

LETTER

Browneite, MnS, a new sphalerite-group mineral from the Zakłodzie meteorite

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ABSTRACT

Browneite (IMA 2012-008), MnS, is a new member of the sphalerite group, discovered in Zakłodzie, an ungrouped enstatite-rich achondrite. The type material occurs as one single crystal (~16 μm in size) in contact with and surrounded by plagioclase; enstatite and troilite are nearby. Low-Ni iron, martensitic iron, tridymite, quartz, cristobalite, sinoite, schreibersite, buseckite, keilite, and graphite, are also present in the type sample. Browneite is yellowish brown and translucent. The mean chemical composition, as determined by electron microprobe analysis of the type material, is (wt%) S 36.46, Mn 62.31, Fe 0.62, Ca 0.10, sum 99.49, leading to an empirical formula calculated on the basis of 2 atoms of $(\text{Mn}_{0.993}\text{Fe}_{0.010}\text{Ca}_{0.002})\text{S}_{0.995}$. Electron back-scatter diffraction patterns of browneite are a good match to that of synthetic β -MnS with the $F\bar{4}3m$ structure, showing $a = 5.601 \text{ \AA}$, $V = 175.71 \text{ \AA}^3$, and $Z = 4$. Browneite is a low-temperature (<200 $^{\circ}\text{C}$) phase, metastable relative to alabandite, that postdates the impact melting and subsequent crystallization of an enstatite-rich rock.

Keywords: Browneite, MnS, new mineral, sphalerite group, EBSD, Zakłodzie meteorite, enstatite achondrite

INTRODUCTION

The Zakłodzie meteorite, which is a moderately weathered find discovered near the village of Zakłodzie, Poland, in September 1998, is an ungrouped enstatite-rich achondrite with likely affinities to enstatite chondrites. Its origin has been ascribed to impact melting (e.g., Keil 2010) and to internal melting within the parent body (Przylibski et al. 2005). During a nano-mineralogy investigation of this meteorite, a new manganese monosulfide mineral, MnS with a $F\bar{4}3m$ sphalerite structure was identified and named “browneite”. Field-emission scanning electron microscope (SEM), electron-backscatter diffraction (EBSD), electron microprobe, and micro-Raman spectroscopic analyses were used to characterize its composition and structure and those of associated minerals. Synthetic β -MnS with space group $F\bar{4}3m$ is a well-known synthetic material (Schnaase 1933; Yang et al. 2012) that has been heavily studied recently because MnS is a P-type semiconductor with a wide band gap (e.g., Yang et al. 2012), making it attractive for applications in short wave optoelectronic devices. It is readily synthesized as a metastable phase at low temperatures (in place of α -MnS or alabandite, which is the stable MnS phase at room temperature) using molecular beam epitaxy and solvothermal reactions (e.g., Skromme et al. 1995; Lu et al. 2001). This study reports the first natural occurrence of MnS with the $F\bar{4}3m$ sphalerite structure, joining alabandite ($Fm\bar{3}m$; NaCl structure) and rambergite ($P6_3mc$, wurtzite structure) as natural polymorphs of Mn monosulfides. We consider the properties and origin of this phase, its relationships to coexisting minerals, and implications through its formation and survival for the evolution of the Zakłodzie meteorite.

MINERAL NAME AND TYPE MATERIAL

The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2012-008) (Ma 2012). The name browneite is in honor of Patrick R.L. Browne (b. 1941), Professor at the University of Auckland, New Zealand, for his contributions to low-temperature mineralogy and petrology. The holotype material in a Caltech Zakłodzie section (ZAK-TS2) has been deposited in the Smithsonian Institution’s National Museum of Natural History, Washington, D.C., and is cataloged under USNM 7607. This section also hosts the type buseckite (IMA 2011-070; Ma et al. 2012).

