

THREE DIMENSIONAL MICROSTRUCTURE AND MINERALOGY OF A COSMIC SYMPLECTITE IN THE ACFER 094 CARBONACEOUS CHONDRITE. M. Matsumoto¹, A. Tsuchiyama^{2,3}, A. Miyake⁴, M. Ito⁵, N. Tomioka⁵, Y. Kodama⁶, K. Uesugi⁷, A. Takeuchi⁷, T. Nakano⁸, J. Matsuno⁴, A. Nakato⁹, E. Vaccaro¹⁰. ¹Department of Earth and Planetary Materials Science, Tohoku University, Miyagi 980-8578, Japan, ²Research Organization of Science and Technology, Ritsumeikan University, Shiga 525-8577, Japan, ³GIG, Chinese Academy of Science, Guangzhou, GD 510640 China, ⁴Division of Earth and Planetary Sciences, Kyoto University, Kyoto 606-8502, Japan, ⁵Kochi Institute for Core Sample Research, JAMSTEC, Kochi 783-0093, Japan, ⁶Marine Works Japan Ltd., Kanagawa 237-0063, Japan, ⁷JASRI, Hyogo 679-5198, Japan, ⁸GSJ/AIST, Ibaraki 305-8567, Japan, ⁹JAXA/ISAS, Kanagawa 252-5210, Japan, ¹⁰Department of Earth Sciences, NHM, London SW7 5BD, UK. (E-mail: m_matsumoto@tohoku.ac.jp)

Introduction: Components of carbonaceous chondrites show wide range of oxygen isotopic compositions that keep nearly constant $\delta^{17}\text{O}/\delta^{18}\text{O}$ ratio of ~ 1 [e.g., 1] (Fig. 1). This mass-independent isotopic fractionation is thought to be derived from mixing of two distinct reservoirs (i.e., ^{16}O -rich and $^{17,18}\text{O}$ -rich reservoirs) in the solar nebula. The nature of these reservoirs can be constrained based on the mineralogical characteristics of the components whose oxygen isotopic compositions are plotted in the two extremes.

Fe-rich material showing extremely $^{17,18}\text{O}$ -rich composition ($\delta^{17,18}\text{O}$: $\sim +180$ ‰) has been reported from the primitive carbonaceous chondrite Acfer 094 [2]. The Fe-rich material consists of nanometer-scaled symplectic intergrowth of magnetite and Fe-Ni sulfides and is named “cosmic symplectite (COS)” [3]. COS grains are typically several to 10 μm in size and widely distributed in the matrix of the Acfer 094 [4]. They probably represent the $^{17,18}\text{O}$ -rich reservoir and are currently hypothesized to have formed by oxidation of Fe-Ni metal and sulfides by $^{17,18}\text{O}$ -rich water or water vapor in the early Solar System. However, mineralogical studies on COS grains are very limited and their origin is still poorly constrained.

In this study, we performed synchrotron radiation-based X-ray computed tomography (SR-XCT), transmission electron microscopy (TEM), and NanoSIMS analysis of a COS grain. The results give new insights into the origin of COS.

Samples and Methods: First, we observed a polished Acfer 094 section (~ 2.2 mm²) using a field emission scanning electron microscope (FE-SEM) equipped with energy dispersive X-ray spectrometer (EDS) and found five COS grains. The COS grains (~ 10 μm) show rope-like structure similar with those reported by Abe et al. (2017) [4]. One of the five grains was extracted as a block ($\sim 25 \times 25 \times 30$ μm) from the polished section using a focused ion beam (FIB) technique. Three dimensional (3D) images of the block sample were obtained using a SR-XCT system with high spatial resolution (~ 100 nm) at SPring-8 BL47XU. After the SR-XCT analysis, one cross section including the COS grain (~ 5 μm in thickness) was extracted

from the block using FIB. The sample was subjected to chemical analysis with FE-SEM-EDS and oxygen isotopic imaging with NanoSIMS. Then, the cross section sample was thinned into < 100 nm thick and analyzed using TEM-EDS.

Results and Discussion: SR-XCT analysis shows that the COS grain has irregular shape with many topographic depressions on the surface and contains small inclusions ($< a$ few micron) (Fig. 2). The inclusions are not three-dimensionally connected to the outside even via fractures, ensuring that they were originally contained in the COS grain.

FE-SEM-EDS analysis of the COS grain reveals that the inclusions have compositions rich in O, Na, and S. We note that any O-Na-S-rich material was not observed outside the COS grain.

NanoSIMS analysis confirms that the COS grain has extremely $^{17,18}\text{O}$ -rich composition [$\delta^{17}\text{O} = +159 \pm 6$ (1σ) ‰, $\delta^{18}\text{O} = +166 \pm 3$ (1σ) ‰] (Fig. 1). However, it could not be confirmed whether there is an oxygen isotopic difference between the inclusions and the host COS grain because the inclusions are too small to obtain their own compositions.

