

EARLIEST SOLID CONDENSATES CONSISTING OF THE ASSEMBLAGE OLDHAMITE, SINOITE, GRAPHITE AND EXCESS ^{36}S IN LAWRENCITE FROM ALMAHATA SITTA MS-17 EL3 CHONDRITE FRAGMENT. Y. Lin¹, A. El Goresy², M. Boyet³, L. Feng¹, J. Zhang¹, and J. Hao¹, ¹Key Laboratory of the Earth's Deep Interior, Institute of Geology and Geophysics, Chinese Academy of Science, Beijing, China, Email: LinYT@mail.iggcas.ac.cn, ² Bayerisches Geoinstitut, Universität Bayreuth, 95447 Bayreuth, Germany, ³Université Blaise Pascal, Lab. Magmas et Volcans, UMR CNRS 6524, BP 10448, F-63000 Clermont-Ferrand, France..

Introduction: We encountered in fragment MS-17 a very primitive EL-3 from Almahata Sitta asteroid, a unique assemblage of earliest solid condensates consisting of oldhamite, sinoite and graphite. Sinoite ($\text{Si}_2\text{N}_2\text{O}$) was previously reported only in equilibrated EL chondrites, including several EL6s [1], one EL4 [2] and an anomalous E-chondrite (Y793225) [3]. The proposed origin of sinoite in these meteorites include thermal metamorphism [4] and claimed crystallization from EL chondrite alleged impact melts [2]. Another scenario is that sinoite condensed from the solar nebula under high temperature and pressure [5]. However, this mineral was not found in any primitive EL3 so far. Here, we report the first occurrence of sinoite in a condensation sequence with oldhamite and graphite in Almahata Sitta MS-17 EL3 chondrite fragment that was preliminarily classified as a shocked and partially melted EL3/4 chondrite [6] but reclassified by us here as a pristine primitive unshocked and unmelted EL3 [7]. This finding puts new constraints as to the origin of sinoite, discarding the thermal metamorphism hypothesis [4] and the impact melt claim [2] and demonstrating the occurrence of clasts in EL-3 unexpectedly highly enriched in volatile elements, *e.g.* N, Cl, and F.

In MS-17 fragment, we also encountered several lawrencite (FeCl_2) grains, allowing a promising chance to determine the initial $^{36}\text{Cl}/^{35}\text{Cl}$ ratio of the solar nebula in the EL meteorite-forming region. By comparing with the initial $^{36}\text{Cl}/^{35}\text{Cl}$ ratios determined from sodalite in CAIs of carbonaceous chondrites [8,9], it is now possible to explore the spatial distribution of ^{36}Cl in the solar nebula, which will be critical evidence for origin of short-lived ^{36}Cl .

Occurrence of Sinoite-bearing condensate assemblages: Sinoite was found in 39 Fe-Ni metal nodules in a polished section (2.3 cm^2) of Almahata Sitta MS-17. It occurs as euhedral prisms with size up to $60 \times 120\ \mu\text{m}$, which often cluster as radial, network-like with interstitial inclusions of oldhamite, sphalerite or troilite, and micron-sized assemblages. All assemblages occur exclusively in the cores of the metal nodules. Inclusions of sinoite prisms (and/or intergrown with oldhamite) inside both enstatite and diopside strongly suggests formation of sinoite prior to enstatite and diopside condensation.

Raman spectra of many sinoite prisms intergrown with oldhamite are significantly different from those coexisting with sphalerite and troilite. This correlation is unlikely due to crystal orientation because such variation was not found among sinoite prisms of the same cluster. We envisage the presence of two distinct sinoite polymorphs. C, N, O, F, Cl, Si, S mapping with nanoSIMS 50L reveals high concentrations of F, Cl and S along the grain boundaries, but their distributions are not completely superimposed.

The above observations indicate that sinoite-bearing assemblage condensed from a solar gas with unusual composition. The inferred condensation sequence could be oldhamite \rightarrow oldhamite + sinoite \rightarrow graphite \rightarrow enstatite \rightarrow diopside \rightarrow sphalerite/troilite, according to the textural relationship. After condensation, the sinoite-bearing assemblages were incorporated in the Fe-Ni metal. The high volume percent of sinoite in the metal nodules (up to 14 vol%) are difficult to explain for the proposed reaction of $\text{SiO}_2 + 3\text{Si} + 2\text{N}_2(\text{g}) = 2\text{Si}_2\text{N}_2\text{O}$ during thermal metamorphism [4] or impact melting [2]. The texture and composition of the assemblages clearly refutes an origin by impact melting [2].

