A STUDY OF OSBORNITE FROM ENSTATITE CHONDRITES AT THE SUBMICROMETER SCALE.

J. Leitner[1], C. Vollmer[2], and P. Hoppe[1], [1]Max Planck Institute for Chemistry, Hahn-Meitner-Weg 1, 55128 Mainz, Germany (jan.leitner@mpic.de), [2]Universität Münster, Institut für Mineralogie, Corrensstr. 24, 48149 Münster, Germany.

Introduction: Osbornite was first reported in the Bustee aubrite [1], and later identified as TiN by [2]. Since then, it has been found in small amounts in several enstatite chondrites (ECs) and achondrites [e.g., 3–7], as well as the metal-rich chondrites Allan Hills (ALH) 85085 (CH3) and Isheyevo (CH/CB) [8–11], and even in refractory particles from comet Wild 2 [e.g., 12]. Abundances are generally not well constrained; osbornite is typically reported as trace component or accessory phase. However, it was suggested that osbornite constitutes one of the major N-carriers in enstatite chondrites [13]. N-isotopic compositions of TiN have been reported so far for two inclusions in the Bustee aubrite [14,15], one in ALH 85085 [9], and one in Isheyevo [11]. TiN in ALH and Bustee showed no deviation from the terrestrial value [9,14] and small ^{15}N-depletion [15], respectively, while the Isheyevo-TiN had a δ^{15}N of –359 ‰, close to the inferred value for the Sun and the protosolar nebula (δ^{15}N = –383 ‰) [16]. This wide range suggests that the N-isotopic compositions of osbornite can reveal information on their formation conditions, making TiN a valuable target for the study of parent body (and potentially nebular) processes. Here, we report first results of our ongoing investigation of osbornite in ECs.

Samples & Experimental: TiN was identified by SEM-EDS element mapping in thin sections of Neuschwanstein (EL6), Thiel Mountains (TIL) 91714 (EL5), and Almahata Sitta MS-17 (EL3) (Fig.1). Recorded EDS-element maps contain only qualitative information, because the N Kα-peak (0.3924 keV) overlaps with the Ti Lα-peak (0.4522 keV) in the energy spectra for our detector´s energy resolution (127 eV @ Mn Kα). Thus, for an unambiguous identification of osbornite, additional information on the N, O, and Ti concentrations is required, and ultimately, investigation by NanoSIMS allows the identification of N-bearing phases (Fig.1).

Suitable grains were selected for C- & N-isotopic analysis with the NanoSIMS 50 at the MPI for Chemistry. A ~100 nm Cs$^+$ primary ion beam (~1 pA) was rastered over selected sample areas, and secondary ion images of ^{12,13}C$^-$, ^{12}C^{14}N$^-$, ^{12}C^{15}N$^-$, and ^{28}Si$^-$ were recorded in multi-collection. In addition, transmission electron microscopy (TEM) analyses were performed on a Zeiss Libra 200FE (200 kV) at the Institute for
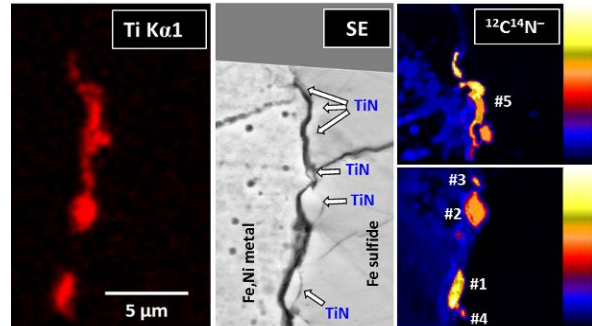

Figure 1. TiN in Neuschwanstein, located at a boundary between Fe,Ni metal and Fe sulfide: SEM-EDS Ti-map (left), secondary electron (SE) image (center), and ^{12}C^{14}N$^-$ secondary ion image (right), representative for the N-distribution in the analyzed area.

Mineralogy at the University of Münster to investigate the mineralogy of selected grains.

