

THE FORMATION OF WASSONITE: A NEW TITANIUM MONOSULFIDE MINERAL IN THE YAMATO 691 ENSTATITE CHONDRITE. K.Nakamura-Messenger^{1,2}, L. P. Keller¹, S. Messenger¹, A. E. Rubin³, B.-G. Choi⁴, M. I. Petaev⁶, S. J. Clemett^{1,5}, S. Zhang⁷, Z. Rahman^{1,2}, and K. Oikawa⁸. ¹Robert M Walker Laboratory for Space Science, Astromaterials Research and Exploration Science Directorate, NASA Johnson Space Center, Houston, TX ²ESCG/ Jacobs Engineering, TX 77058, USA, ³Institute of Geophysics and Planetary Physics, University of California, Los Angeles, CA 90095-1567, USA, ⁴Earth Science Education, Seoul National University, Seoul 151-748, South Korea, ⁵ESCG/ ERC Inc., TX 77058. USA, ⁶Department of Earth & Planetary Sciences, Harvard University & Solar, Stellar, & Planetary Sciences, Harvard-Smithsonian CfA, 20 Oxford St., Cambridge MA 02138, USA, ⁷Texas Material Institute, University of Texas, Austin, TX 78712, USA, ⁸Dept. of Metallurgy, Graduate School of Engineering, Tohoku University, Sendai, 980-8579, Japan. keiko.nakamura-1@nasa.gov

Introduction: Wassonite, ideally stoichiometric TiS, is a titanium monosulfide not previously observed in nature, that was discovered within the Yamato 691 EH3 enstatite chondrite [1]. Because of the submicrometer size of the wassonite grains, it was not possible to determine conventional macroscopic properties. However, the chemical composition and crystal structure were well constrained by extensive quantitative energy dispersive x-ray analysis and electron diffraction using transmission electron microscopy (TEM). The crystal system for wassonite is rhombohedral ($a = 3.42 \pm 0.07$, $c = 26.50 \pm 0.53$ Å) with space group: $R\bar{3}m$ (R9 type), cell volume: 268.4 ± 0.53 Å³, $Z=9$, density (calculated): 4.452 g/cm³, empirical formula: $(\text{Ti}_{0.93}, \text{Fe}_{0.06}, \text{Cr}_{0.01})\text{S}$.

In this study, we discuss possible formation mechanisms of wassonite and its associated minerals based on the petrology, mineralogy, crystallography, thermodynamic calculations, Al/Mg isotopic systematics and the O-isotopic composition of the wassonite-bearing BO chondrule.

General mineralogy of the wassonite-bearing BO chondrule: Major phases of the wassonite-containing BO chondrule include olivine (Fa 0.7) and a feldspathic, moderately sodic mesostasis. All 12 of the wassonite candidate grains occur within the mesostasis of the BO chondrule. In field-emission scanning TEM (FE-STEM) observations of the focused ion-beam (FIB) section (Fig.1), we identified a wassonite grain (50 × 450 nm in size, hereafter wassonite grain #1) cutting through the middle of an unknown Ti-rich layer phase having approximately the same cell parameters as schöllhornite [2] ($a=3.32$, $c=26.6$, $\text{Na}_{0.3}\text{CrS}_2 \cdot \text{H}_2\text{O}$) and wassonite ($a=3.4$, $c=26.6$). Attached to one side of this assemblage, schöllhornite and another unknown Ti-rich hydrated phase occur (the unknown phase has a different composition but the same cell parameters as schöllhornite). Minor phases in the FIB section are enstatite, troilite, Fe-Ni alloy, osbornite, schöllhornite, and three unknown titanium-sulfide phases in the me-

sostasis. All of the minerals associated with wassonite grain #1 are illustrated in Fig. 1b.

