^{36}Cl-^{36}S SYSTEMATICS IN *CURIOUS MARIE*: A ^{26}Mg-RICH U-DEPLETED FINE-GRAINED CAI FROM ALLENDE. H. Tang[1], M-C. Liu[1], K.D. McKeegan[1], F.L.H. Tissot[2,3] and N. Dauphas[2], [1]Ion Probe Group, Department of Earth, Planetary, and Space Sciences, UCLA; [2] Origins Lab, Department of the Geophysical Sciences and Enrico Fermi Institute, the University of Chicago; [3]Department of the Earth, Atmospheric and Planetary Sciences, MIT, Cambridge. (haolantang@ucla.edu).

Introduction: Chlorine-36 ($t_{1/2}$=0.3 Myr) decays to either ^{36}Ar (98%, β^-) or ^{36}S (1.9%, ε and β^+). This radionuclide can be produced either by local irradiation of gas and/or dust of solar composition [1-2] or by stellar nucleosynthesis in AGB stars or Type II supernovae [3]. Evidence for the presence of ^{36}Cl in the early Solar System (ESS) comes from radiogenic excesses of ^{36}Ar [4] and/or ^{36}S [5-9] in secondary phases (*e.g.*, sodalite and wadalite) in ESS materials such as Calcium, Aluminum-rich inclusions (CAIs) and chondrules. Though the presence of ^{36}Cl in the ESS has been demonstrated, the inferred initial ^{36}Cl/^{35}Cl ratios vary a lot (from 1.0×10^{-7} to 2×10^{-5}) from one inclusion to another [5-9]. Interestingly, all secondary phases measured so far lack resolvable ^{26}Mg excesses that could be due to the decay of ^{26}Al ($t_{1/2}$ = 0.7 Myr), implying that ^{36}Cl and ^{26}Al may not have been derived from the same source. Given that ^{26}Al could have come from a stellar source [10] and that secondary phases should have formed late, we are left with either a very high ^{36}Cl/^{35}Cl initial ratio ($\sim 10^{-2}$) in the ESS, or a late (> 3 Myr after CAI formation) irradiation scenario for the production of ^{36}Cl [9]. ^{36}Cl/^{35}Cl $\sim 10^{-2}$ far exceeds the predictions from any model (stellar nucleosynthesis or irradiation); therefore, a late irradiation scenario producing ^{36}Cl at the observed level is favored. In this framework, ^{36}Cl is produced in the early solar nebula and incorporated into CAIs via aqueous activities, which could also lead to the formation of sodalite.

The Allende *Curious Marie* fine-grained (non-FUN) CAI is a special sample. It is characterized by an extremely large ^{235}U excess (δ^{235}U $\sim$59 ‰ rel. to CRM-112a) [11], providing strong evidence that ^{247}Cm was alive in the ESS, as previously suggested by [12]. This CAI lacks primary refractory phases, but instead contains a wide distribution of chlorine-rich phases (sodalite and nepheline), which are characterized by large, yet uniform, ^{26}Mg excesses (δ^{26}Mg*) of $\sim$43‰ over a large range of ^{27}Al/^{24}Mg values [Fig 1A; 13]. This observation contrasts largely with previous findings and implies that ^{26}Al could have still been alive when sodalite formed, and the homogeneous δ^{26}Mg* found in all spots measured could have resulted from later closed-system resetting [13]. Therefore, this CAI offers an excellent opportunity to investigate the relationship between ^{26}Al and ^{36}Cl, as well as the evolution of this strange CAI. We performed isotopic analysis for the ^{36}Cl-^{36}S systematics, and the preliminary results are reported here.

Method: Secondary minerals such as nepheline, sodalite, Fe-rich pyroxene, and Fe-rich spinel were observed in *Curious Marie*. Analyses for the Cl-S system were performed on the new Cameca ims-1290 ion probe in UCLA. Sulfur isotopes (^{33}S, ^{34}S, and ^{36}S) as well as chlorine isotopes (^{35}Cl and ^{37}Cl) in sodalite were measured in a peak jumping mono-collection mode, with the mass sequence of 32.8, ^{33}S, ^{34}S, ^{35}Cl, ^{36}S and ^{37}Cl. Negative secondary ions were produced by a 0.6 nA Cs$^+$ primary ion beam focused to a <10 μm spot. A long pre-sputtering time was required (>20 mins) to minimize the surface S contamination. A mass resolving power of 5000 was used to resolve interferences from the peaks of interest. Besides, of special importance in the measurement of ^{36}S is the potential contribution from the scattered ions of ^{12}C$_3$ and ^{35}ClH, but this did not appear to be a problem under our analytical condition. The instrumental mass fractionation (IMF) was internally corrected by using standards of Balmat pyrite, Canyon Diablo troilite, CAR 123 pyrite, and NIST 610 glass. The transmission was decreased to avoid QSA effect (Quasi-Simultaneous Arrival) in pyrite and troilite standards and data were reduced from total counts. The excesses of ^{36}S were calculated by following a linear law with a mass fractionation exponent of -0.489 obtained from standards. In addition, a terrestrial sodalite (^{35}Cl/^{34}S = 15,000) was applied to verifying the validity of mass spectrometry. The relative sensitivity factor of ^{35}Cl/^{34}S ($\sim$0.93) used throughout this study was determined from NIST 610 glass (Cl/S=1).

Results and discussion: Significant excesses in ^{36}S are clearly resolved in *Curious Marie* over a large range of ^{35}Cl/^{34}S values (from 500 to 20,000). However, the ^{36}S excesses are uniformly elevated, with a weighted average of 95±28‰ (2σ error, reduced χ^2 = 3), independent of the Cl/S ratio. Therefore, no isochron is observed and no initial ^{36}Cl/^{35}Cl ratio can be inferred for this CAI.

