EXCESS ^{36}S IN LAWRENCITE AND NITROGEN ISOTOPIC COMPOSITIONS OF SINOITE FROM ALMAHATA SITTA MS-17 EL3 CHONDRITE FRAGMENT.

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Introduction: Almahata Sitta is an unique meteorite shower, the remnants of asteroid 2008 TC_3 that was observed before it hit the Earth [1]. The meteorite is a breccia containing mainly ureilitic lithologies with many chondritic clasts, and MS-17 fragment was first described as EL3/4 [2] and later as primitive EL3 [3].

The very fresh feature of MS-17 fragment promises preservation of lawrencite ($FeCl_2$), the only known Cl-rich, S-poor condensate of the solar nebula, hence a key to determine the initial abundance of short-lived ^{36}Cl (half life of 0.3 Ma) of the solar system. Excess ^{36}S due to decay of ^{36}Cl has been reported in sodalite [4] and wadalite [5], but both are the secondary alteration phases in Ca-, Al-rich inclusions (CAIs).

The MS-17 EL3 fragment also supplies with a good chance to clarify the origin of sinoite (Si_2N_2O) that was previously reported in equilibrated ELs [6-8]. The proposed formations of sinoite include condensation of the solar nebula [9], thermal metamorphism [10] and crystallization from alleged EL impact melts [7].

We conducted a combined nanoSIMS, FESEM, microRaman studies of the MS-17 EL3 fragment [11]. Several grains of lawrencite were found, and three of them have large excesses of ^{36}S with the highest inferred ^{36}Cl/^{35}Cl ratios of 0.92×10^{-4} -1.42×10^{-4}. In addition, a large number of sinoite crystals were observed in various assemblages in the cores of metallic Fe-Ni nodules, intergrown with oldhamite, sphalerite, or troilite. Here, we report more ^{36}Cl/^{35}Cl ratios in lawrencite from a new polished section of MS-17 and the first analysis of N isotopic composition of sinoite in an EL3 chondrite.

Samples: Beside the polished section (2.3 cm^2) studied in the previous work [11], a new polished section prepared from the same MS-17 fragment was investigated. More than 50 grains of lawrencite were encountered in the new section. Although no water was used during the sample preparation, many lawrencite grains are moderately weathered.

Another 38 sinoite-bearing assemblages were found in the new section. The sinoite occurs as euhedral prisms often cluster as radial, network-like with interstitial grains of oldhamite, sphalerite or troilite in the cores of metal nodules, similar to the previous observations of the other section. Several metal assemblages contain concentric layers of fine-grained sinoite crystallites in an aggregated conglomerate of small metal fragments in the FeNi-metal nodules. In addition, very fine-grained sinoite were found in a few troilite assemblages in silicate matrix or at the rims of metal nodules. All observations of the sinoite-bearing assemblages, the occurrence of fluffy crystallite accretionary rims around metal nodules and absence of metal-sulfide eutectic textures in MS-17 EL3 chondrite fragment clearly indicate sequential condensation of sinoite and troilite, and against shock-induced melting.

Experimental: ^{32}S, ^{33}S, ^{34}S, ^{36}S and ^{37}Cl of lawrencite were analyzed by the nanoSIMS 50L at the Institute of Geology and Geophysics, Chinese Academy of Sciences. A primary Cs^+ beam of ~2 pA was used, and the secondary S isotopes and ^{37}Cl were counted with electron multipliers (EM) in multi-collection mode. Possible charging was compensated by using e-gun. The ^{33}S peak was well resolved from ^{32}S^{1}H at a mass resolving power (MRP) of 6000 (CAMECA definition). Between analyses of lawrencite in different assemblages, troilite nearby (assuming a normal S isotopic composition) and synthetic $FeCl_3$ deposited on purified Au foil were repeatedly measured as standards of S isotopes. Dead-time and background of each EM were corrected. The relative yield of Cl/S of lawrencite is unknown, instead, that of NIST glass of ~0.8 was applied.

Because of very low yield of CN^- of sinoite, ^{14}N^{16}O$^-$ and ^{15}N^{16}O$^-$ were measured to determine the ^{15}N/^{14}N ratios. Interferences of ^{14}N^{16}O by ^{30}Si, and ^{15}N^{16}O by ^{30}Si^{1}H and ^{14}N^{17}O can be well separated at MRP of ~9000. ^{14}N^{16}O$^-$ was counted by FC and ^{15}N^{16}O$^-$ by EM. Synthetic sinoite prepared from an equimolar mixture of Si_3N_4 and SiO_2 at 1850ºC [12] was used as the standard of N isotopes.

Results: Sulfur isotopic compositions were normalized to ^{34}S, and the excesses of ^{36}S were determined with $\Delta^{36}S/^{34}S=\delta^{36}S/^{34}S+2\times\delta^{33}S/^{34}S$. All analyses were plotted as ^{36}S/^{34}S vs ^{35}Cl/^{34}S in Fig. 1, with the error bars of 2σ. The synthetic $FeCl_3$ has the highest ^{35}Cl/^{34}S ratios up to 1×10^6, with no significant excess of ^{36}S. The synthetic $FeCl_3$ analyses define a detection limit of $^{36}Cl/^{35}Cl$ of $(2.9\pm0.4)\times10^{-7}$. Except for the analyses without ^{36}S excess, the other grains of lawrencite appear to cluster into three "isochron" lines (Fig. 1), with the inferred $^{36}Cl/^{35}Cl$ ratios of $(2.5\pm0.2)\times10^{-6}$, $(1.1\pm0.08)\times10^{-5}$ and $(0.94\pm0.08)\times10^{-4}$, respectively. It is noted that the higher Cl/S ratios of lawrencite the lower inferred $^{36}Cl/^{35}Cl$ ratios. In addition, the moderately weathered grains usually reveal small or no excess of ^{36}S. It is possible that the S isotopic compositions of some lawrencite grains have been contaminated by the neighboring sulfides due to weathering. Hence, the highest $^{36}Cl/^{35}Cl$ ratio of $(0.94\pm0.08)\times10^{-4}$ can be referred to as the closest to the initial value of the solar system.

