MAGNESIUM AND OXYGEN ISOTOPIC STUDY OF THE WARK-LOVERING RIM AROUND A FLUFFY TYPE-A INCLUSION FROM ALLENDE. M. Cosarinsky\textsuperscript{1}, K. D. McKeegan\textsuperscript{1}, I. D. Hutcheon\textsuperscript{2}, P. Weber\textsuperscript{3} and S. Fallon\textsuperscript{2}, \textsuperscript{1}Dept. of Earth & Space Sciences, University of California Los Angeles, Los Angeles, CA - 90095-1567; \textsuperscript{2}Chemical Biology & Nuclear Science Division, Lawrence Livermore National Laboratory, Livermore, CA - 94551-0808. mariana@ess.ucla.edu

\textbf{Introduction:} The abundance of $^{26}$Al in chondritic materials in principle permits a determination of the relative timing of events that occurred during the early stages of solar system formation \cite{1}. In particular, Ca-Al-rich inclusions (CAIs) from CV chondrites experienced complex histories and many suffered flash thermal events that resulted in the formation of Wark-Lovering rims (WLRs) or sequences of thin layers, each composed of a single mineral phase \cite{2}. The timing of these high temperature processes is important for understanding CAI formation and thermal structures in the nebula, but is relatively poorly constrained by data. High-precision results obtained by ion microprobe on an Efremovka inclusion suggest a time difference of $\sim$0.5 My between the formation of the CAI and the WLR \cite{3}. However, the difficulty to obtain high-precision analyses on single phases represents a major challenge because of the relatively large beam size compared to the target phases. A promising approach to obtain both high-precision and high-spatial resolution results is to perform multiple collector analyses on low Al/Mg minerals with the ims 1270 ion microprobe combined with NanoSIMS analyses on high Al/Mg phases in the same objects. The goals of this study are to determine the primary $^{26}$Al/$^{27}$Al at the time of CAI formation, and the timing and nature of WLR formation. Additionally, Mg and O isotope mass fractionations among WLR layers and CAI phases will provide further constraints on the processes involved in the evolution of refractory materials in the early solar system and the gaseous reservoirs with which they interacted. Here we report preliminary data on a type-A CAI from Allende.

\textbf{Petrography:} Allende TS25F1 is a large (15 x 5 mm) and oblong fluffy type-A CAI consisting of large, reversely zoned melilite ($\text{Ak} \sim 30$ in the core to $\text{Ak} \sim 10$ near the rim) crystals with inclusions of spinel, hibonite, and perovskite. Spinel occurs as euhedral grains, 10-15 $\mu$m in size, sometimes grouped in clusters. Hibonite occurs as smaller ($<10 \mu$m) laths, mostly concentrated near the WLR. Perovskite grains are rounded and very small ($<5 \mu$m). Alteration minerals are abundant in this inclusion and include nepheline, anorthite, grossular, sodalite, and wollastonite. A well-developed and continuous WLR surrounds the inclusion. It consists of a sequence of thin layers of relatively constant thickness (Fig. 1): (1) an innermost layer (10 to 50 $\mu$m thick) of spinel intergrown with minor euhedral hibonite and perovskite grains; (2) a thin ($<10 \mu$m) layer of melilite ($\text{Ak}\sim 10$), most of which is altered to anorthite; and (3) an outer layer (10 to 15 $\mu$m) of pyroxene of fassaitic composition that progressively becomes more Al-diopside-rich outwards. Over the WLR, there is a continuous accretionary rim composed of an inner layer of forsteritic olivine and an outer layer of fayalitic olivine similar to the matrix \cite{4,5}.

\textbf{Isotopic Analyses:} Several phases from the WLR and the interior CAI were analyzed by ion microprobe techniques to determine O and Mg isotopic compositions.

\textbf{Magnesium.} The Mg isotopic composition of WLR spinel and pyroxene and interior CAI spinel and melilite were measured with the Cameca ims 1270 ion microprobe at UCLA (multicollection mode; spot diameter of $\sim$50 $\mu$m). All phases but pyroxene show resolvable excess $^{26}$Mg*. In the case of melilite, this excess does not correlate with Al/Mg, most likely as a result of isotopic redistribution during alteration. Interior and rim phases seem to define distinct isotopic systems, with higher $\Delta^{26}$Mg* values for spinel from the CAI core than for rim spinel (Fig. 2). However, isochrons are difficult to obtain because rim pyroxene shows no $^{26}$Mg* and melilite is disturbed by secondary alteration. Forcing the isochrons through the origin, spinel grains from each petrographic setting yield different slopes, corresponding to an initial $^{26}$Al/$^{27}$Al = \((7.25\pm0.74) \times 10^{-5}\) for the interior CAI and \((4.32\pm0.85) \times 10^{-5}\) for the WLR. In terms of Mg mass fractionation, the WLR phases are normal ($^{25}$Mg $\sim$ 0 $\%_e$) and more than 10 $\%_e$/amu lighter than interior spinel.

Mg isotopes were also measured on spinel and hibonite grains from the core and spinel from the rim of TS25F1 with the Cameca NanoSIMS at LLNL (multicollection mode; rastered area of 5 $\mu$m). Interior phases, mostly hibonite, define an isochron with a slope that yields \((^{26}\text{Al}/^{27}\text{Al})_0 = (7.08\pm0.95) \times 10^{-5}\) for the interior CAI and \((4.32\pm0.85) \times 10^{-5}\) for the WLR. In terms of Mg mass fractionation, the WLR phases are normal ($^{25}$Mg $\sim$ 0 $\%_e$) and more than 10 $\%_e$/amu lighter than interior spinel.
Oxygen. O isotopes were also measured on spinel, pyroxene, melilitic and melilite alteration (anorthite) from the WLR with the UCLA ins 1270 ion microprobe by peak jumping (monocollection mode; spot size ~15 µm). All data spread along the CCAM line and show a strong mineralogical control (Fig. 3): spinel is the most $^{18}$O-rich ($\delta^{18}$O = $\delta^{17}$O ~ –45 ‰), pyroxene is slightly $^{18}$O-depleted ($\delta^{18}$O = $\delta^{17}$O ~ –35 ‰), and anorthite and melilite are $^{18}$O-poor ($\delta^{18}$O = $\delta^{17}$O ~ –10 and 0 ‰, respectively).

Discussion: The two analytical techniques used yield consistent high ($^{26}$Al/$^{27}$Al)$_0$ values for the interior CAI phases, higher than the "canonical" value and in agreement with recent high-precision data in bulk CV CAIs [6]. WLR formation apparently postdated CAI formation by ~0.6 My. In terms of Mg mass fractionation, most of the inclusion phases are isotopically similar to the WLR phases and have nearly normal compositions. It is possible that some interior spinels that are isotopically heavier represent relict grains. Rim phases are mostly $^{16}$O-rich and probably formed from the same O reservoir as CAIs [7]. It is likely that WLR melilite and pyroxene exchanged O to variable extents with a heavier reservoir during alteration of the inclusion, after the formation of the WLR and accretionary rim [5].


Fig. 1 BSE image of a portion of the Allende TS25F1 inclusion composed of melilite (mel), spinel (sp), hibonite (hib) and perovskite (pv). The WLR sequence consists of spinel+hibonite, melilite partially altered to anorthite (an), and pyroxene (px), mostly Al-rich diopside.

Fig. 2 Al/Mg evolution diagrams for phases from (a) the CAI interior and (b) from the WLR.

Fig. 3 O isotopic compositions of WLR phases. Reference lines are the terrestrial fractionation (TFL) and to the carbonaceous chondrites anhydrous mineral (CCAM) lines.