

### Discovery of Buseckite, (Fe,Zn,Mn)S, a New Mineral in Zakłodzie, an Ungrouped Enstatite-rich Achondrite.

Chi Ma\*, John R. Beckett, George R. Rossman; Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena CA 91125, USA; \*chi@gps.caltech.edu.

**Introduction:** The Zakłodzie meteorite, a moderately weathered find discovered near the village Zakłodzie, Poland, is an ungrouped enstatite-rich achondrite ascribed to an impact melt [1] or internal melting within the parent body [2]. During our nano-mineralogy investigation of the Zakłodzie meteorite, a new Fe-dominant monosulfide mineral, (Fe,Zn,Mn)S with the  $P6_3mc$  wurtzite-type structure was identified and named “buseckite”. We used electron probe microanalysis (EPMA), high-resolution scanning electron microscope (SEM), electron backscatter diffraction (EBSD), and micro-Raman to characterize its composition and structure. (Fe,Zn,Mn)S phases similar in composition to buseckite were previously found through EPMA of sulfides in Zakłodzie [3], Yilmia (EL6) [4], and Grein 002 (EL4/5) [5]. We report here the first confirmed (Fe,Zn,Mn)S mineral with a wurtzite-type structure and consider the origin of this phase and implications through its formation and survival for the evolution of the Zakłodzie meteorite. The mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2011-070). The name is in honor of Peter R. Buseck, a mineralogist at the Arizona State University, for his many contributions to mineralogy, meteorite research and transmission electron microscopy.

**Appearance, Chemistry and Crystallography:** Buseckite occurs as scattered irregular to subhedral crystals (4 - 20  $\mu\text{m}$  in dia.) along grain boundaries between two or more of enstatite, sodic feldspar [K-rich ( $\text{An}_{2.2}\text{Ab}_{85.1}\text{Or}_{12.7}$ ) to low-K, moderately calcic plagioclase ( $\text{An}_{20.9}\text{Ab}_{76.6}\text{Or}_{2.5}$ )], quartz, tridymite, and troilite (Figs. 1-2). One buseckite grain contains euhedral laths of sinoite.

Type buseckite is black and opaque with a mean chemical composition of (wt%) S 35.84, Fe 28.68, Zn 23.54, Mn 10.04, Mg 1.18, sum 99.28. The empirical formula, based on 2 atoms *pfu*, is:  $(\text{Fe}_{0.46}\text{Zn}_{0.32}\text{Mn}_{0.16}\text{Mg}_{0.04})\text{S}_{1.01}$ , yielding a simplified formula of (Fe,Zn,Mn)S. We observed no significant within grain or grain-to-grain differences in composition among buseckites.

EBSD patterns of buseckite can only be indexed using the wurtzite structure and this yields a best fit based on unit cell data for synthetic  $(\text{Zn}_{0.558}\text{Fe}_{0.442})\text{S}$  [6]. Buseckite has a hexagonal close packed structure, Space Group:  $P6_3mc$ , showing  $a = 3.8357 \text{ \AA}$ ,  $c = 6.3002 \text{ \AA}$ ,  $V = 80.27 \text{ \AA}^3$  and  $Z = 2$ .

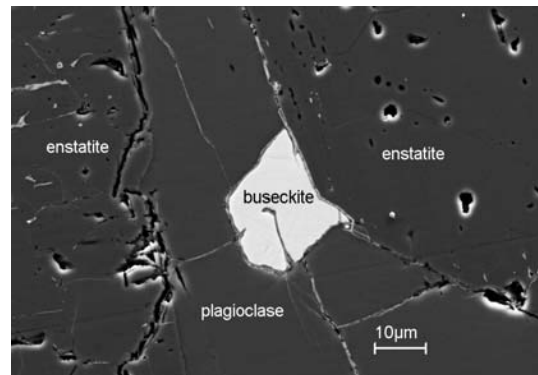


Fig. 1. SEM secondary electron (SE) image showing a buseckite grain with plagioclase and enstatite.

