

ORIGIN OF P-O-RICH SULFIDE IN CM CHONDRITES: MORE CONSTRAINTS FROM MINERALOGY AND OXYGEN ISOTOPE COMPOSITIONS. A. C. Zhang^{1,2}, S. Itoh², H. Yurimoto², W. B. Hsu³, Y. B. Guan⁴, R. C. Wang¹, and L. A. Taylor⁵, ¹Nanjing University, China (aczhang@nju.edu.cn); ²Hokkaido University, Japan; ³Purple Mountain Observatory, China; ⁴California Institute of Technology, USA; ⁵University of Tennessee, Knoxville, USA.

Introduction: Materials in chondrites provide important clues for understanding conditions and processes that prevailed in the early solar nebula and/or on their parent bodies. Phosphorus-rich sulfide is a unique and ubiquitous object in CM chondrites [1-3]. Various formation mechanisms have been proposed for the origins of this P-rich sulfide in CM chondrites: a) a condensation phase from the solar nebula [1]; b) a sulfidization product of a precursor phase of extrasolar origin prior to condensation of FeNi metal [2]; and c) an alteration product during formation of tochilinite on the parent body of the CM chondrites [3]. Recently, we found that P-rich sulfide grains in two CM chondrites (Grove Mountains (GRV) 021536 and Murchison) are also O-rich. Here, we report their detailed petrographic features, chemical compositions, TEM observations, *in-situ* oxygen isotope compositions, and discuss possible processes of formation.

Analytical methods: Petrographic observations of P-O-rich sulfide were performed by using a Hitachi S-3400N II SEM at Purple Mountain Observatory and a JSM 7000F FE-SEM at Hokkaido University. Mineral compositions were determined using a Cameca SX100 EPMA (with hematite as a standard for Oxygen measurement) at University of Tennessee, Knoxville and a JEOL 8100 EPMA (5 kV for breznaitite) at Nanjing University. The FIB-TEM observations were performed at the National Center for NanoScience and Technology, Beijing. Oxygen isotope compositions were measured initially by using a Cameca NanoSIMS 50L at Caltech without standards and later, measured by a Cameca IMS-1270 instrument at Hokkaido University with a magnetite standard.

Results: P-O-rich sulfide (abbrev as POS hereafter) grains are observed in both GRV 021536 and Murchison. POS in GRV 021536 occurs only as individual fragments or aggregates in the matrix. However, POS in Murchison has at least three types of occurrences. 1) The first type of P-O-rich sulfide grains in Murchison is similar in occurrence to those in GRV 021536; 2) The second is in the matrix and surrounded by tochilinite (Fig. 1). Cracks in these POS grains may contain fine Ca-phosphate grains (<3 μm in size). They are partly surrounded by forsterite and enstatite grains. In some cases, irregular POS is closely associated with calcite (Fig. 1). Fine-grained (<2 μm in size) grains of breznaitite (Cr_3S_4), chromite, and esko-

laite (Cr_2O_3) occur as inclusions in one POS aggregate, which is also associated with fine-grained magnetite and FeNi-phosphide; 3) The third occurs in type I chondrules and are usually surrounded by tochilinite.

The FIB-TEM observations show that POS grains are aggregates of 5-10 nm nano-phases (Fig. 2) with a few subhedral-euhedral Cr-rich phase, which is probably breznaitite or eskolaite. Selected-area electron diffraction (SAED) patterns of POS have concentric and sharp rings with decreasing diffraction intensities at 1.80 \AA , 3.01 \AA , 3.15 \AA , 5.91 \AA , 2.00 \AA , 2.38 \AA , and 1.58 \AA .

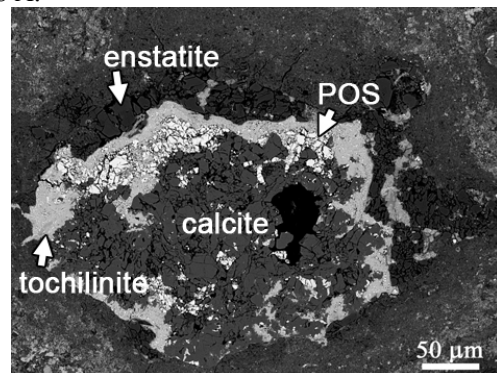


Fig. 1. BSE image of P-O-rich sulfide in Murchison.

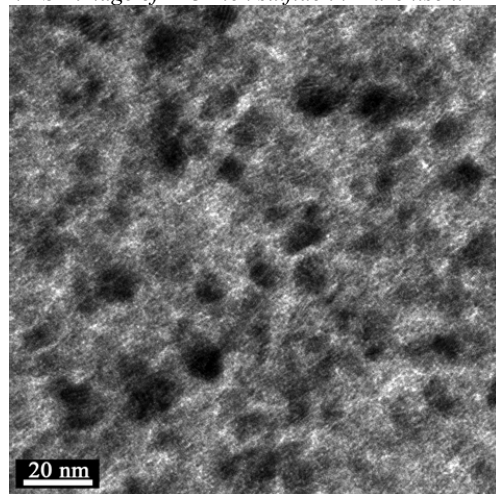


Fig. 2. Bright Field image of P-O-rich sulfide.