Relative to the atmosphere, the synthetic sinoite has $\delta^{15}N_{air}$ of 47.6±5.3‰ (1SD, n=9), and five large sinoite grains from Almahata Sitta MS-17 fragment vary from (1SD) 8.3±6.3‰ to 33.6±9.5‰ with an average of 22.7±10‰. We assume that the synthetic sinoite has a similar N isotopic composition of the atmosphere, because it was prepared at very high temperature under a N_2 pressure of 0.98MPa [12]. After the IMF corrected, the sinoite in MS-17 fragment has $\delta^{15}N$ of -24.9±15‰.

Discussion: The analysis of more lawrencite grains from the new MS-17 section confirms the previous discovery of large excess of ^{36}S in this mineral [11]. The highest inferred $^{36}Cl/^{35}Cl$ ratio of $(0.94\pm0.08)\times10^{-4}$ can be referred to as the initial value of the solar nebula at the E-chondrite forming region, because lawrencite is a primary phase. Excess of ^{36}S was reported in sodalite [4] and wadalite [5] in CAIs from carbonaceous chondrites. After calibrating the time difference between CAI formation and alteration, the initial $^{36}Cl/^{35}Cl$ ratio of $>1.4\times10^{-6}$ at the C-chondrite forming region was calculated [4]. E-chondrites probably formed closer to the Sun than C-chondrites, because the former are much more reduced. In this case, the initial $^{36}Cl/^{35}Cl$ ratio of the solar nebula shows no increasing trend toward the Sun, arguing against irradiation of ^{36}Cl by the proto-Sun.

The $\delta^{15}N$= -24.9±15‰ of sinoite measured in this study is consistent with the analysis of sinoite in a EL6 chondrite [-18±3‰, 13], indicative of no significant fractionation of N isotopes during thermal metamorphism in the parent body. Our analysis is also consistent with bulk N isotopic composition of E-chondrites [14]. The similarity of N isotopic compositions between E-chondrites and the Earth is another line of evidence for contribution of an E-meteorite-like precursor during accretion of the Earth.

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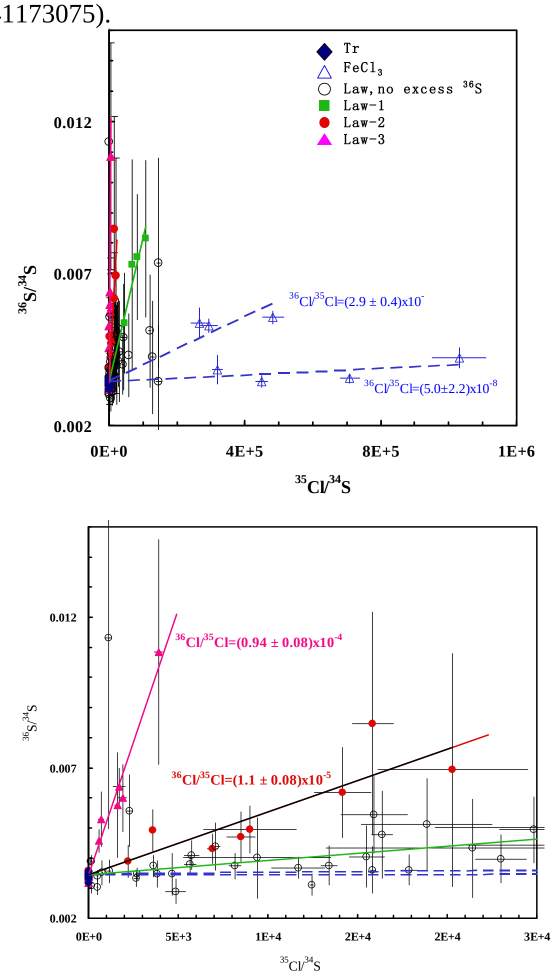

Fig. 1. $^{36}S/^{34}S$ vs $^{35}Cl/^{34}S$ plot of lawrencite from Almahata Sitta MS-17 EL3 fragment. Troilite (Tr) and synthetic $FeCl_3$ were standards of S isotopes. Error bars are in 2σ.

References: [1] Jenniskens P., et al. 2009. *Nature* 458: 485-488. [2] Bischoff A., et al. 2010. *Meteoritics & Planetary Science* 45: 1638-1656. [3] El Goresy A., et al. 2011. *Meteoritics & Planetary Science* 46: #5079. [4] Lin Y., et al. 2005. *Proc. National Academy of Sciences* 102: 1306-1311. [5] Jacobsen B., et al. 2011. *The Astrophysical Journal Letters* 731: L28. [6] Keil K. and Andersen C. A. 1965. *Nature* 207: 745-745. [7] Rubin A. E. 1997. *American Mineralogist* 82: 1001-1006. [8] Kimura M., et al. 2002. *Meteoritics & Planetary Science* 37: A78. [9] Sears D. W. 1980. *Icarus* 43: 184-202. [10] Muenow D. W., et al. 1992. *Geochimica et Cosmochimica Acta* 56: 4267-4280. [11] Lin Y., et al. 2011. *Workshop on Formation of the first solids in the solar system* #9094. [12] Sekine T., et al. 2006. *American Mineralogist* 91: 463-466. [13] Hoppe P., et al. 1989. *Meteoritics* 24: 278. [14] Thiemens M. H. and Clayton R. N. 1983. *Earth and Planetary Science Letters* 62: 165-168.