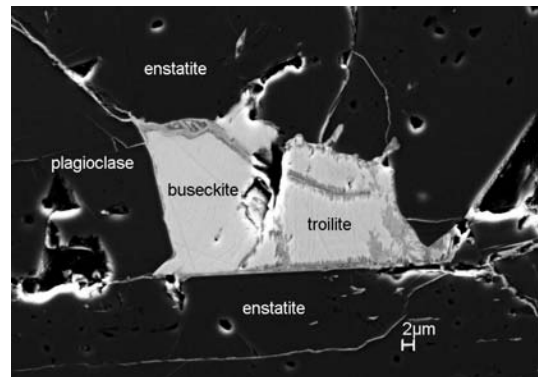


Fig. 2. SE image showing buseckite with troilite, plagioclase and enstatite.

**Occurrence and Associated Minerals:** Buseckite occurs with enstatite, plagioclase, sinoite, troilite  $[\text{Fe}_{0.86}\text{Cr}_{0.06}\text{Mn}_{0.02}\text{Ti}_{0.02}\text{S}]$ , quartz, tridymite, cristobalite, low-Ni iron, martensitic iron, schreibersite, keilite, and graphite. One or both of enstatite and silica are in contact with each buseckite grain but alloys, which comprise roughly 20 volume % of the meteorite [2], are not. From EBSD and/or Raman, silica in Zakłodzie is mostly tridymite. Quartz is associated with sinoite; we observed one cristobalite grain next to tridymite.

**Origin and Significance:** Zakłodzie is generally thought to be an impact melt of an enstatite-rich precursor (e.g., [1] but see [2]). Overall, the silicates imply peak temperatures above  $\sim 1500^\circ\text{C}$  followed by rapid cooling. High temperature phase relations for the opaque assemblage can be treated, ignoring graphite and minor Mn-Zn-Ca sulfides, in terms of the Fe-Ni-S system. For 20 volume % alloy and 10 % sulfide, average densities of 8 and 4  $\text{g/cm}^3$ , respectively, and assuming that the sulfide is dominated by troilite, we

obtain a bulk composition of ~70 mole % Fe, 2% Ni and 28 % S. The model of [7] for the Fe-Ni-S system yields an alloy as the liquidus phase for this bulk composition, appearing at ~1300°C, well below peak temperatures for the silicate melting event and consistent with alloys and sulfides occurring interstitially between silicates. No sulfides crystallize above 1000°C (i.e., sulfides form at temperatures below the solidus for silicates). Initially, Zn, along with other minor elements such as Cr, Ti, and Mn, is likely accommodated in pyrrhotite so that a separate Zn-rich phase does not form. However, pyrrhotite breaks down at lower temperatures and sulfides such as troilite, alabandite, keilite, and niningerite, so produced, have no significant solubility for Zn. Daubréelite, a Cr sulfide, can accommodate considerable Zn [8] but this phase is not observed in Zakłodzie. Apparently, under the relatively high temperatures of equilibration for Zakłodzie, keilite and troilite were able to accommodate the Cr and cooling was sufficiently fast so that exsolution of Cr-rich phases such as daubréelite did not occur. The lack of a sulfide with a significant solubility for Zn ultimately led to the formation of buseckite, probably as a breakdown product of pyrrhotite. This scenario would be consistent with the observed association of troilite with buseckite in Zakłodzie.

[5] found that Zakłodzie keilites equilibrated down to 500-600°C. This provides a likely approximate temperature range for which chemical exchange between buseckite and troilite also ceased and it provides a significant line of evidence for rapid cooling rates as equilibrium among metal, troilite, and (Ca,Mg,Mn,Fe) monosulfides is readily achieved in days to months at 500-600°C [9-10].

