

On an unnamed Mg-Mn-Sb oxyborate from the blatterite locality of the Kitteln mine, Nordmark, Filipstad, Värmland, Sweden

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Introduction

Blatterite was described as a new mineral species from the Kitteln mine (Kittelgruvan) at Nordmark, north of Filipstad, Sweden, by Raade et al. (1988). It is an orthorhombic Mg-Mn-Sb oxyborate, differing from related minerals of the orthopinakiolite group by its large unit cell with $a \approx 37.7 \text{ \AA}$. It was shown by an HRTEM investigation (Olsen & Raade 1987, Raade et al. 1988) that blatterite has the structure type $8t8t$ where the numbers equal the number of octahedral layers between a twin plane t .

Cooper & Hawthorne (1998) solved and refined the blatterite structure in space group $Pnmm$ to an R index of 0.043 and established the refined formula $\text{Sb}^{5+}_3(\text{Mn}^{3+}, \text{Fe}^{3+})_9(\text{Mn}^{2+}, \text{Mg})_{35}(\text{BO}_3)_{16}\text{O}_{32}$, based on material from the Långban deposit.

The blatterite-bearing material in the Kitteln mine has evidently been dumped there from a nearby mine (Fig. 1). It was suggested by Raade et al. (1988) that the source might have been the Brattfors mine (Brattforsgruvan). However, the closely situated Moss mine (Mossgruvan) is perhaps more likely, from which Bovin et al. (1986, 1996) have described a blatterite-like mineral (see below).



Figure 1. The Kitteln mine.
Photo by G. Raade 19. June 2010

Already at the time when blatterite was described, it was clear that a different oxyborate mineral existed in the material from the Kitteln mine. Blatterite from Kitteln is embedded in calcite or manganosite and forms very characteristic crystals in the form of {110} prisms that are striated along the length and have a flat, diamond-shaped cross-section (Fig. 2). Crystals up to 5 mm long and 1 mm wide have been reported. They often have dull surfaces. The other mineral is present as much smaller, shiny, prismatic crystals which look well-formed under the binocular microscope but are in fact composed of two or more individuals (Fig. 3). The two oxyborate minerals do not occur together.

The unknown mineral is black with submetallic lustre and occurs in calcite. A small specimen was treated with weak hydrochloric acid, and the extracted crystals were hand-picked under a binocular microscope. We had great hopes that these nice crystals might turn out to be a new species. Mark Cooper of the University of Manitoba has examined a large number of the supposedly individual crystals with a single-crystal diffractometer (personal communication August 2010). Unfortunately, the crystals are not single prisms but complexly intergrown polycrystals (Fig. 3). Only one very small crystal gave a unit cell similar to an Sb-bearing pinakolite from Långban ($a \approx 21.8 \text{ \AA}$) described by Hansen et al. (1988) and Norrestam & Hansen (1990). For some crystals, a unit-cell repeat of 37 \AA was observed, which is equal to that of blatterite, but all spots did not fit a single simple cell. We are reporting here on the work done so far and especially on the chemical composition of the mineral.



Figure 2. BSE image of a striated blatterite crystal from Kitteln. A small cross section is visible below the prismatic crystal.

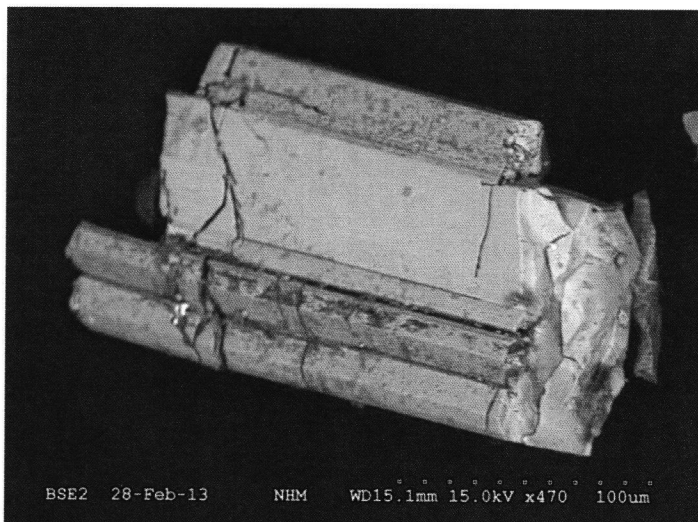


Figure 3. BSE image of an extremely complex aggregate of the unknown oxyborate from Kitteln, displaying five intergrown crystals.