The EPMA results show that POS in CM chondrite has a small variation in composition. The POS is dominated by Fe (28.6-33.8 wt%), Ni (28.5-31.6 wt%), and S (22.6-26.5 wt%), with O and P varying in 5.12-7.59 wt% and 4.71-6.28 wt%, respectively. The Co content varies from 0.86 to 1.68 wt%, with a Co/Ni value

(0.048) similar to the solar value (~ 0.045 , [4]). Compositions of tochilinite plot at the tochilinite end on the Tochilinite-Crostedtite mixing line (Fig. 3). Brezinaite (Cr_3S_4) contains 51.9-53.3 wt% Cr, 44.7-45.5 wt% S, and 1.42-1.62 wt% Fe.

Oxygen isotope compositions of the POS plot almost on the TF line (Fig. 4), with an average $\delta^{18}\text{O}$ value of -22.5 ‰ and an average $\Delta^{17}\text{O}$ value of 0.2 ± 4.6 ‰ (1σ). However, the $\delta^{18}\text{O}$ value of POS in this study may include an instrumental mass fractionation, since the matrix effect between POS and magnetite is exactly unknown. Meanwhile, carbonate minerals associated with POS and tochilinite have an average $\delta^{18}\text{O}$ value of 16.1 ‰ and an average $\Delta^{17}\text{O}$ value of -2.4 ± 1.7 ‰ (1σ).

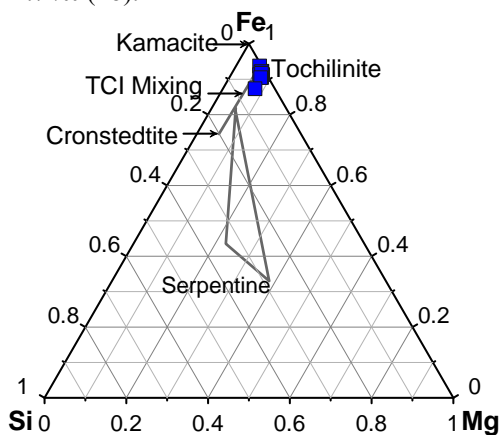


Fig. 3. Si-Mg-Fe ternary diagram for distinguish hydrated minerals in CM chondrites [5].

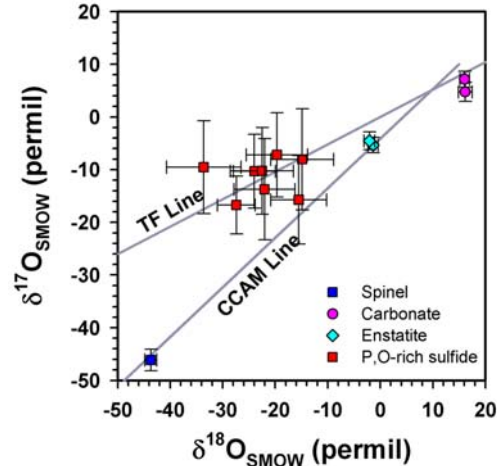


Fig. 4. Oxygen isotope compositions of POS, carbonate, enstatite, and spinel in Murchison. The error bar is 2σ .

Discussion: Our petrographic observations are generally consistent with those of P-rich sulfide in previous investigations [1-3]. All minerals associated with POS in this study have been reported in [2], although some of their associations are different. Therefore, it is very likely that P-rich sulfide reported by [1-

2] are also POS. In agreement with [1], TEM observations indicate that POS in CM chondrites are polycrystalline aggregates. However, there is no convincing evidence that POS is a mixture of different phases. Indeed, no simple mineral assemblage of known minerals could account for both the compositions and d values of POS, although some Cr-rich phases are included in POS. It is hereby concluded that POS is a single phase.

Previous investigations preferred that POS in CM chondrites is of condensation origin based on the very fine-grained and compact texture [1] and unusual trace-element patterns [2]. However, it is more likely that POS is a low-temperature alteration product rather than a high-temperature condensation mineral based on our observations that. 1) POS is observed in chondrule; 2) POS is closely associated with low-temperature minerals, such as carbonate, brezinaite, eskolaite, and magnetite; 3) The $\Delta^{17}\text{O}$ value of POS is similar to that of carbonate within analytical errors; 4) The Co/Ni value of POS which is similar to the solar Co/Ni ratio [4]. The Co/Ni value could be a heritage from its possible precursor (chondritic FeNi metal).

Based on the Co/Ni value of POS, it is probable that chondritic FeNi metal in CM chondrites is the precursor of POS, also supported by [3], although no FeNi metal that is included by POS was observed in this study. However, POS does not appear to be an accessory product during formation of tochilinite, as proposed by [3]. This inference was supported by two facts: 1) Almost all POS in GRV 021536 and the majority of POS in Murchison occur as individual fragments or aggregates and no associated tochilinite was observed; 2) For those POS grains associated with tochilinite, the POS is always enclosed by the tochilinite. The association between POS and tochilinite in CM chondrites indicates that tochilinite could have formed after formation of POS. Since brezinaite, eskolaite, and chromite are included in POS, they might have been formed simultaneously, probably during sulfurization and oxidation of P-rich FeNi metal. In this event, Fe and Ni mainly form POS while minor Cr in primitive FeNi metal was sulfurized and oxidized to brezinaite and eskolaite, and even chromite. After this event, CM chondrites may have experienced further low-temperature alteration events that caused the formation of carbonate and tochilinite.

References: [1] Devouard B. and Buseck P. R. (1997) *MAPS*, 32(4) supplement: A34. [2] Nazarov M. A. et al. (2009) *Petrology*, 17, 101-123. [3] Palmer E. E. and Lauretta D. S. (2011) *MAPS*, 46, 1587-1607. [4] Anders E. and Grevesse N. (1989) *GCA*, 53, 197-214. [5] McSween H. Y. Jr. (1987) *GCA*, 51, 2469-2477.