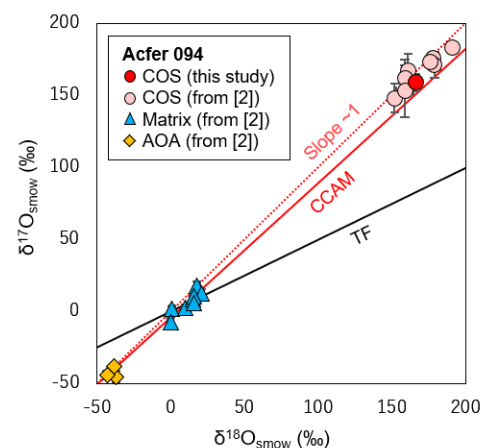


Fig. 1. Oxygen isotopic compositions of the components of the Acfer 094 carbonaceous chondrite. AOA = amoeboid olivine aggregates. CCAM = carbonaceous chondrite anhydrous mineral mixing line. TF = terrestrial fractionation line.

TEM analysis was performed on an ultra-thin section of the COS grain. The ultra-thin section contains one relatively large O-Na-S-rich inclusion (~2 μm in diameter) embedded in the host COS grain. Based on the chemical composition and selected area electron diffraction patterns, the inclusion was identified as a single crystal of Na-sulfate (Na_2SO_4).

Nanometer-scale quantitative compositional maps of the COS grain were obtained using a scanning-TEM (STEM) system combined with EDS. The map analysis reveals that the COS grain exhibits multi-layered structure surrounding the large O-Na-S-rich inclusion core (Fig. 3). We identified three-types of layers; (1) inner-most Ni-poor layer consisting of 100–200 nm size magnetite and pyrrhotite grains, (2) Ni-rich layer consisting of nanometer-scaled intergrowth of magnetite and Fe-Ni sulfides with symplectic texture, and (3) outer-most Fe-(hydro)-oxide layer. The Ni-rich symplectite layer can be divided into 100–300 nm size domains on the basis of crystal orientation of magnetite. This domain structure is probably derived from the precursor Fe-Ni-rich grains currently replaced by the symplectite.

These microstructure can give new insights into the origin of COS. Experimental studies on Fe-metal corrosion by Na-sulfate [e.g., 5] have shown that high temperature (>600 $^{\circ}\text{C}$) heating events in $\text{N}_2\text{-O}_2\text{-SO}_2$ gas condition form scales consisting of FeS and Fe oxides at the contacting surface between Fe-metal and Na-sulfate. The scales exhibit a symplectic intergrowth of FeS and Fe oxide in some part. These are similar with the mineralogy of the COS grain in this study. This suggests that the COS grain might have been formed by some heating events in the presence of Na-sulfate and Fe-Ni metal. Such heating events must have preceded the incorporation of the COS grain into the Acfer 094 parent body although we cannot specify the place at this time. After the incorporation, the COS grain went through aqueous alteration in the Acfer 094 parent body [e.g., 6]. This process might have formed the outer-most Fe-(hydro)-oxide layer of the COS grain.

References: [1] Clayton R. N. (1993) *Annu. Rev. Earth Planet. Sci.*, 21, 115–149. [2] Sakamoto N. et al. (2007) *Science*, 317, 231–233. [3] Seto Y. et al. (2008) *Geochim. Cosmochim. Acta*, 72, 2723–2734. [4] Abe K. et al. (2017) *Geochem. Jour.*, 51, 3–15. [5] Buscaglia V. et al. (1990) *Corros. Sci.*, 30, 327–349. [6] Matsumoto M. et al. (2019) *Sci. Adv.*, 5, eaax5078.

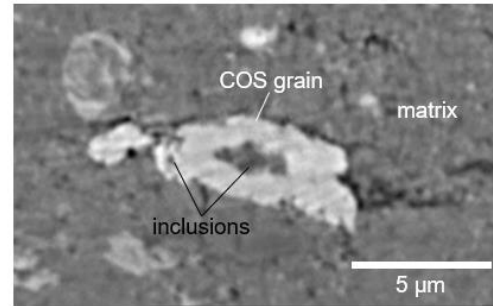


Fig. 2. SR-XCT slice image of a COS grain taken at X-ray energy 8 keV. The COS grain (white) contains small inclusions (dark gray).

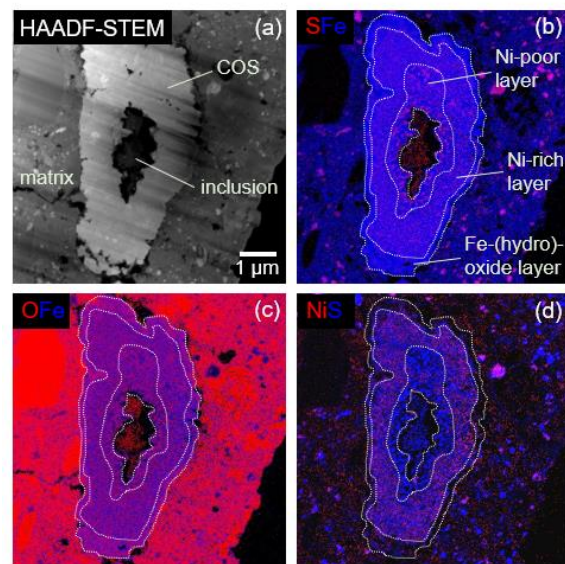


Fig. 3. (a) A high angle annular dark field (HAADF)-STEM image of a COS grain, and combined STEM-EDS maps (b) for S (red) and Fe (blue), (c) for O (red) and Fe (blue), and (d) for Ni (red) and S (blue). The COS grain exhibits multi-layered structure. The boundaries between the layers are indicated by white dashed lines.