Chemical data

The chemical composition was determined with a Cameca SX100 electron microprobe (EMP) in wavelength-dispersive mode at 15 kV acceleration voltage, 15 nA beam current and with a beam diameter of 1 μm . The probe standards are reported in Table 1. The peaks of the major elements Mg, Mn and Sb were counted for 10 s, and the counting time for the minor elements Fe and Al was 20 s. Ca and Ti were sought but not detected.

The mean result of 17 individual EMP analyses on three grains is presented in Table 1. Two of the grains are irregular whereas a longitudinal section of a prismatic crystal consists of two parts in parallel growth, possibly a twin. Most importantly, the mineral did not show any chemical zonation, and the ranges and standard deviations of the analytical results are quite small.

The two irregular grains have inclusions of a Mg-Mn silicate with a ratio of (Mg+Mn):Si close to 9:4, corresponding to sonolite, $\text{Mn}_9(\text{SiO}_4)_4(\text{OH})_2$, except that the mineral has $\text{Mg} > \text{Mn}$ and the F content is not known. It might well be a new species, the Mg analogue of sonolite. Alleghanyite, sonolite and manganhumite have previously been identified in the blatterite-bearing specimens by X-ray powder diffraction and EMP analyses, and they all have $\text{Mn} > \text{Mg}$. It should be noted that the unknown oxyborate has an appreciably higher Mg content than blatterite, about 24 versus 12 wt% MgO. Thus the blatterite-bearing assemblage is poorer in Mg compared to the assemblage of the unknown oxyborate.

A black, porous Mn oxide associated with the unknown oxyborate turned out to be nearly X-ray amorphous, but the strongest reflection of hausmannite is probably present. Bovin et al. (1996) reported their blatterite-related mineral to be associated with hausmannite and calcite. This is in contrast to blatterite from Kitteln which occurs together with manganosite (Raade et al. 1988). Any associated minerals of blatterite from Långban are not reported.

Table 1. Electron-microprobe analytical data of an unknown oxyborate from Kitteln.

Constituent	Wt%	Range	St. dev.	Standard	Line
MgO	24.11	22.79-25.06	0.66	MgO	Mg-K α
MnO	29.85	39.04-41.64*	0.89*	Pyrophanite	Mn-K α
B ₂ O ₃ **	15.26				
Al ₂ O ₃	0.27	0.24-0.31	0.02	Al ₂ O ₃	Al-K α
Mn ₂ O ₃ ***	11.49				
Fe ₂ O ₃	0.45	0.36-0.59	0.06	Fe metal	Fe-K α
Sb ₂ O ₅	18.15	17.31-18.55	0.32	Sb ₂ S ₃	Sb-L α
Total	99.58				

* Raw data with total Mn as MnO (mean 40.17 wt% MnO)

** Calculated to give B:O = 1:5 (i.e. B = 16 *apfu*)

*** Calculated such that the sum of cations (except B) equals 47 *apfu*.

Tentatively based on a blatterite cell with 80 O atoms, the empirical formula is $\text{Sb}^{5+}_{4.10}(\text{Mn}^{3+}_{5.31}\text{Fe}^{3+}_{0.21}\text{Al}_{0.19})_{\Sigma 5.71}(\text{Mg}_{21.83}\text{Mn}^{2+}_{15.36})_{\Sigma 37.19}(\text{BO}_3)_{16}\text{O}_{32}$. The simplified formula has reasonable subscripts: $\text{Sb}^{5+}_4(\text{Mn}^{3+}, \text{Fe}^{3+})_6(\text{Mg}, \text{Mn}^{2+})_{37}(\text{BO}_3)_{16}\text{O}_{32}$. This can be compared to the composition of blatterite from Långban (Cooper & Hawthorne 1998): $\text{Sb}^{5+}_3(\text{Mn}^{3+}, \text{Fe}^{3+})_9(\text{Mn}^{2+}, \text{Mg})_{35}(\text{BO}_3)_{16}\text{O}_{32}$. The unknown mineral is higher in Sb, has a lower content of trivalent cations and, most importantly, $\text{Mg} > \text{Mn}^{2+}$.