Wassonite and surrounding hydrated phase: Schöllhornite, associated with wassonite, also occurs in the Norton County aubrite with other Cr-rich minerals, probably formed by terrestrial weathering of caswellsilverite (NaCrS_2) [2]. Caswellsilverite has been observed previously as inclusions in enstatite crystals and in the brecciated matrix of the Norton County aubrite [6], and between coarse pyroxene grains in chondrules in the Qingzhen EH3 enstatite chondrite [7]. The unknown Ti-rich hydrated mineral surrounding the wassonite (Fig.1) may have formed by alteration of wassonite under conditions similar to the replacement of caswellsilverite by schöllhornite. However, no other minerals show evidence of aqueous alteration in the BO chondrule.

NiAs-type TiS vs. Wassonite (R9-type): In synthetic (Fe,Ti)S monosulfide studies, the NiAs structure occurs in compositions 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 [8]. The a - and c -axis of the NiAs structure monotonically increases and decreases with increasing TiS content, respectively [9]. The R9 structure phase is a NiAs-type superstructure transformed from the NiAs phase during cooling. The phase transformation from NiAs-type to R9-type is very sensitive to the cooling rate [10]. TiS tends to be R9-type rather than NiAs-type when cooled slowly (from 1200°C to water quenched vs. 30°C/min [11]). When the original melting T is low (800-1000 °C), TiS becomes R9-type, regardless of the cooling rate [11].

Formation of wassonite: The wassonite-bearing BO chondrule was originally a totally molten object and the low Fa content of the olivine is indicative of its high melting temperature. It probably formed from a reduced olivine-rich precursor dust-ball assemblage with very little FeO. The other phases in the BO chondrule are highly reduced and indicate formation at low oxygen fugacities.

We evaluated potential wassonite formation processes using thermodynamic constraints derived

from the associated mineral assemblage. The presence of coexisting enstatite and forsterite and lack of Ti-oxides provide constraints on the oxygen fugacity. It is clear that the ferromagnesian silicates and the Ti-bearing sulfide-nitride assemblage are not in equilibrium with each other, with f_{O_2} and f_{N_2} values differing by orders of magnitude. This discrepancy suggests melting of a TiS- and TiN-bearing silicate precursor under oxidizing conditions. The stability of wassonite at high temperatures in S-rich and H-depleted systems suggests that it can form as a refractory residue in a system depleted in Ca. The wassonite likely formed as a residue during evaporation of Ti-bearing troilite, and most likely is a relict phase in the BO chondrule.

Because chondrules in different chondrite groups have different O-isotopic compositions, different mean sizes and different proportions of textural types [12], 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.

Wassonite may only occur in this type (BO) of chondrule because most other chondrules may have too

much FeO or may not have reached such high temperatures. Wasson [13] noted that volatile elements such as Na and S occur in chondrules in their cosmic proportions. Thus, most 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 synthetic TiS polymorph studies.

References: [1] Nakamura-Messenger K. et al. (2011) *Amer. Mineral.*, submitted. [2] Okada A. et al. (1985) *Amer. Mineral.*, 70, 638-643. [3] Keil, K. (1968) *J. Geophys. Res.*, 73, 6945-6976. [4] Keil, K. (1969) *Earth and Planetary Science Letters*, 7, 243-248. [5] Keil K. and Brett R. (1974) *Amer. Mineral.*, 59, 467-470. [6] Okada, A. & K. Keil (1982) *Amer. Mineral.*, 67, 132-136. [7] Grossman J.N. et al. (1985) *Geochim. Cosmochim. Acta*, 49, 1781-1795. [8] Nolze G. & Kraus W. (1998) *Powder Diffr.* 13 256. [9] Mitsui H., et al. (2009) *J. Iron Steel Japan*, 49 936-941. [10] Jacquin Y. & Jeannin Y. (1963) *Compt. Rend.* 256. 5362. [11] Mitsui H. (2003) PhD thesis, Tohoku Univ. Japan. [12] Rubin A. E. (2000) *Earth-Sci. Rev.*, 50 3-27. [13] Wasson J.T. (1996) *Chondrules and the protoplanetary disk* (Hewins R. H. et al. eds)p.45-55.

Fig1: Associated minerals with wassonite in the FIB section from the BO chondrule in Y 691. (a) A mosaic of bright field STEM micrographs. (b) Mineral distribution image generated from the x-ray spectral mappings superimposed over Fig 1a.