In our previous study we proposed that the presence of homogeneous δ^{26}Mg* to be 43±6‰ (2σ error, reduced χ^2 = 3) and negative δ^{25}Mg (from $\sim$-9‰ to -19‰) in *Curious Marie* indicates that Mg isotope exchange must have taken place in a closed system to avoid dilution with chondritic Mg [13]. Although the uniform ^{26}Mg excess independent of Al/Mg precludes the determination of an isochron, a model ^{26}Al/^{27}Al ratio = $(6.2\pm0.9)\times10^{-5}$ can still be inferred by using the bulk ^{27}Al/^{24}Mg ratio ($\sim$95, measured by solution ICPMS; [11]) and assuming δ^{26}Mg$_0$ = 0. This suggests

that either the secondary phases in the *Curious Marie* CAI formed while [26]Al was still at the canonical level, or the CAI remained intact until a late-alteration event, which took place after [26]Al had completely decayed away, homogenized the [26]Mg excesses and formed sodalite. The latter scenario would be less likely as the elevated uniform $\delta^{26}Mg*$ requires closed-system homogenization, contrary to the fact that the formation of sodalite requires an external Cl-rich fluid. Besides, the significant Mg loss resulted from this alteration can achieve a higher bulk [27]Al/[24]Mg ratio in this CAI relative to the normal range (~2-10) with the $\delta^{26}Mg*$ value similar to or lower than that in the primary mineral (<5‰). Therefore, we propose that alteration resulting in the formation of sodalite in *Curious Marie* must have taken place extremely early, probably right after the condensation of this CAI, so that the Cl-rich fluid involved in this process can wash Mg (and perhaps U) away without diluting $\delta^{26}Mg*$.
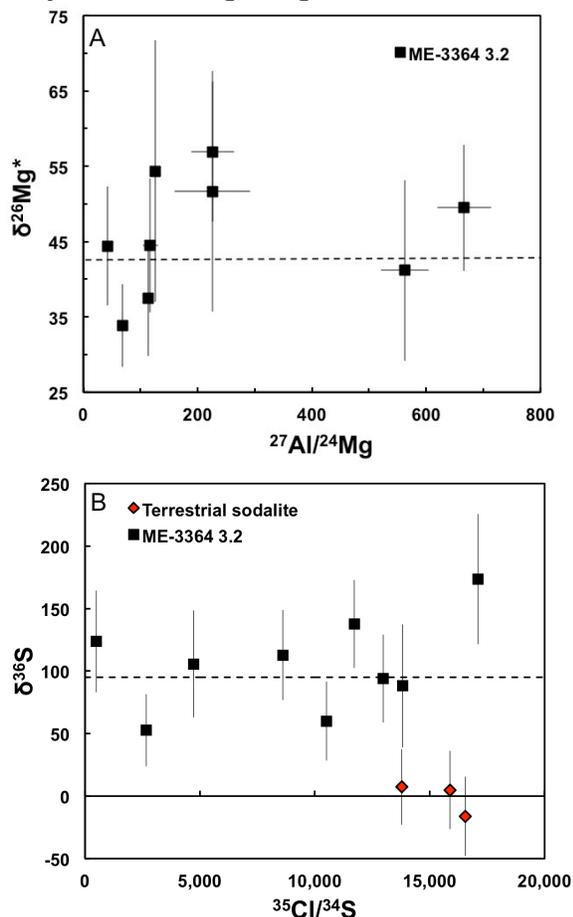

Fig. 1. (A) [26]Al-[26]Mg and (B) [36]Cl-[36]S systematics in Allende CAI *Curious Marie* (2σ error). The black dash line in A indicates the average $\delta^{26}Mg$ of ~43‰ in *Curious Marie*. The black dash line in (B) represents the average $\delta^{36}S$ of ~95‰.

The Cl-S result can also be understood in the context of the aforementioned alteration scenario. Although it is impossible to form an isochron, and thus an initial [36]Cl/[35]Cl ratio, based on the CAI's Cl-S isotopic results, the [36]S excesses in the sodalite would still require the presence of [36]Cl. This radionuclide can be introduced into the CAI via a Cl-rich fluid involved in the formation of secondary phases or be produced by late local irradiation on the sodalite. The former interpretation implies that [36]Cl was present in the early solar nebula at the time of CAI condensation, which would require that [36]Cl originated from a stellar source or early local irradiation. In the context of the latter explanation, [36]Cl would be produced in-situ inside sodalite by late irradiation, similar to the proposed scenarios in [5-9]. However, knowledge about the Cl and S elemental abundances is required to estimate the [36]Cl/[35]Cl production ratio for *Curious Marie*. The final event would be that both $\delta^{26}Mg$ and $\delta^{36}S$ were homogenized in the entire CAI in a closed system after the complete extinction of [26]Al and [36]Cl.

Conclusion: We find elevated and uniform excesses in [36]S, similar to those for [26]Mg excesses, in the U-depleted fine-grained CAI *Curious Marie*, implying a complicated multi-stage history. The CAI precursor condensed with the [26]Al/[27]Al canonical ratio and might have experienced an extremely early alteration process with a Cl-rich, Mg-free fluid to form the secondary phases including sodalites and nephelines. The presence of [36]S excesses can be interpreted as a decay product of [36]Cl, which was either introduced from a Cl-rich fluid in early alteration or produced through in situ local irradiation on the CAI after sodalite formed. Further studies of the Al-Mg and Cl-S systematics in other fine-grained CAIs are ongoing to investigate their condensation in the early solar nebula and alteration in the chondritic parent bodies as well as the origin of [36]Cl in different early-formed objects.

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