# A sakhaite-like mineral from the Kombat Mine in Namibia

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## Abstract

Sakhaite from the Kombat Mine in Namibia is cubic, with $a = 14.749(1)$Å; the space group is a subgroup of $Fd3m$, the density is 2.88 g/cm$^3$, and the index of refraction is $n = 1.642(2)$. It is apparently more highly hydrated than previously described sakhaite, and has more aluminosilicate substitution. The idealized composition is $Ca_{24}Mg_8(BO_3)_8[(BO_3)_y\{AlSi_4(O,OH)_{<16}\}_x](CO_3)_8 \cdot < 8H_2O$ with $x = 0.73$ and $y = 5.0$.

KEYWORDS: sakhaite, Kombat Mine, Namibia.

## Introduction

THE crystallographic and chemical data for sakhaite were summarised by Giuseppetti *et al.* (1977), who showed that harkerite and sakhaite have respective unit cell contents of $Ca_{24}Mg_8$ $[AlSi_4(O,OH)_{16}]_2(BO_3)_8(CO_3)_8(H_2O,Cl)$ and 2 $\{Ca_{24}Mg_8[(BO_3)_8(BO_3)_8](CO_3)_8 (H_2O)\}$. They differ primarily in that half of the BO$_3$ groups of sakhaite are replaced by AlSi$_4$(O,OH)$_{16}$ in harkerite. The crystallographic data are concerned with complex substructure/superstructure relations that are in part related to the chemical substitution mechanism. Because the crystallographic data and their relation to the chemical substitutions are not completely known, in part because

these minerals have been little studied, we have carried out a detailed examination of the sakhaite from a new occurrence at the Kombat Mine in Namibia.

Our results show that this 'sakhaite' is much more highly hydrated than previously described sakhaite, suggesting that it is a separate species. However, because the relations between symmetry and crystal chemistry are still incompletely defined, we refer to it as sakhaite until further distinctions, if any, can be made; in this manner, nomenclatural simplicity is maintained. All of the results reported herein were obtained from the core of one 4 mm diameter crystal. The cores of crystals are transparent and appear to be homo-

geneous, but the rims of these crystals are nearly opaque white, implying some heterogeneity.

## Occurrence

The sakhaite specimen described herein was found at the Kombat Mine, which is located 49 km south of Tsumeb, in Namibia. The sakhaite crystals were extracted from massive, friable hausmannite collected in the Asis West mining sector in June of 1984. Individual crystals are up to 8 mm in size, and many are connected by thin (<0.2 mm thick) cross-fibre, thread-like seams of sakhaite traversing the hausmannite matrix. The other associated minerals are copper, calcite, and kombatite.

The specific locality was the 1208 metre elevation of the W90 (south-east) stope on 12 level in the Asis West sector of the mine. This is also the type locality for kombatite (Dunn *et al.*, 1986). At a higher elevation in the same stope, on the same stratigraphic level, altered octahedra of sakhaite to 3.2 cm were collected from the same granular, friable hausmannite ore. Some crystals had inclusions of vesuvianite and hausmannite.

Sakhaite was noted to occur only in a single, thin (3–10 cm thick) zone sited about 0.6 m above the sharp contact between the layered manganese ores and the footwall-sited, massive hematite-magnetite ores. A 4 cm thick zone of pale blue, granular glaucochroite associated with crystals of vesuvianite and copper was sited 10 cm stratigraphically above the sakhaite zone, separated from it by granular hausmannite–calcite ore.

## Description

The Kombat Mine sakhaite occurs as euhedral crystals abundantly distributed in bands and as isolated crystals, as described above. The crystals are octahedral; no other forms are discernible. Many such octahedral crystals are zoned; sakhaite occurs as light pink, transparent glassy cores of composite crystals. The exteriors of such composite crystals are turbid and nearly opaque; they are composed of either a new mineral or a mixture of minerals unknown to us, but cannot be characterised at this time due to the extremely fine grain size and poor quality of the material. The density of Kombat sakhaite is 2.88 g/cm$^3$, determined using heavy liquid techniques; the lustre is vitreous; and no cleavage was observed. The index of refraction is $n = 1.642(2)$ and calculation of the Gladstone-Dale relationship (Mandarino, 1981) yields $K_C = 0.216$ and $K_P = 0.223$ indicating excellent compatibility of the optical and physical data.

Sakhaite also occurs in smaller pink crystals which are clear throughout and have no overgrown mineral present, as evidenced by X-ray powder diffraction patterns. However, most of these crystals are quite impure, containing crystals of calcite, hausmannite, and what may be a brucite-like mineral, all identified using X-ray diffraction methods.