Sb-bearing oxyborates from Långban-type deposits in Sweden have been described on several occasions. In order to make a comparison with these minerals, the empirical formula of the Kitteln mineral is divided by 16 and rearranged, with di- and trivalent Mn combined: $\text{Mg}_{1.36}\text{Mn}_{1.29}\text{Fe}_{0.01}\text{Al}_{0.01}\text{Sb}_{0.26}(\text{BO}_3)\text{O}_2$ (with rounding errors).

→ An unnamed oxyborate from an unspecified locality at Nordmark was described by Dunn et al. (1983): $(\text{Mg}_{1.19}\text{Mn}_{0.81})(\text{Mn}^{3+}_{0.73}\text{Sb}^{3+}_{0.15}\text{Fe}^{3+}_{0.11}\text{Al}_{0.01})(\text{BO}_3)\text{O}_2$ (Sb should be pentavalent). This composition does not match well with our mineral.

→ Sb-rich pinakiolite (space group *C2/m*) from Långban (Norrestam & Hansen 1990) has the structurally refined composition $\text{Mg}_{1.90}\text{Mn}_{0.91}\text{Sb}_{0.19}\text{O}_2\text{BO}_3$, which also does not correspond to our mineral, but see the discussion below.

→ The blatterite-like mineral from Mossgruvan (Bovin et al. 1996) is much closer, $\text{Mg}_{1.33}\text{Mn}_{1.44}\text{Fe}_{0.05}\text{Sb}_{0.17}\text{O}_2\text{BO}_3$, especially with regard to the Mg content.

New single-crystal data

Additional material of the unknown Kitteln mineral was investigated by Mark Cooper in March 2013 (personal communication). On a tiny, twinned crystal it was possible to establish a monoclinic cell with $a = 21.866$, $b = 6.212$, $c = 5.382$ Å, $\beta = 94.38^\circ$, which agrees well with Sb-rich pinakiolite from Långban (Hansen et al. 1988, Norrestam & Hansen 1990). However, it was not possible to come up with a meaningful structure result.

Discussion and conclusion

Bovin et al. (1996) described the structure of a mineral from Mossgruvan, which they called both "blatterite" and "a blatterite mineral", based on a combined single-crystal X-ray and electron microscopy study. The structural model, deduced from HRTEM images, was refined to an *R* value of 0.056. This mineral, with space group *Pnmm* and $a = 37.384$ Å, can be considered as an unnamed Mg analogue of blatterite. Since a structural model was proposed, it could have been defined as a new species. Our unnamed mineral, which is Mg-rich compared to blatterite and is probably also from Mossgruvan, has turned out to be related to Sb-rich pinakiolite from Långban.

The Sb-rich pinakiolite was first described as a new structural variety, although it was noted that it probably fulfilled the requirements of being considered as a new species (Hansen et al. 1988). A structural solution and refinement to *R* = 0.047 was achieved by Norrestam & Hansen (1990). Three chemical formulae have been presented for this mineral. One is based on a combined EMP/WDS and ICP investigation (Hansen et al. 1988), and the two others are derived from single-crystal X-ray data (quoted above) and the result of SEM/EDS analysis (Norrestam & Hansen 1990). Comparing the chemical data of Hansen et al. (1988) with those of the Kitteln mineral reveals an almost identical Sb content but different Mg/Mn ratios (wt%; data for the Kitteln mineral in parentheses): MgO 32.02 (24.11), total Mn as MnO 31.60 (40.17), Sb_2O_5 18.09 (18.15), Al_2O_3 0.22 (0.27), Fe_2O_3 0.06 (0.45).

The fact that some crystals of the Kitteln mineral have cell parameters close to those of Sb-rich pinakiolite from Långban means that they are structurally related but they are not necessarily the same species. This depends on the specific distribution of elements among the various structure sites. It is an important factor that the Långban mineral is quite different in appearance. It has a tabular, micaceous habit and is light olive-green to yellowish brown and bronze-like (Hansen et al. 1988).

Both studies of Sb-rich pinakiolite from Långban report some structural disorder. For the Kitteln crystals, it can be concluded that they have much more severe defects that have prevented a structural solution, and they may be intergrowths of several structure types, as has been shown previously for other oxyborates by HRTEM (Bovin & O'Keeffe 1981, Bovin et al. 1981).

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