

**NEW TITANIUM MONOSULFIDE MINERAL PHASE IN YAMATO 691 ENSTATITE CHONDRITE.**

K. Nakamura-Messenger<sup>1,2</sup>, S. J. Clemett<sup>1,3</sup>, A. E. Rubin<sup>4</sup>, B.-G. Choi<sup>5</sup>, S. Zhang<sup>1,6</sup>, Z. Rahman<sup>1,2</sup>, K. Oikawa<sup>7</sup>, and L. P. Keller<sup>1</sup>. <sup>1</sup>Astromaterials Research and Exploration Science Directorate /NASA Johnson Space Center, Houston, TX 77058, USA, <sup>2</sup>ESCG/ Jacobs Engineering, TX 77058, USA, <sup>3</sup>ESCG/ ERC Inc., TX 77058, USA, <sup>4</sup>Institute of Geophysics and Planetary Physics, University of California, Los Angeles, CA 90095-1567, USA, <sup>5</sup>Earth Science Education, Seoul National University, Seoul 151-748, South Korea, <sup>6</sup>Lunar and Planetary Institute, Houston, TX 77058, USA, <sup>7</sup>Lunar and Planetary Institute, Houston, TX 77058, USA, <sup>7</sup>Dept. of Metallurgy, Graduate School of Engineering, Tohoku University, Sendai, 980-8579, Japan. keiko.nakamura-1@nasa.gov

**Introduction:** Yamato 691, an EH3 enstatite chondrite, was among the first meteorites discovered by chance in Antarctica by the Japanese Antarctic Research Expedition (JARE) team in 1969. This discovery led to follow-up searches for meteorites in Antarctica [1]. These international searches have been very successful recovering over 40,000 total specimens (and still counting), including martian and lunar meteorites.

Titanium is partly chalcophile in enstatite-rich meteorites. Previous occurrences of Ti-bearing sulfides include troilite, daubréelite and ferroan alabandite in enstatite chondrites and aubrites [2], and heideite with 28.5 wt% Ti in the Bustee aubrite [3]. Here we report a new mineral from Yamato 691, ideally stoichiometric TiS, titanium monosulfide, a simple two-element mineral phase, yet with a very unique crystal structure that, to our knowledge, has not been observed previously in nature.

**Sample and Methods:** Twelve Ti-S phase grains were identified in a rare barred olivine (BO) chondrule (72  $\mu\text{m}$  in diameter) in petrographic thin section Yamato 691,79-1 using the UCLA electron microprobe. No other Ti-S grains were located in the thin section. We used the JSC FEI Quanta 3D-FEG dual beam focused ion beam (FIB) instrument to extract, *in situ*, a  $5 \times 10 \mu\text{m}$  cross section of two Ti-S grains within the BO chondrule. The FIB section was prepared using a 30 keV focused Ga ion beam. After mounting on a TEM grid, the section was thinned to 50 nm thickness.

Imaging and selected area electron diffraction (SAED) were performed using a JEOL 2000FX transmission electron microscope (TEM) (200keV) and a JEOL 2500SE field-emission scanning TEM (FE-STEM). The FE-STEM is equipped with a large area, thin window energy-dispersive X-ray detector (EDX) analysis system and Gatan Imaging Filter used to collect electron energy-loss spectroscopy (EELS) data. Nanometer-scale compositional maps of the sample were acquired with a 4 nm incident probe whose dwell time was minimized to avoid beam damage and element diffusion during mapping. Image layers of each mapped region were acquired and combined in order to achieve sufficient counting statistics for major elements in each pixel to derive quantitative abundances. All the EDX data were reduced using the Cliff-Lorimer ratio

method [4]. We used EELS to determine whether C, N, or O were detected in the new TiS mineral phase and to determine the Ti valence state. In EDX analysis, the N  $K_{\alpha}$  X-ray is strongly absorbed by the thin windows in the EDX detector, and the position of the O  $K$  peak overlaps with that of the Ti  $L$  peak. We determined the Ti valence in the new mineral by comparison of its Ti  $L_{2,3}$  energy loss near edge structure with those from the reference materials with known Ti valence. Ilmenite,  $\text{Ti}_2\text{O}_3$ , and TiO, served as references for  $\text{Ti}^{4+}$ ,  $\text{Ti}^{3+}$  and  $\text{Ti}^{2+}$ , respectively. All spectra were processed by power-law background subtraction followed by removal of plural scattering using the low-loss region.

**General mineralogy of the TiS-containing BO chondrule:** Major phases include olivine (Fa 0.7) and a feldspathic, moderately sodic mesostasis. Minor phases in the FIB section are enstatite, troilite, Fe-Ni alloy, osbornite, schöllhornite, and three unknown titanium sulfide phases in the mesostasis.