## X-ray crystallography

Irregularly shaped fragments were separated from the core of a single crystal and studied using precession and Weissenberg techniques. The resulting photographs indicated that this sakhaite is cubic, with $a = 14.82$Å. The intense reflections give rise to extinctions consistent with space group $Fd3m$, the pseudosymmetry of harkerite and sakhaite (Giuseppetti *et al.*, 1977). However, the presence of the weak reflection 640 (and its symmetry-equivalents) shows that the $d$-glide is not present, and that the space group must therefore be a subgroup of $Fd3m$. The true space group cannot be defined beyond that restriction. However, we note that Chichagov *et al.* (1974) refined the crystal structure of a 'synthetic sakhaite' in space group $F4_132$, a sub-group of $Fd3m$. Furthermore, Barbieri *et al.* (1977) reported that harkerite from Albano, Italy, is cubic with $a = 14.82$Å and has space group $Fm3m$, $F432$, or $F\bar{4}3m$. The latter is a subgroup of $Fd3m$ and therefore also consistent with the diffraction relations of this study. Drs D. Appleman and J. Post (pers. comm.) have studied the diffraction relations of part of the same crystal we have studied; the resulting intensity data, obtained using a four-circle diffractometer, are consistent with the results of this study.

Giuseppetti *et al.* (1977) showed that harkerite from Skye, Scotland, is trigonal with space group $R\bar{3}m$. There is a pronounced cubic substructure having $a = 14.78$Å, and a pseudocubic superstructure having $a = 2 \times 14.78$Å. Single-crystal photographs of the present study were therefore obtained with long exposures in order to detect weak superstructure reflections, but none was observed. Furthermore, photographs from different orientations that are related by cubic symmetry were obtained and directly compared, but no deviations from cubic symmetry were detected, nor was there any indication of the twinning found by Giuseppetti *et al.* (1977) that would be consequent on the reduction in symmetry to that of the trigonal system.

Powder diffraction data were obtained using a Philips powder diffractometer fitted with a graphite monochromator and using Si as an internal

standard. The data are presented n Table 1, and were used in a refinement of the lattice parameter, giving rise to the value $a = 14.749(1)$Å.

Table 1. Powder X-ray diffraction data for sakhaite from the Kombat Mine [*]

| $I/I_o$ | d(Obs) | d(Calc) | hkl |
|---|---|---|---|
| 13 | 8.50 | 8.51 | 111 |
| 22 | 5.21 | 5.21 | 220 |
| 4 | 4.256 | 4.257 | 222 |
| 3 | 3.687 | 3.687 | 400 |
| 16 | 3.382 | 3.383 | 331 |
| 10 | 3.010 | 3.010 | 224 |
| 6 | 2.837 | 2.838 | 115, 333 |
| 100 | 2.607 | 2.607 | 440 |
| 5 | 2.458 | 2.458 | 442, 600 |
| 6 | 2.331 | 2.332 | 620 |
| 3 | 2.249 | 2.249 | 335 |
| 3 | 2.224 | 2.223 | 226 |
| 40 | 2.129 | 2.129 | 444 |
| 15 | 2.066 | 2.065 | 551, 117 |
| 9 | 1.971 | 1.971 | 642 |
| 14 | 1.844 | 1.844 | 800 |
| 4 | 1.739 | 1.738 | 228, 066 |
| 2 | 1.704 | 1.703 | 555, 751 |
| 2 | 1.693 | 1.692 | 662 |
| 5 | 1.650 | 1.649 | 048 |
| 2 | 1.619 | 1.619 | 357, 119 |
| 2 | 1.573 | 1.572 | 664 |
| 12 | 1.505 | 1.505 | 448 |
| 2 | 1.445 | 1.446 | 268, 02,10 |
| 5 | 1.419 | 1.419 | 666, 22,10 |
| 10 | 1.303 | 1.304 | 088 |
| 3 | 1.289 | 1.289 | 179, 599, 13,11 |

[*]Diffractometer data obtained using $CuK_\alpha$ radiation, graphite monochromator, Si internal standard, d-values calculated with the lattice parameter a=14.749 Å.

## Chemical composition

Kombat sakhaite was chemically analysed using a variety of methods. Because the compositions of the sakhaite–harkerite series demonstrate very complex solid-solution relations, and because the precision of our determinations is essential to our interpretation, we provide more detail on the chemical analytical methods employed than is normally given.

The elements Ca, Mg, Al, and Si were determined using an ARL-SEMQ electron microprobe, utilizing an operating voltage of 15 kV and a sample current of 0.025 µA, measured on brass. A wavelength-dispersive microprobe scan indicated the absence of other elements with atomic number greater than 8, except those reported here. The standards used were wollastonite (Ca), and hornblende (Si,Al,Mg). The data were corrected using a modified version of the *MAGIC*-4 program. A number of crystals were analysed and were all found to be very similar in composition.

Carbon was determined with a Leco WR-112 carbon analyser. In this procedure the sample is burned in an induction furnace and swept with a stream of oxygen into a molecular sieve trap. At the end of the burn the trap is heated to release the $CO_2$, which is swept through a thermal conductivity cell. A dolomite limestone, NBS 88a, was used to standardize the instrument.

