THE ^{36}Cl – ^{36}S SYSTEMATICS OF WADALITE FROM THE ALLENDE METEORITE.

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Introduction: The origin of short-lived radionuclides in the early Solar System is currently the subject of considerable debate. Their ultimate nucleosynthetic sources [c.f. 1-4] have important implications regarding the usability of these nuclides as high-resolution chronometers for dating early Solar System events. If these radionuclides originated from a nearby exploding star(s) and were well mixed into the molecular cloud from which our Solar System was born [e.g. 1,5], variations in abundances may reasonably be ascribed to the passage of time from an initial uniform inventory. However, models producing short-lived radionuclides via energetic particle bombardment [e.g., 3] accommodate widely variable abundances of radionuclide with no chronological significance. The issue is far from resolved and considerable efforts are required.

Chlorine-36 (^{36}Cl) decays to ^{36}Ar (98.1%, β^-) and ^{36}S (1.9%, electron capture and β^+) with a half-life of 0.3 Ma. Along with ^{10}Be [6], ^{36}Cl is one of two short-lived radionuclides most likely produced by energetic particle irradiation within the Solar System [7]. Calculations [8] suggest that the collective fluence of protons, ^{3}He and ^{4}He needed to produce ^{10}Be is comparable to that needed for production of ^{36}Cl at the inferred initial ^{36}Cl/^{35}Cl ratio reported by [7,9]. This fluence does not produce significant ^{26}Al, consistent with the near absence of ^{26}Al in sodalite ($Na_8Al_6Si_6O_{24}Cl_2$). It is not clear, however, when, where and how volatile ^{36}Cl was incorporated into the refractory mineral assemblages of Ca-Al-rich refractory inclusions (CAIs) in carbonaceous chondrites. The Pink Angel CAI studied by Hsu et al. [7] contains pure radiogenic ^{129}Xe from the decay of ^{129}I ($t_{½}$ = 15.7 Ma) but does not contain radiogenic ^{36}Ar from the decay of ^{36}Cl or radiogenic ^{26}Mg from decay of ^{26}Al. Nor is it clear if the variable ^{36}Cl/^{35}Cl initial ratios, ranging between $(<1.6\text{-}4)\times10^{-6}$ [e.g. 7,9,11], are due to temporal variations, disturbance to the ^{36}Cl-^{36}S system in secondary, halogen-rich minerals, or a heterogeneous distribution of ^{36}Cl in the early Solar System.

To further investigate and better constrain the abundance and distribution of ^{36}Cl in the early Solar System, we have studied the ^{36}Cl-^{36}S systematics in wadalite, a Cl-rich ($Ca_6(Al,Si,Fe,Mg)_7O_{16}Cl_3$) secondary phase recently discovered in the Allende Type B CAI AJEF [12]. Wadalite was initially characterized by electron microprobe and SEM, followed with Focused Ion Beam (FIB) sectioning and scanning transmission electron microscope (STEM) analyses [12]. The Cl-rich (12-13%), as well as Ca-Al-rich chemistry (~40% for CaO, and ~20% for Al_2O_3), make wadalite a unique candidate for isotopic studies of ^{36}Cl-^{36}S, ^{26}Al-^{26}Mg and ^{41}Ca-^{41}K systematics. Rarely is there a single mineral that could allow investigation of three very short-lived radionuclides (^{36}Cl: $t_{1/2}$=0.3 Ma, ^{26}Al: $t_{1/2}$=0.73 Ma, and ^{41}Ca: $t_{1/2}$=0.1 Ma). The wadalite in AJEF occurs adjacent to melilite in secondary veins associated with grossular, monticellite, and wollastonite (Fig. 1). The formation of wadalite in CAIs is not fully understood, but petrography suggests it most likely involved interaction of grossular with Cl-rich fluids at modest temperature and pressure [12].

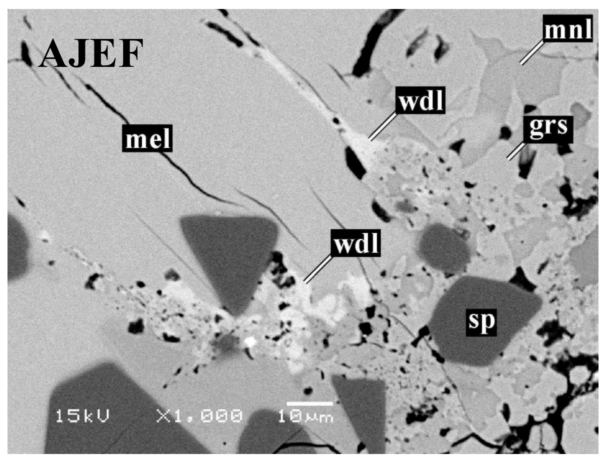

Figure 1. Backscattered electron image of wadalite (wdl) in AJEF. Wadalite occurs in secondary veins adjacent to melilite (mel) together with grossular (grs) and monticellite (mnl). Dark minerals are spinel (sp).

