DISTRIBUTION AND ORIGIN OF ^{36}Cl IN ALLENDE CAIS. J.E.P. Matzel[1], B. Jacobsen[1] I.D. Hutcheon[1], A.N. Krot[2], K. Nagashima[2], Q.-Z. Yin[3], E.C. Ramon[1], P.K. Weber[1], and G.J. Wasserburg[4], [1]Lawrence Livermore National Lab, 7000 East Ave, Livermore, CA 94550, USA, matzel2@llnl.gov, [2]School of Ocean, Earth Science and Technology, Hawai'i Institute of Geophysics and Planetology, University of Hawai'i at Manoa, Honolulu, HI 96822, USA, [3]Department of Geology, University of California, Davis, CA 95616, USA, and [4]Lunatic Asylum, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA.

Introduction: The abundance of short-lived radionuclides (SLRs) in early solar system materials provide key information about their nucleosynthetic origin and can constrain the timing of early solar system events. Excesses of ^{36}S (^{36}S*) correlated with ^{35}Cl/^{34}S ratios provide direct evidence for *in situ* decay of ^{36}Cl ($\tau_{1/2} \sim 0.3$ Ma) and have been reported in sodalite ($Na_8Al_6Si_6O_{24}Cl_2$) and wadalite ($Ca_6Al_5Si_2O_{16}Cl_3$) in CAIs and chondrules from the Allende and Ningqiang CV carbonaceous chondrites [1-4]. While previous studies demonstrate unequivocally that ^{36}Cl was extant in the early solar system, no consensus on the origin or initial abundance of ^{36}Cl has emerged. Understanding the origin of ^{36}Cl, as well as the reported variation in the initial ^{36}Cl/^{35}Cl ratio, requires addressing *when, where and how* chlorine was incorporated into CAIs and chondrules. These factors are key to distinguishing between stellar nucleosynthesis or energetic particle irradiation for the origin of ^{36}Cl.

Wadalite is a chlorine-rich secondary mineral with structural and chemical affinities to grossular. The high chlorine (~12 wt%) and very low sulfur content (<<0.01 wt%) make wadalite ideal for studies of the ^{36}Cl-^{36}S system. Wadalite is present in Allende CAIs [5] exclusively in the interior regions either in veins crosscutting melilite or in zones between melilite and anorthite associated with intergrowths of grossular, monticellite, and wollastonite [6]. Wadalite and sodalite most likely resulted from open-system alteration of primary minerals with a chlorine-rich fluid phase [6].

We recently reported large ^{36}S* correlated with ^{35}Cl/^{34}S in wadalite in Allende Type B CAI AJEF, yielding a (^{36}Cl/^{35}Cl)$_0$ ratio of (1.7±0.3)×10^{-5} [4]. This value is the highest reported ^{36}Cl/^{35}Cl ratio and is ~5 times greater than values for sodalite in some CAIs and chondrules [1-3]. We report here new ^{36}Cl-^{36}S isotope measurements of wadalite in two Type B CAIs (TS34 and Egg-6) and sodalite in a fine-grained CAI (Pink Angel) from Allende.

Analytical Techniques: The ^{36}Cl-^{36}S isotope abundances were determined using the Lawrence Livermore National Laboratory *Cameca* NanoSIMS 50. An ~7 pA primary Cs$^+$ beam was rastered over areas between 4×4 μm^2 and 8×8 μm^2 in size to produce quantitative secondary ion images. Each ion image was subdivided into two or three regions based on the ^{37}Cl/^{34}S ratio. Negative secondary ions were acquired

in a combined peak jumping, multi-collection mode, simultaneously measuring ^{12}C$^-$ or ^{18}O$^-$, ^{28}Si$^-$, ^{32}S$^-$, ^{34}S$^-$ and ^{36}S$^-$, and subsequently stepping the magnetic field to measure ^{37}Cl$^-$. The secondary ion intensities were corrected for background and counting system dead time. Measured ^{37}Cl$^-$/^{34}S$^-$ ion ratios were converted to atomic ratios using a relative sensitivity factor determined from repeated measurements of terrestrial scapolite and hauynite. A mass resolving power of ~3600 was used in order to eliminate contribution from ^{12}C$_3^-$ and ^{35}ClH$^-$ on ^{36}S$^-$.
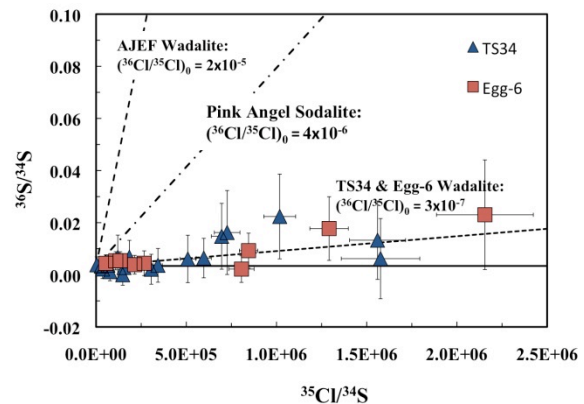

Fig. 1. Plot of ^{36}S/^{34}S *vs.* ^{35}Cl/^{34}S in wadalite grains from TS34 and Egg-6. Representative initial ^{36}Cl/^{35}Cl ratios for AJEF wadalite [4], Pink Angel sodalite [2], and TS34 and Egg-6 wadalite [this study] are shown with dashed lines. Error bars are 2σ.