Excess ^{36}S of Lawrencite: Minor lawrencite was found in metal, mainly in the sinoite-bearing metal nodules. Most of the grains are very small ($<1\ \mu\text{m}$) and partially weathered. ^{32}S , ^{33}S , ^{34}S , ^{36}S and ^{37}Cl of lawrencite were analyzed by nanoSIMS 50L, but only six grains are relatively large ($1\sim 2\ \mu\text{m}$) and reveal $^{35}\text{Cl}/^{34}\text{S}$ ratios > 1000 (1500-5300). Three analyses show significant excess of ^{36}S , with $\delta^{36}\text{S}^*$ (2σ) of 830 ± 170 , 2230 ± 1810 and 510 ± 260 . The inferred $^{36}\text{Cl}/^{35}\text{Cl}$ ratios are $(0.92\pm 0.2)\times 10^{-4}$, $(3.8\pm 3.1)\times 10^{-4}$ and $(1.42\pm 0.74)\times 10^{-4}$, taking the relative sensitivity factor of Cl/S of 0.8 measured on NIST 610. The other two analyses have no detectable excess of ^{36}S .

The value of $(1.42\pm 0.74)\times 10^{-4}$ can be referred to as the initial $^{36}\text{Cl}/^{35}\text{Cl}$ ratio of the solar nebula in EL-chondrite forming region, without calibration for time difference between condensation of CAIs and lawrencite assuming fast condensation of the solar nebula. This is consistent with the initial $^{36}\text{Cl}/^{35}\text{Cl}$ ratio of $\geq 1.4\times 10^{-4}$ determined from sodalite in CAIs of Ningqiang carbonaceous chondrite [8]. The result in-

dicates no increase of the initial $^{36}\text{Cl}/^{35}\text{Cl}$ ratios toward the Sun as predicted by irradiation of the proto-Sun.

Conclusions: The first discovery of sinoite-bearing assemblages and its occurrences in the Almahata Sitta MS-17 EL3 fragment indicate its origin as earliest condensates and definitely not by shock melting of ambiguous precursors. Formation of sinoite and high concentrations of F and Cl associated with the sinoite-bearing assemblages require high-fugacities of volatiles (*e.g.* N, Cl, F) in the region where this meteorite formed. The presence of sinoite and the inferred condensation sequence will put more stringent parameters on the condensation calculation of the solar nebula under highly reducing conditions. The high abundance of Cl and F further predicts high abundance of I and could open the way of measuring the $^{129}\text{I}/^{129}\text{Xe}$ radiometric system.

Large excesses of ^{36}S were measured in two lawrencite grains isolated in Fe-Ni metal. The inferred $^{36}\text{Cl}/^{35}\text{Cl}$ ratio of $(1.42 \pm 0.74) \times 10^{-4}$ is consistent with the initial ratio of $\geq 1.4 \times 10^{-4}$ calculated from sodalite in CAIs of Ningqiang carbonaceous chondrite [8]. This result confirms our previous conclusion that no increase of the initial $^{36}\text{Cl}/^{35}\text{Cl}$ ratios towards the Sun [9], arguing against irradiation of ^{36}Cl by the proto-Sun.

References: [1] Keil K. and Andersen C. A. 1965. *Nature* 207: 745-745. [2] Rubin A. E. 1997. *American Mineralogist* 82: 1001-1006. [3] Kimura M., et al. 2002. *Meteoritics & Planetary Science* 37: A78. [4] Muenow D. W., et al. 1992. *Geochimica et Cosmochimica Acta* 56: 4267-4280. [5] Sears D. W. 1980. *Icarus* 43: 184-202. [6] Bischoff A., et al. 2010. *Meteoritics & Planetary Science* 45: 1638-1656. [7] El Goresy A., et al. 2011. *Meteoritics & Planetary Science* 46: #5079. [8] Lin Y., et al. 2005. *Proc. National Academy of Sciences* 102: 1306-1311. [9] Lin Y., et al. 2009. *Meteoritics & Planetary Science* 44: 5179.