Experimental procedures: Cl–S isotope data were obtained using the LLNL NanoSIMS in image rastering mode with a primary Cs$^+$ beam at ~8 pA and diameter of ~200 nm. Measurements were preformed in combined peak jumping, multi-collection mode, simultaneously measuring ^{28}Si, ^{32}S, ^{34}S and ^{36}S, and subsequently stepping the magnetic field to measure ^{37}Cl. A mass resolving power of ~3600 was used, sufficient to eliminate any contribution from $^{12}C_3^-$ or ^{35}ClH$^-$; the intensity of the ^{35}Cl^{37}Cl^{-2} dimer was estimated to be <0.01 sec^{-1}. Due to the low intensity of ^{36}S$^-$, the background at mass 36 was carefully evaluated; the mean background intensity for wadalite, 0.002 sec^{-1}, is ~10x lower than for sodalite. No significant background correction was required for any wadalite data. Measured $^{37}Cl^-/^{34}S^-$ ion ratios were converted to atom ratios using a relative sensitivity factor of 0.71 ± 0.04, determined from measurements of terrestrial scapolite $(Na,Ca)_4(Al_3Si_9O_{24})Cl$ and hauynite $(Na,Ca)_{4-8}Al_6Si_6(O,S)_{24}(SO_4,Cl)_{1-2}$. This relative sensitivity factor is similar to that reported by [11].

Results: The AJEF wadalite shows very large ^{36}S excesses ($\delta^{36}S$>209,500 ‰) correlated with the respective $^{35}Cl/^{34}S$ ratios (as high as 2,000,000). The slope of the best-fit line through the data yields an inferred $^{36}Cl/^{35}Cl$ ratio at the time of wadalite formation of $(17.2±2.5)\times10^{-6}$ (Fig. 2). This slope is ~4–10 times higher than the inferred $^{36}Cl/^{35}Cl$ ratio for the Pink Angel [7,11] and ~10x higher than that found for sodalite in Allende CAI #2 [13].

Discussion: The use of ^{36}Cl as a chronometer for early solar system events has appeared unfeasible due to the absence of any correlation between the inferred initial abundances of ^{36}Cl and ^{26}Al. The high initial ^{36}Cl abundance found here, in a CAI displaying the canonical $^{26}Al/^{27}Al$ initial ratio, suggests ^{36}Cl may yet help constrain the timing of halogen-rich alteration affecting CAIs. A comparison of data for the Allende CAIs AJEF and #2 (data from [13]) is illustrative. Both CAIs contain $^{26}Mg^*$ in primary anorthite and $^{36}S^*$ Cl-rich secondary phases. The difference in initial $^{26}Al/^{27}Al$ ratios for the two CAIs corresponds to a difference in crystallization age of ~1.4 Ma, while the difference in initial $^{36}Cl/^{35}Cl$ ratios corresponds to difference of ~1.1 Ma in the "age" of secondary minerals; AJEF is "older" according to both the ^{26}Al and ^{36}Cl clocks. More data, especially for ^{26}Al in wadalite or coexisting grossular in AJEF are needed to explore this possibility and to provide a more tightly constrained value for the initial abundance of ^{36}Cl in the solar nebula.

Solar energetic particle irradiation is the most likely source for ^{36}Cl production [1,7]. The $^{36}Cl/^{35}Cl$ ratio ($\sim17\times10^{-6}$) determined from wadalite in AJEF is close to the value expected in a long-term irradiation scenario [8] and to the value predicted in the X-wind model of [14].

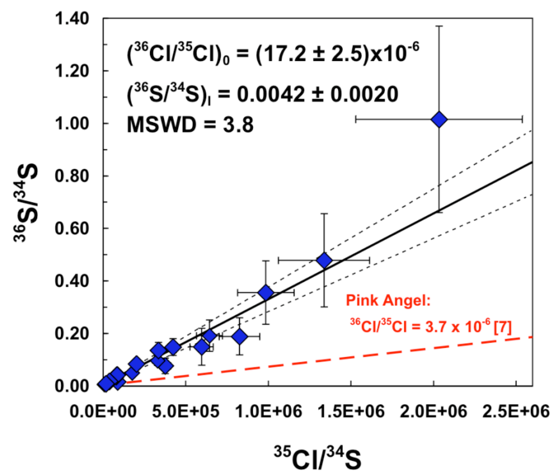

Figure 2. ^{36}Cl-^{36}S isotope correlation diagram of wadalite from Allende CAI AJEF. The black solid line is the best-fit regression through the data. The black dashed lines represent the error envelope. The uncertainties are 2σ. The red dashed line represents the inferred $^{36}Cl/^{35}Cl$ ratio for Pink Angel sodalite [7].

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