APPEARANCE, PHYSICAL AND OPTICAL PROPERTIES

The type material is a fractured single crystal (as revealed by EBSD) in USNM 7607, occupying a triangular (in section) region with a maximum dimension of 20 μm . A portion of the crystal has a partially polished surface, ~8 μm across. The phase is surrounded by plagioclase. Troilite (as close as ~2 μm) and enstatite (within ~10 μm), are nearby (Fig. 1).

Browneite is yellowish brown, translucent, and brittle (observed during final phases of section polishing). Synthetic β -MnS, is red or pink (e.g., Yang et al. 2012). Luster, streak, hardness, cleavage, fracture, and details of the optical properties were not determined because of the small grain size. The density, calculated from the empirical formula, is 3.291 g/cm^3 . The crystal is non-fluorescent under the electron beam in an SEM.

CHEMICAL COMPOSITION

Quantitative elemental microanalyses were conducted with a JEOL 8200 electron microprobe operated at 10 and 15 kV and

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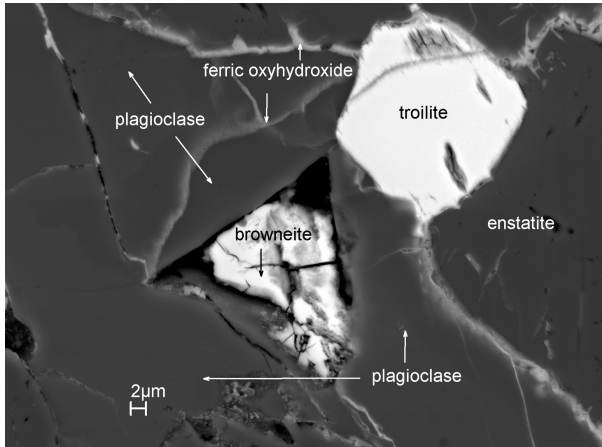


FIGURE 1. SEM backscattered electron image showing a fractured brownite single crystal with associated plagioclase, enstatite, and troilite. When first observed, the brownite crystal occupied most of the central triangular area of the image with no additional phases noted during SEM examination but losses of material during subsequent vibro-polishing left only a small portion of the original brownite crystal intact.

5 nA in focused beam mode. Analyses were carried out in WDS mode and processed with the CITZAF correction procedure of Armstrong (1995). The average of six individual analyses of the type brownite is reported in Table 1. No other elements with atomic number greater than four were detected by WDS scans. In particular, Mg concentrations were below detection levels (<0.07 wt%). The empirical formula, based on two atoms per formula unit, is: $(\text{Mn}_{0.993}\text{Fe}_{0.010}\text{Ca}_{0.002})\text{S}_{0.995}$, yielding a simplified formula of MnS. We observed no evidence for zoning within the type grain.

Alabandite (MnS with the NaCl structure) is a common accessory mineral in enstatite-rich meteorites, although it has not been reported in Zakłodzie. As shown in Figure 2, the compositions of meteoritic alabandites are, based on data of previous studies, far more ferroan (10–25 wt%) and, generally, far more magnesian (0.3–13 wt%; all but one analysis with >1 wt%) than brownite, whose composition is much closer to that of pure MnS, with 0.6 wt% Fe and <0.07 wt% Mg (Table 1). Keilite, which is observed in Zakłodzie (they are at the Mn-rich end of the keilite field shown in Fig. 2), and niningerite are also compositionally distinct from brownite.

CRYSTALLOGRAPHY

Crystallography by EBSD at a sub-micrometer scale was carried out using methods described in Ma and Rossman (2008,

TABLE 1. Mean electron microprobe analytical results for the type brownite

Constituent	wt%*	Range	SD†	Probe standard
S	36.46	36.18–36.73	0.22	MnS
Mn	62.31	61.80–62.90	0.48	MnS
Fe	0.62	0.41–0.92	0.18	FeS
Ca	0.10	0.08–0.15	0.02	anorthite
Mg	b.d.‡			forsterite
Total	99.49			

* Average of six analyses.

† Standard deviation of the mean.

‡ Below detection. Detection limit at 99% confidence is Mg 0.07 wt%.