Results & Discussion: Five µm-sized TiN grains and one vein-like structure were found in Neuschwanstein; TIL 91714 contained one grain and one vein-like assemblage, and the ongoing EDS investigation of Almahata Sitta MS-17 revealed >70 TiN candidate grains so far. The C- & N-isotopic compositions of osbornite in Neuschwanstein were studied by NanoSIMS. The fact that it was feasible to measure the N-isotopic compositions via ^{12}C^{14,15}N$^-$ indicates the presence of C in the grains, consistent with the observations by [2] and [11]. Carbon isotopic compositions range from δ^{13}C = –17±8 ‰ to 42±30 ‰, with a weighted average of –2 ‰, and N-isotopes lie in the range of δ^{15}N = –37±6 ‰ to 10±26 ‰, with a weighted average of –30 ‰ (Fig. 2). This average δ^{15}N lies close to both the average bulk-δ^{15}N of ECs and the N-isotopic composition of Bustee-TiN determined by [15] (Fig.2), and is also comparable to the N-isotopic composition of sinoite (Si$_2$N$_2$O) in ECs (δ^{15}N = –18±3 ‰) [e.g.,17]. A recent study of Solar System Si$_3$N$_4$ from ECs found a significantly lighter average composition of δ^{15}N$_{Si3N4}$ ~ –62 ‰ [18], indicating differing N-isotopic compositions of these EC constituents. In previous studies, osbornite has been reported in ECs of petrologic types 5-6 but not in ECs of types 3-4 [18]. In the current study, we found TiN to be significantly less abundant than Si$_2$N$_2$O in Neuschwanstein and TIL 91714. Thus, TiN is apparently not a major carrier of nitrogen in the
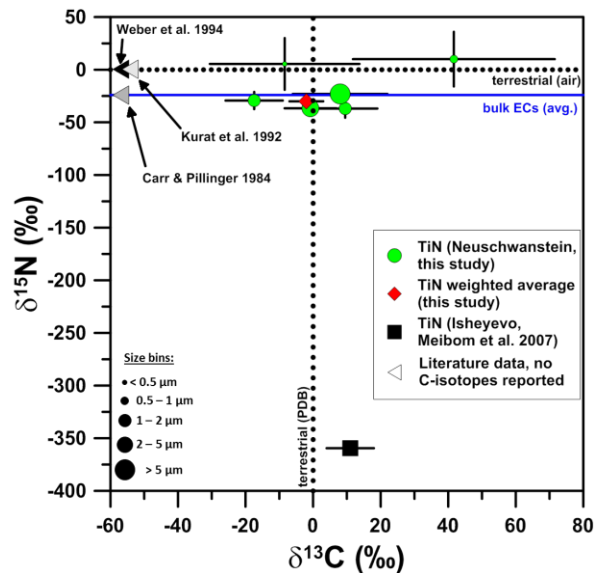
Figure 2. C-N-isotope plot for TiN in Neuschwanstein from this study, together with literature data for TiN from Bustee (aubrite) [14,15], ALH85085 (CH3) [9], and Isheyevo (CH/CB) [11]. Terrestrial values are marked by the dotted lines. All errors are 1σ.

enstatite chondrites. Almahata Sitta MS-17, appears to be a special case. It is the only EL3 so far that contains abundant osbornite and sinoite, but only a few Si_3N_4 grains. Quantitative EDS analyses indicate that several of the osbornite grains also contain V.

TEM investigation of one grain from Neuschwanstein revealed it to be a single crystal of TiN with the typical rock salt structure without any defects, clearly demonstrated by selected area electron diffraction. EDS and EELS analyses showed that no other elements besides Ti and N are present (Fig. 3). In contrast, the Wild 2 TiN was a solid solution of TiN and TiO, with significant amounts of V, but no C. For these osbornite grains, formation by condensation was considered [19].

Conclusions: With the exception of Almahata Sitta MS-17 (EL3), osbornite has been only observed in ECs of high petrologic types (5-6). The N-isotopic composition of TiN from Neuschwanstein is slightly depleted in ^{15}N and is, on average, compatible with both the bulk N isotopes of ECs and the N-isotopic composition of sinoite from EL chondrites. Osbornite is not a major carrier of nitrogen in the ECs studied here, in contradiction to the conclusion drawn by [13]. The same conclusion was inferred for Si_3N_4 [18], indicating that other carrier phases (e.g., Fe,Ni metal or sulfides) have to be considered. The fact that the vast majority of TiN grains studied here occur at boundaries between Fe,Ni metal and Fe sulfides could be indicative for formation by exsolution, with Ti contributed from the sulfides and N from the metal phase. It ap-

pears that osbornite occurs in primitive Solar System materials as both secondary phase (this study), and as condensation product [11,19], and can preserve a wide range of N-isotopic compositions. Thus, a detailed study of TiN can provide deeper insights into parent body and nebular processes in the early Solar System.
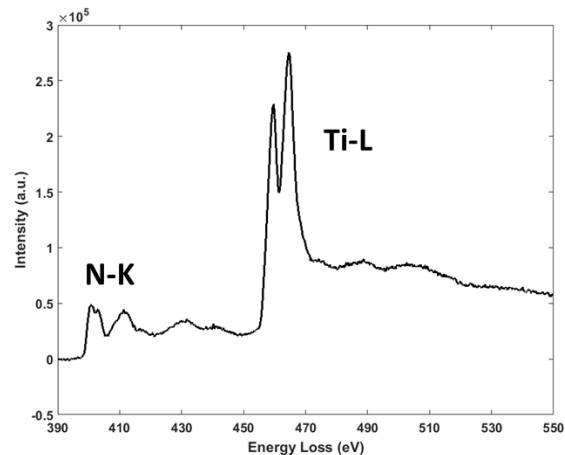

Figure 3. Electron energy loss (EEL) spectrum of grain NEU-C31 from Neuschwanstein. The N and Ti edges are clearly recognizable and the EELS fine structure is consistent with pure TiN bonding. No other elements like V (513/521 eV) or O (532 eV) are present in the osbornite.

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