ion microprobe measurements have provided great insight into the Al-Mg chronology of CAIs, but are limited to minerals with high Al/Mg [2]. Since the major constituent minerals of the majority of CAI are melilite, fassite (Ti-rich pyroxene) and spinel, applications of the Al-Mg method have generally relied upon the analysis of minor, primary accessory phases, such as gehlenitic melilite, anorthite and grossite, and secondary phases such as nepheline and sodalite.

Herein we have used laser ablation MC-ICP-MS which enables the *in situ*, high precision measurement of Mg isotope ratios, and the determination of Al-Mg ratios on mineralogically characterised materials. The direct comparison of Mg isotope ratios with those in standards enables isotope fractionation to be determined and the high precision of the isotope ratios allows the measurement of Al-Mg ages on the abundant low Al/Mg (<10) minerals melilite, spinel and fassaite. Conversely the instrumental requirements are such that Mg in high Al/Mg phases cannot be reliably determined.

Samples and methods: Leoville MRS-6 is a Type B CAI, approximately 30x10mm. It comprises a central region (*ca.* one third the diameter) of intergrown melilite (Ak4-55), Al-rich diopside (Al_2O_3 16-23%, TiO_2 2-11%) and less abundant anorthite (An 98.8-99.6). These phases enclose abundant spinel crystals, typically 1-15µm. This central region is entirely surrounded by a melilite-rich mantle devoid of diopside and anorthite and with only minor small spinel grains. The inclusion is rimmed by a *ca.* 10µm layer of spinel, surrounded by Ti-Al-rich diopside, zoned to more Al-rich toward the outside. The CAI is very pristine; the only secondary minerals present are rare calcium carbonate grains and a rare sub-micron Na-rich phase.

A slab of the CAI was mounted and polished. Mineralogy and textures of the CAIs and chondrules were obtained by SEM and electron microprobe. For Mg isotope ratio determination samples were ablated into a He stream using an ArF excimer laser (193nm) by rastering a 25µm - 35µm beam to produce a 60-100µm, *ca.*5µm deep pit. Mg isotopes and Al/Mg ratios were measured using a Nu Instruments MC-ICP-MS; Na, Ca, Fe abundances were also monitored.
All magnesium isotope ratios are given in per mil (‰) relative to the SRM-980 international magnesium isotope standard (Mg metal which appears to be isotopically light compared with geological samples). Solutions of internal laboratory standards were directly compared with SRM-980 solutions. Analyses of these materials by laser ablation enabled the direct standard-sample-standard comparisons to be made during sample measurement. The errors were determined by the repeated measurement of internal standards. Comparisons of the elemental abundances, determined by electron probe, of two augites, melilite, spinel, cordierite and pyrope, with those measured by LA-ICPMS show that the Al/Mg is reproducible to within 3%. We use δ^{25}Mg and δ^{26}Mg in the same way as other stable isotope systems and Δ^{26}Mg* to denote the excess ^{26}Mg derived from the decay of ^{26}Al assuming the fractionation of ^{25}Mg is related to that of ^{26}Mg by a factor of 0.52 [3].

The precision for δ^{25}Mg and δ^{26}Mg were determined by repeat analysis of standards and give a range of ±0.8‰. The range in Δ^{26}Mg* for these samples is ±1‰.

Results: Mg isotope results for the Leoville MRS-6 are shown in Figure 1. These are compared with results from an Allende Type B CAI and an Allende Type A CAI. Most of the CAI has a uniform δ^{25}Mg of +7.6‰. However there are significant deviations for Mg derived from the outermost 100µm of the CAI. Data from this outer portion of the CAI lie on a fractionation line running through the chondrules, matrix and isolated matrix olivines of Leoville and Allende. Looking at these data on an Al-Mg evolution diagram (Fig. 2) it can be seen that analyses from the core of the CAI, those with the uniform δ^{25}Mg, show evidence for having contained "live" ^{26}Al material, consistent with an initial ^{26}Al/^{27}Al of $5x10^{-5}$. Data from the material lying on the fractionation line show no evidence for the presence of live ^{26}Al.

Discussion: The majority of Solar System materials have a limited range in Mg isotopes, with Mars, Earth, bulk chondrites and achondrites having similar ^{25}Mg values of *ca.* +1.6‰ [4]. In contrast Leoville MRS-6 has a δ^{26}Mg of +7.6‰, consistent with evaporative loss of Mg from an initially chondritic melt. That the spinel, fassaite and melilite have identical δ^{25}Mg values implies that there was no significant evaporation during crystallisation. It has been demonstrated that evaporation from a melt in a low pressure environment leads to Rayleigh isotope fractionation for Mg [5]. However in MRS-6 the isotope and chemical data are irreconcilable for simple evaporative fractionation.

The lack of ^{26}Mg* in the outermost 80-100µm of the inclusion show that open system re-equilibration of Leoville MRS-6 took place after ^{26}Al decay. The narrow margin of resetting indicates that the event was brief, but intense enough to reset, but not melt, the outermost 100µm. The presence of an evaporative rim on the CAI shows that the CAI was briefly after the initial igneous crystallisation. This may have been the same event which reset the Al-Mg systematics, if so then it occurred after ^{26}Al decay, thereby divorcing rim formation from the CAI forming process.

Conclusions: The major minerals in CAIs have an initial ^{26}Al/^{27}Al consistent with that observed for minor high Al/Mg minerals. Fractionation of Mg isotopes occurred before igneous crystallisation of the CAI. These observations are consistent with the formation of CAIs by condensation as "fluffy" Type I CAIs which were soon melted and evaporated in a low pressure environment, as evinced by the fractionated Mg isotopes and the presence of live ^{26}Al during melting with the canonical Solar System initial ^{26}Al/^{27}Al value. Re-melting of the outermost portions of the CAI after the complete decay of ^{26}Mg in an environment with a high pressure of Mg resulted in exchange with the CAI, thereby obliterating any signature of live ^{26}Al.

The heating producing the evaporation rim and the resetting of the Al-Mg of the margins of the CAI was brief as evinced by the fact that the core of the CAI remains unaffected. This, in turn, indicates a nebula rather than parent body phenomenon for the re-heating. Hence a phase of CAI nebula heating took place after the complete decay of ^{26}Al had occurred. Thus the source of heating for any ice melting, water circulation and hydration/dehydration cannot have been from the decay of ^{26}Al, unless there was a post alteration nebula modification phase in the evolution of carbonaceous chondrites.

References: [1] Grossman et al., (2000) *GCA* **64**, 2879-2894. [2] MacPherson *et al.*, (1995) *Meteoritics* **30**, 365. [3] Galy *et al.*, (2000) *Science* **290**, 1751 [4] Galy & O'Nions (2000) *J. Conf. Abstr. (Goldschmidt 2000)* **5**, 424. [5] Wang *et al.* (2001) *GCA* **65**, 479.