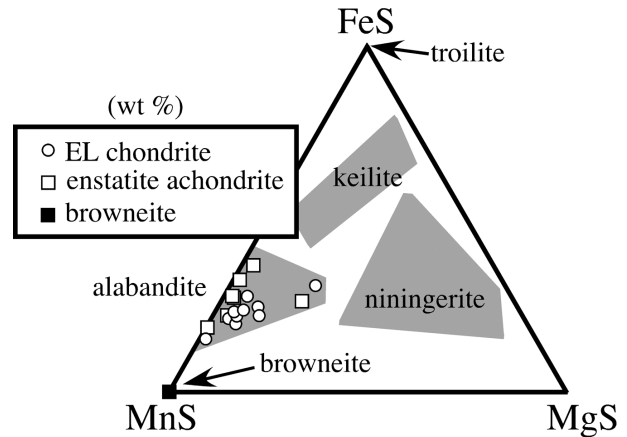


FIGURE 2. Meteoritic brownite and alabandite compositions cast in terms of the ternary MgS-FeS-MnS (wt% basis). Brownite data are from this study. Alabandite compositions are taken from Buseck and Holdsworth (1972), Fogel (2005), Keil and Brett (1974), Lin and El Goresy (2002), McCoy et al. (1995), Okada et al. (1988), Patzer et al. (2004), Rubin (1983b, 1983c, 1984), Rubin and Wasson (2011), and Watters and Prinz (1979). Also shown are fields for keilite and niningerite. These were constructed from published analyses in Ehlers and El Goresy (1988), Gannoun et al. (2011), Ikeda (1989), Karwowski et al. (2007), Keil and Snetsinger (1967), Leitch and Smith (1982), Lin and El Goresy (2002), Ma et al. (2012), Przylibski et al. (2005), Rubin (1983a), Rubin and Wasson (2011), and Shimizu et al. (2002).

2009) with an HKL EBSD system on a ZEISS 1550VP scanning electron microscope operated at 20 kV and 6 nA in focused beam with a 70° tilted stage and in a variable pressure mode (25 Pa). The structure was determined and cell constants were obtained by matching the experimental EBSD pattern (Fig. 3a) against the structures of synthetic alabandite (α -MnS, $Fm\bar{3}m$) (Mehmed and Haraldsen 1938; Sweeney and Heinz 1993), synthetic β -MnS ($F\bar{4}3m$, $F\bar{4}3c$) (Mehmed and Haraldsen 1938), and synthetic rambergite (γ -MnS, $P6_3mc$) (Mehmed and Haraldsen 1938). Among these, only the EBSD of the $F\bar{4}3m$ sphalerite structure yields a good fit for the EBSD pattern of brownite (Fig. 3b). Brownite has a cubic $F\bar{4}3m$ structure, with $a = 5.601 \text{ \AA}$, $V = 175.71 \text{ \AA}^3$, and $Z = 4$. The mean angular deviation is 0.46. No errors are given for the cell parameters because they are taken directly from the data of the matching synthetic phase in Mehmed and Haraldsen (1938). The type material appears to consist of a single crystal with the [111] axis oriented approximately perpendicular to the plane of the thin section. The outline of the cavity within which the brownite is found is roughly triangular,

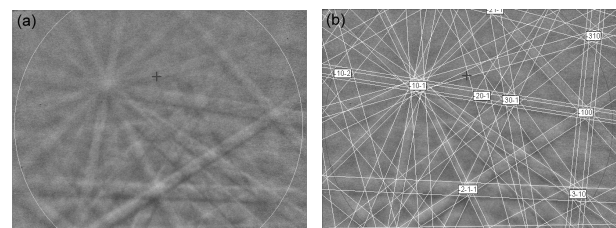


FIGURE 3. (a) EBSD pattern of the brownite crystal shown in Figure 1 and (b) the pattern indexed with the $F\bar{4}3m$ β -MnS structure.

which would be consistent with a single crystal formed prior to incorporation within the surrounding feldspars. However, two of the three bounding surfaces form arcs, so it is much more likely that browneite is occupying an opportunistic void formed by the feldspars. Also, as discussed below, browneite is a low-temperature phase and could not have formed before feldspars that crystallized from a melt. If the triangular region were to be interpreted as the outline of a large, freely formed single crystal, then the browneite is a low-temperature pseudomorph after the putative high-temperature phase.