Results: A set of measurements were made on six wadalite grains from TS34 and three wadalite grains from Egg-6 (Fig. 1). The slope of a best-fit line through the data yields an inferred (^{36}Cl/^{35}Cl)$_0$ ratio of (2.7±2.4)×10^{-7} for TS34 and (2.6±2.0)×10^{-7} for Egg-6. These ratios are approximately two orders of magnitude lower than wadalite in AJEF [4]. We analyzed an additional wadalite grain from AJEF within the same analytical session as Egg-6 and confirmed our previous result of (1.7±0.3)×10^{-5}.

We also analyzed five sodalite grains from Pink Angel. The majority of the measurements show no ^{36}S* outside analytical uncertainty (Fig. 2). The slope of a best-fit line through the Pink Angel data yields an inferred ^{36}Cl/^{35}Cl ratio at the time of sodalite formation of (6.5±7.4)×10^{-7}. This result is distinctly lower than

the $^{36}Cl/^{35}Cl$ ratio reported by [2] for Pink Angel sodalite, but within the range of observed sodalite measurements from another Allende CAI [3] and other measurements of Pink Angel sodalite [7]. Note that four of our measurements were obtained from different parts of a single sodalite grain, in which only one of the three analyses shows resolvable $^{36}S^*$ (Fig. 2).
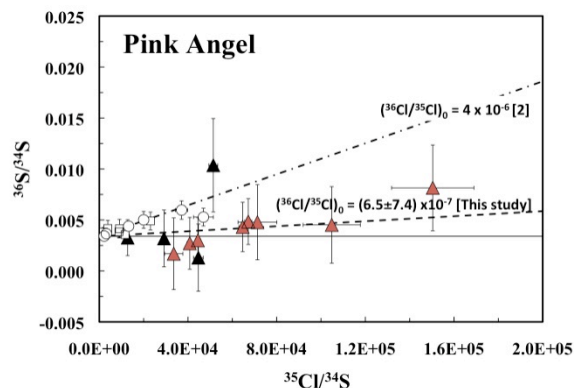

Fig. 2. Plot of $^{36}S/^{34}S$ *vs.* $^{35}Cl/^{34}S$ in sodalite grains from Pink Angel. Representative initial $^{36}Cl/^{35}Cl$ ratios shown with dashed lines, and previously published data from Pink Angel ([7] - open circles and [2] - open squares) are shown for reference. Our data are presented as red and black triangles. The black triangles represent measurements made in different regions of the same large grain. Only one subregion shows a resolvable $^{36}S^*$. Error bars are 2σ.

Discussion: Grossular associated with wadalite in AJEF shows no resolvable ^{26}Mg excess [6], and the absence of radiogenic ^{26}Mg in grossular contrasts with the primary minerals (melilite, anorthite, pyroxene) which show a well-defined internal isochron with $(^{26}Al/^{27}Al)_0$ ~5×10^{-5} [8]. These data indicate that the wadalite-grossular paragenesis in AJEF formed >2.6 Myr after crystallization of the CAI.

These observations lead to the following conclusions: (1) The initial abundance of $^{36}Cl/^{35}Cl$ was at least 1.7×10^{-5} at the time of wadalite-grossular paragenesis in AJEF and (2) wadalite and sodalite continued to form or re-equilibrate with a Cl, S-rich fluid over a > 2 Ma time period on the parent body, *or* (3) the ^{36}Cl-^{36}S system was modified by later diffusive redistribution of ^{36}S making the ^{36}Cl-^{36}S chronometer unreliable. The data from Pink Angel support the latter conclusion.

The well-defined chronology for primary and secondary minerals within AJEF imposes important constraints on the origin of ^{36}Cl. If ^{36}Cl was introduced together with ^{26}Al at the birth of the solar system, the late formation of wadalite inferred from the low $(^{26}Al/^{27}Al)_0$ ratio in grossular, would require an extremely high initial $^{36}Cl/^{35}Cl$ ratio of >8.7×10^{-3}. This value is not achievable by either a SNe or AGB source

[9]. The results for Allende CAI AJEF thus require late production of ^{36}Cl decoupled from ^{26}Al in primary CAI minerals. Spallation reactions induced by energetic particles from the young Sun have been previously suggested as the source of SLRs, most notably ^{7}Be and ^{10}Be [10-11]. From considering results from [12], energetic particle bombardment can produce $^{36}Cl/^{35}Cl$ up to 5×10^{-3} with negligible production of ^{26}Al, assuming that the fluence ratio of gradual to impulsive events is small (<10).

Our preferred model to explain the ^{36}Cl observations involves late irradiation of material that is then incorporated in to proto-asteroid bodies containing a wide spectrum of objects (CAIs, chondrules, igneous differentiates, matrix). The ^{36}Cl is then redistributed during thermal metamorphic processes during formation of halogen-rich phases.

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