Boron was determined by atomic absorption spectrophotometry following the procedure described by Weger et al. (1969). The sample was fused with $Na_2CO_3$, leached with water, filtered, and acidified with HC1. The boron was extracted with a five percent solution of 2-ethyl-1,3-hexane diol in chloroform. The extracted boron was aspirated into an acetylene–nitrous-oxide flame and the absorption compared with that of similarly extracted standard solutions prepared from borosilicate glass NBS #93.

Thermogravimetric and evolved gas analyses were performed using a Mettler TA-1 Thermoanalyzer/Inficon IQ200 quadrupole mass spectrometer. Fragments free of translucent whitish exterior zones were selected for analysis. A 5 mg sample was equilibrated at 80% relative humidity; it then lost 0.5wt.% in vacuum at 21°C. Upon heating at 10°/min., in high vacuum, a complex loss of $H_2O$ and $CO_2$ took place between room temperature and the experimental limit of 1030°C. The sample gradually lost 0.4 wt.% to 450°C. This was followed by a rapid continuous loss to 1030°C, at which temperature the loss was considerably slowed but incomplete. The total loss to 1030°C was 17.4wt.%. Water pressure peaks occurred as follows: a minor peak at 245°, a moderate peak at 750°, and possibly a peak at 980°C. $CO_2$ peaks occurred as follows: a minor peak at 550°, a moderate peak at 850°, and a major peak at 995°C. Total water content was estimated at 3 wt.% from the thermal data, of which amount 2 wt.% was tightly bonded (500–900°C). However, subtraction of the independently-derived

$CO_2$ value from the total TG loss leaves 4.8 wt.%, a figure significantly higher than the estimated water content of 3 wt.%. This may be due to a possible loss of undetected B-rich volatiles. Calculations are based on a water content of 4.8 wt.%, with the recognition that the true value may be as low as 3 wt.%.

The resultant analyses yielded: CaO 46.4, MgO 11.7, $Al_2O_3$ 1.3, $SiO_2$ 6.2, $B_2O_3$ 15.9, $CO_2$ 12.6, $H_2O$ 4.8, total = 98.9 wt.%. As noted above, the TGA-EGA analysis did not go to completion below the 1030 °C limit of the instrument, and approximately 1 wt.% of material may have been unaccounted for; thus, the slightly low summation of the analyses is quite acceptable, especially considering the difficulties inherent in analyses of light elements.

Calculation of unit cell contents, utilizing the observed density and refined unit cell parameter, for determined elements yields results in good agreement with the 64 octahedral cations in the formula given by Chichagov *et al.* (1974). Their structural formula of sakhaite, determined on synthetic material, is $Ca_{24}Mg_8(BO_3)_8(BO_3)_8$ $(CO_3)_8 \cdot H_2O$, for the end-member. However, few sakhaites conform to this idealized formula (Barbieri *et al.*, (1977). Giuseppetti *et al.* (1977) have noted that, in the very closely related mineral harkerite, $(BO_3)_8$ is replaced by $[AlSi_4(O,OH)_{16}]_2$. We have interpreted the Kombat sakhaite as having the same replacement, such that nearly 1/4 of the $(BO_3)$ groups have been so replaced. The formula of Kombat sakhaite, calculated on the basis of 82 oxygens, with Z = 2, is: $Ca_{23.51}Mg_{8.25}$ $(BO_3)_8[(BO_3)_{4.98}Al_{0.72}Si_{2.93}O_{11.15}]$ $(CO_3)_{8.13}$ · $7.57H_2O$, in which the contents of the square brackets [] represent the partial replacement of $(BO_3)_8$ of idealized sakhaite by ~4$(BO_3)$ groups and aluminosilicate. The idealized formula for this Kombat sakhaite is $Ca_{24}Mg_8(BO_3)_8[(BO_3)_y$ $\{AlSi_4(O,OH)<_{16}\}_x](CO_3)_8$ · <8$H_2O$, with x = 0.73 and y = 5.0.

Aside from the complex borate-aluminosilicate substitution, the other most notable aspect of this Kombat sakhaite is the apparent high water content, which is released at relatively high temperatures. Although we have calculated the above formula in accordance with the most recent structure determination, we agree with Barbieri *et al.* (1977) that few sakhaites approach this composition; most have Cl, which is unaccounted for in the structural formula, and all have less water (or hydroxyl) than the Kombat material. Most sakhaites have approximately 26–28 boron atoms per cell, as does the Kombat material, which extends the known aluminosilicates substitution within the sakhaite symmetry beyond that given by Barbieri *et al.* (1977).

Much work remains to be done on the structure of sakhaite, the significance and site of Cl, the presence or absence of (OH), and the possible existence of tightly bonded $H_2O$. Although the Kombat material may represent a unique composition, and thus be a new phase, until such structural relations are clear, we consider it best not to name it, and to use the appelation sakhaite so as to keep the literature neat and uncluttered.

## Acknowledgements

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