[11] showed that Fe dominant Zn-rich monosulfides in Indarch (EH4) have the cubic  $F\bar{4}3m$  sphalerite structure (rudashevskyite), whereas the Fe dominant Zn-rich monosulfides in Zakłodzie are buseckites ( $P6_3mc$  wurtzite structure), a difference in structure that reflects differences in composition and formation conditions. In general, for a given bulk composition, the  $P6_3mc$  wurtzite structure is stable at high temperatures and the  $F\bar{4}3m$  sphalerite structure at lower temperatures. Although generally treated as a monosulfide, Zn-S sphalerite is also slightly metal deficient and wurtzite slightly sulfur deficient relative to a metal/sulfur ratio of 1:1, so that higher sulfur fugacities favor the sphalerite structure [10]. The effect of different metals on the transition temperature is quite variable. For pure ZnS, wurtzite is stable only above ~1020°C but the minimum transition temperature drops to as low as ~850°C in FeS-ZnS [12] and ~820°C in Ga<sub>2</sub>S<sub>3</sub>-ZnS [13]. Thus, both Fe and Ga sta-

bilize the  $P6_3mc$  wurtzite-structured compounds relative to the  $F\bar{4}3m$  sphalerite structure. Mn and Mg are very strong wurtzite structure stabilizers [14-15]. In MnS-ZnS, the minimum temperature for a stable wurtzite structure monosulfide is only ~350°C. Thus, other things being equal, Zn-enriched monosulfides with high Mn or Mg (e.g., buseckite from Zakłodzie), are more likely to have the wurtzite structure than are monosulfides plotting closer to the FeS-ZnS join.

Buseckite in Zakłodzie is relatively Mn-rich and, although it owes its name to its Fe-dominant composition, Mn is actually more important than Fe for its formation and survival. In Indarch (EH4), rudashevskyite formed during relatively low temperature metamorphism [11]. Given the relatively low Mn content, the  $P6_3mc$  -  $F\bar{4}3m$  transition is probably greater than ~800°C (i.e., higher than peak metamorphic temperatures), so it is unlikely that buseckite ever formed during metamorphism of this meteorite. In the more primitive EH3 chondrites, however, Zn-enriched monosulfides may have formed under a variety of high and low temperature planetary and nebular environments. The more Mn-rich of these grains may be buseckites and, if there is a mixture of buseckites and rudashevskyites, the distribution of structure types among the grains could be used to constrain thermal history, although this can't be quantified at present. In EL4-6 chondrites, the Zn-rich monosulfides have high Mg+Mn, comparable to concentrations observed in Zakłodzie. The structure type(s) for these sulfides have not been determined but the high Mn+Mg favors buseckite. Overall, high formation temperatures, fast cooling rates, to avoid inversion to the sphalerite structure on cooling, high Mn(+Mg) contents to lower the inversion temperature, and low sulfur fugacities favor buseckite over rudashevskyite.

**References:** [1] Keil K. (2010) *Chem. Erde* 70, 295. [2] Przylibski T.A. et al. (2005) *MAPS* 40, A185. [3] Karwowski L. et al. (2007) *Amer. Mineral.* 92, 204. [4] Buseck P.R. and Holdsworth E.F. (1972) *Meteoritics* 7, 429. [5] Patzer A. et al. (2004) *MAPS* 39, 1555. [6] Kullerud G. (1953) *Norsk Geol. Tidssk.* 32, 61. [7] Waldner P. and Pelton A.D. (2004) *Metall. Trans.* 35B, 897. [8] Lin Y. and El Goresy A. (2002) *MAPS* 37, 577. [9] Skinner B.J. and Luce F.D. (1971) *Amer. Mineral.* 56, 1269. [10] Scott S.D. and Barnes H.L. (1972) *Geochim. Cosmochim. Acta* 36, 1275. [11] Britvin S.N. et al. (2008) *Amer. Mineral.* 93, 902. [12] Knitter St. and Binnewies M. (1999) *Z. Anorg. Allg. Chem.* 625, 1582. [13] Zhang J.M. et al. (1990) *J. Amer. Ceram. Soc.* 73, 1544. [14] Brightwell J.W. et al. (1984) *J. Mater. Sci. Lett.* 3, 951. [15] Tauson V.L. et al. (1977) *Geochem. Int.* 14 (3), 33.