X-ray powder-diffraction data ($\text{CuK}\alpha 1$) were calculated from the cell parameters of Mehmed and Haraldsen (1938) and the empirical formula of the type browneite from this study using Powder Cell version 2.4 (2000). The strongest X-ray powder diffraction lines are [relative intensity (I), d in Å, (hkl)] (100) 3.234 (111); (63) 1.980 (220); (39) 1.689 (311); (19) 1.143 (422); (14) 1.285 (331); (14) 0.947 (531), (14) 0.886 (620); (9) 1.400 (400). A Raman spectrum for browneite is devoid of either strong or sharp features. It is given in the supplementary material¹.

OCCURRENCE AND ASSOCIATED MINERALS

Przylibski et al. (2005) and Karwowski et al. (2007) provide general descriptions of Zakłodzie, its petrography and chemistry and Ma et al. (2012) give additional data and details specific to polished thin section USNM 7607, within which the type browneite crystal resides. Zakłodzie is an enstatite-rich meteorite with moderate amounts of feldspar and low-Ni iron (formerly known as “kamacite”). It contains minor to trace amounts of martensitic iron, sinoite, schreibersite, and graphite, the silica polymorphs quartz, tridymite, and cristobalite, and the sulfides troilite, keilite, buseckite, and browneite. The position of the type browneite within the Zakłodzie meteorite is not known, although it could be an important clue to its formation because the mineralogy varies significantly with location (Przylibski et al. 2005). The presence of keilite, $(\text{Fe}^{2+}, \text{Mg})\text{S}$, in USNM 7607 (Ma et al. 2012) argues against the sample being from the central portion of the meteorite (Karwowski et al. 2007). The browneite grain is in contact with plagioclase with compositions ranging from K-bearing albite ($\text{An}_6\text{Ab}_{87}\text{Or}_7$ where An, Ab, and Or refer to $\text{CaAl}_2\text{Si}_2\text{O}_8$, $\text{NaAlSi}_3\text{O}_8$, and KAlSi_3O_8 components in the feldspar) to K-poor, moderately calcic plagioclase ($\text{An}_{35}\text{Ab}_{64}\text{Or}_1$). Nearby enstatite is $(\text{Mg}_{0.972}\text{Ca}_{0.007}\text{Fe}_{0.002}\text{Al}_{0.002})\text{Si}_{1.008}\text{O}_3$. The nearby troilite grain shown in Figure 1 has a formula of $(\text{Fe}_{0.86}\text{Cr}_{0.07}\text{Mn}_{0.02}\text{Ti}_{0.01})\text{S}$.

ORIGIN AND SIGNIFICANCE

Browneite ($F\bar{4}3m$), alabandite ($Fm\bar{3}m$), and ramborgite ($P6_3mc$) are all polymorphs of MnS and two, alabandite and (now) browneite, occur in enstatite-rich meteorites. Browneite is also a new member of the sphalerite group.

The Zakłodzie meteorite is an igneous rock that was subjected to very high temperatures, exceeding ~ 1500 °C, followed by rapid cooling. It is generally thought to have formed as an impact-

melt, although Przylibski et al. (2005) preferred melting in the interior of the parent body. Here, we emphasize the lower temperature portions of the thermal history recorded by the sulfides and discuss the origin of browneite within this framework. The interested reader is referred to Ma et al. (2012) and references therein for discussions regarding the igneous history.