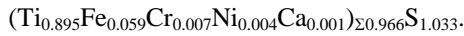
**Ti-S crystalline grains:** All Ti-S grains occur within the mesostasis of the BO chondrule. One of the Ti-S grains extracted by FIB is  $50 \times 450 \text{ nm}$  in size, and completely encapsulated by two different types of fibrous or platy titanium sulfide crystals, possibly hydrates or hydroxides (Fig. 1a). The other Ti-S grain was lost during the FIB sample preparation, but there were osbornite and kamacite grains in close proximity to the location of the lost Ti-S grain, so these minerals might have been associated with the Ti-S grain.

Based on quantitative EDX mapping (Fig. 1b,c), the major elements of the Ti-S grain are (in wt%): Ti 52.0, S 40.2, with minor Fe 4.0, Cr 0.47, Ni 0.31, and Ca 0.05.

Oxygen and nitrogen are below detection limits for EELS analysis (Fig. 1d), thus excluding the presence of Ti-nitride or Ti-oxide in the grain. The Ti  $L_{2,3}$  EELS spectra are consistent with only  $\text{Ti}^{2+}$  in the Ti-S grain.

Extensive SAED (Fig. 1e) revealed that the Ti-S grain is a single crystal (Fig. 1f) with a rhombohedral structure with the unit cell parameter of:  $a = 3.42 \pm 0.07$ ,  $c = 26.50 \pm 0.53 \text{ \AA}$ , space group  $R\bar{3}m$ . The crystallographic data are in excellent agreement with those for synthetic TiS (JCPDS 25-561).

**TiS summary:** The empirical formula of this new Ti-S mineral phase in the Yamato 691 BO chondrule is



The simplified formula is  $\text{Ti}_1\text{S}_1$ , which requires Ti 59.88, S 40.12, for total 100.00 wt%.

In synthetic titanium sulfides ( $\text{Ti}_x\text{S}_y$ ),  $x$  and  $y$  take a variety of values and the crystal structure changes, depending on  $x$  and  $y$ ; however, only TiS and  $\text{Ti}_8\text{S}_9$  assume these elongated ( $a=3.42$ ,  $c=26.5$ ) unit cells. TiS can crystallize in two polymorphs: the TiS with space group  $R\bar{3}m$  that we discovered in Yamato 691 is sometimes referred to as the “R9-type” in the literature studies of synthetic Ti-S, in contrast to the nominal NiAs/B8-type crystal structure.

**High T NiAs-type TiS vs. Low T R9-type TiS:** In synthetic (Fe,Ti)S monosulfide studies, the NiAs structure is observed in a composition region from pure FeS to  $(\text{Fe}_{0.4}\text{Ti}_{0.6})\text{S}$  and pure TiS, while high Ti-content ( $\text{Ti}>\text{Fe}$ )S shows the R9 structure [5]. The  $a$ - and  $c$ -axis of the NiAs structure monotonously increases and decreases with increasing TiS content, respectively [6]. The R9 structure phase is a NiAs-type superstructure transformed from the NiAs structure phase during the cooling, and the phase transformation from the NiAs-type to the R9-type which is very sensitive to the cooling rate [7]. TiS tends to be the R9-type rather than the NiAs-type when cooled slowly (from 1200°C to water quenched vs. 30°C/min [8]). When the original melting T is low (800 to 1000 °C), all of the TiS tends to become R9-type no matter how fast the cooling rate [8].

**Petrogenesis of R9-type TiS:** Because chondrules in different chondrite groups have different O-isotopic compositions, different mean sizes and different proportions of textural types [9], it seems likely that chondrules formed locally in the nebula. Thus, this BO chondrule including its TiS grains presumably formed in the same inner-solar-system location where the EH asteroid accreted. The TiS grains crystallized from the chondrule melt and thus formed in the nebula and not on the parent asteroid. The phases in the chondrule are highly reduced and indicate formation at low oxygen fugacity. Wasson [10] noted that volatile elements such as Na and S occur in chondrules in their cosmic proportions. Thus, chondrules were not devolatilized and could not have been heated above 1000 K for longer than ~100 s. This corresponds to a mean cooling rate exceeding 30,000 °C/hr. This scenario is consistent with the results from synthetic TiS polymorph studies.

**References:** [1] Kojima H. (2006) In the history of meteoritics and key meteorite collections: fireballs, falls and finds. *256* 291-304. [2] Keil K. (1969) *EPSL* 7 243-248. [3] Keil K. & Brett R. (1974) *Am Min.* **59** 467-470. [4] Cliff, G. & Lorimer, G.W. (1975) *J. Microscopy*, **103** 203-207. [5] Nolze G. & Kraus W. (1998) *Powder Diffraction*. **13** 256. [6] Mitsui H., et al. (2009) *J. Iron Steel Japan*, **49** 936-941. [7] Jacquin Y. & Jeannin Y. (1963) *Compt. Rend.* **256** 5362. [8] Mitsui H. (2003) PhD thesis, Tohoku Univ. Japan. [9] Rubin A. E. (2000) *Earth-Sci. Rev.*, **50** 3-27. [10] Wasson J.T. (1996) Chondrules and the protoplanetary disk (Hewins R. H. et al. eds)p.45-55.