Keilites in Zakłodzie are characterized by compositions indicative of high temperatures of equilibration, 500–600 °C, according to Karwowski et al. (2007) and Keil (2007) inferred that the keilite would have re-equilibrated to much lower temperatures had Zakłodzie not formed as a rapidly cooled impact melt. Skinner and Luce (1971) and others (e.g., Scott and Barnes 1972) were readily able to achieve equilibrium at these temperatures among metal, troilite, and (Ca, Mg, Mn, Fe) monosulfides in days to months at temperatures of 500–600 °C. So, the expectation is that slow cooling under planetary conditions would have led to much lower equilibration temperatures for the sulfides. If significant diffusive interactions between sulfides ceased at roughly 500 °C then this would also be true of the troilite and browneite grains shown in Figure 1, even if they were in contact in the third dimension.

At ambient pressure, alabandite (α -MnS) is the stable MnS polymorph from room temperature up to the melting point of 1655 °C (Staffansson 1976; Kang 2010). It is also stable with increasing pressure up to ~ 26 GPa, at which point it breaks down to a phase with lower than hexagonal symmetry (i.e., not to β -MnS, which is cubic; Sweeney and Heinz 1993). This makes it unlikely that browneite could form through shock metamorphism of alabandite, even if the lack of other shock features in the meteorite were to be ignored. β -MnS and presumably browneite, given the near-end-member composition, is a metastable phase formed at or near ambient pressure.

β -MnS is readily synthesized by bubbling H_2S through hot Mn-enriched aqueous solutions at 50–100 °C (e.g., Schnaase 1933), via solvothermal reactions at somewhat higher temperatures (190–200 °C; Lu et al. 2001) and through thin film deposition using molecular beam epitaxy (Prior et al. 2011; Skromme et al. 1995). In all cases, the phase reverts to the stable α -MnS if given half a chance. If the thin film gets too thick, it reverts to an amorphous form or to α -MnS (i.e., alabandite). If the crystals synthesized at 50–200 °C are then annealed at 200–400 °C, they transform into α -MnS (Kennedy et al. 1980). A browneite crystal could, presumably, survive annealing for longer periods of time at lower temperatures but the basic point is that the formation of browneite is restricted to very low temperatures. Thus, bulk exchange between the troilite and browneite grains shown in Figure 1 did not occur, even if they were in contact in the third dimension, because the required temperatures, $> \sim 500$ °C, are too high. Since browneite is a metastable polymorph, scenarios in which alabandite is later transformed into browneite are also not plausible. Once formed, a crystal of browneite could not have been subjected to temperatures above ~ 200 °C.

Based on the above discussion, browneite is a low-temperature metastable phase but the specific mechanism of formation is uncertain. One should be careful of taking a too literal transposition of laboratory synthesis techniques as a direct guide to the mechanism of formation of the natural material as the crystal dimensions for these products, when specified, are in the few tens

¹ Deposit item AM-12-099, supplementary material and figure. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

to few hundreds of nanometer range; the natural material appears, based on orientation determined through EBSD, to consist of a single crystal as much as 20 μm across. We observe no evidence for additional phases in the cavity occupied by the browneite crystal (Fig. 1) that could provide additional clues as to the origin of the browneite and we argued above that the nearby troilite was not a direct participant in the formation of browneite due to the large difference between plausible exchange temperatures involving troilite (~ 500 °C) and the browneite formation temperature (< 200 °C), although it is certainly possible that troilite was involved in the formation of a high-temperature precursor to browneite. Nor can browneite be a simple low-temperature transformation product of high-temperature alabandite because this would require the transformation of a stable phase into a metastable phase. One possible mode of origin for browneite is that it represents a terrestrial weathering product. Ferric oxyhydroxide veins, presumably of terrestrial provenance, occur in the general vicinity of the browneite crystal, including one that contacts the troilite grain next to the browneite crystal shown in Figure 1 and another that appears to intersect one corner of the browneite crystal's cavity. The production of the browneite shown in Figure 1 through terrestrial weathering seems unlikely, because it is a large single crystal. Indeed, the fact that buseckite, a Mn-enriched Fe-Zn monosulfide described by Ma et al. (2012) is partially altered to ferric oxyhydroxide (see their Fig. 1) suggests that the browneite may also be susceptible to terrestrial alteration.

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