

The crystal structure of kamphaugite-(Y)

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Abstract: The crystal structure of kamphaugite-(Y) from Hørtekollen, Norway, $\text{CaY}(\text{CO}_3)_2(\text{OH})\cdot\text{H}_2\text{O}$, $P4_12_12$, $a = 7.434(1)$, $c = 21.793(3)$ Å, $Z = 8$, has been refined isotropically to $R = 0.067$ for 2566 observed reflections. The structure is built of corrugated sheets parallel to (001), consisting of CO_3^{2-} groups and polyhedra of Y in 9-coordination and Ca in 8-coordination. The hydrogen bonding scheme is predicted from bond-valence calculations. A higher water content, corresponding to $\text{Ca}_2\text{Y}_2(\text{CO}_3)_4(\text{OH})_2\cdot 3\text{H}_2\text{O}$, was obtained from chemical analysis, but is not confirmed by the structure investigation. Channels present between the corrugated sheets are not large enough to accommodate an extra water molecule in a special position.

Key-words: kamphaugite-(Y), crystal structure, hydrogen bonding, carbonate.

Introduction

The new mineral kamphaugite-(Y) has been described from the Hørtekollen helvite occurrence, a contact-metamorphic skarn deposit of the Oslo region, Norway (Raade & Brastad, 1993). Chemical analysis by electron microprobe and CHN elemental analyser yields the empirical formula $\text{Ca}_{1.95}(\text{Y}_{1.61}\text{REE}_{0.27})_{\Sigma 1.88}(\text{CO}_3)_{4.00}(\text{OH})_{1.54}\cdot 3.22\text{H}_2\text{O}$ and the ideal formula

$\text{Ca}_2(\text{Y,REE})_2(\text{CO}_3)_4(\text{OH})_2\cdot 3\text{H}_2\text{O}$. The mineral has been previously reported – but with insufficient data for full characterization – from Kazakhstan (Stepanov, 1961), Transvaal, South Africa (Verwoerd, 1963), and from the Evans-Lou pegmatite, Quebec, Canada (Hogarth, 1972). A second Norwegian occurrence is an amazonite pegmatite at Tørdal, Telemark, where it occurs as an alteration product of kuliokite-(Y) (Raade *et al.*, 1993). A third Norwegian locality is the Tangen granite pegmatite quarry near Kragerø (Raade & Brastad, 1993).

Kamphaugite-(Y) from the Hørtekollen locality is well crystallized. The crystals, which are platy on {001} and rarely more than 1 mm across, typically form divergent or rosette-shaped aggregates. This mode of crystallization makes it dif-

ficult to select crystal fragments suitable for single-crystal study. What might appear as single crystals turn out in most cases to be composed of subparallel platelets. We have succeeded in isolating a crystal fragment from which it was possible to determine the crystal structure, as reported below.

Single-crystal X-ray data

The single-crystal X-ray data were collected on a SYNTEX P1 diffractometer at room temperature, using graphite crystal monochromatized $\text{MoK}\alpha$ radiation. Cell parameters were determined by a least-squares fit to the diffractometer settings for 15 general reflections with $2\theta > 33^\circ$. The crystal data are shown in Table 1. Intensity data were collected by the ω scan technique, with a scan speed of 2°min^{-1} and scan width 2° with an additional dispersion term; background counts were taken for 0.35 times the scan time at each of the scan limits. All reflections within a quadrant of reciprocal space out to a $\sin\theta/\lambda$ value of 0.90 Å^{-1} were measured. Three standard reflections were measured at regular intervals during data collection; a systematic variation of up to 2% was corrected in the data reduction procedure. Out of

Table 1. Crystal data and experimental details.

(A) Crystal cell data	
<i>a</i> (Å)	7.434(1)
<i>c</i> (Å)	21.793(3)
<i>V</i> (Å ³)	1204.4(4)
Space group	<i>P</i> 4 ₁ 2 ₁ 2 (No. 92)
Ideal formula	CaY(CO ₃) ₂ (OH)·H ₂ O
<i>Z</i>	8
Density <i>D</i> _x (g cm ⁻³)	3.11
μ (MoK α) (cm ⁻¹)	105.8
(B) Intensity measurements	
Crystal size (mm)	ca. 0.4 × 0.4 × 0.02
Diffractometer	SYNTEX P1
Radiation; wave	
length λ (Å)	MoK α ; 0.71069
Scan mode	ω
Scan speed (° min ⁻¹)	2.0
Scan range (°)	2.0
Maximum $\sin\theta/\lambda$ (Å ⁻¹)	0.90
Independent reflections	2675
Obs. reflections	
<i>m</i> [<i>I</i> > 3 σ (<i>I</i>)]	2566
Refined parameters <i>n</i>	51
(C) Structure refinement	
$R = \sum(F_o - F_c) / \sum F_o $	0.067
$R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$	0.081
$S = [\sum w(F_o - F_c)^2 / (m - n)]^{1/2}$	5.8

2675 measured unique reflections, 2566 with $I > 3.0\sigma(I)$ were retained for the structure analysis. An estimate of the standard deviation is based on counting statistics with an additional term of 2% of the net intensity. The intensities

are corrected for Lorentz and polarization effects and an empirical absorption correction is also applied (Walker & Stuart, 1983). A summary of the experimental details is listed in Table 1. Descriptions of the computer programs applied are given by Mallinson & Muir (1985) and by Gilmore (1984).

Structure determination

Atomic coordinates of all non-hydrogen atoms were determined by direct methods (Gilmore, 1984) and refinements were performed by least-squares calculations. Dispersion corrections were taken into account in order to ascertain the correct space group. The electron probe analysis (Raade & Brastad, 1993) indicates a certain amount of rare-earth elements, and the least-squares procedure continued with the assumption of some Gd in the Y position and some Y in the Ca position (see Discussion). The population was refined for each of the metal sites with the restriction that the sum of the metal ions is 1. The isotropic refinement converged to the parameters given in Table 1, the conventional *R*-factor being 0.067. No significant improvement of the *R*-factor was obtained by introducing anisotropy into the thermal parameters. The relatively high absorption correction ($\mu = 105.8 \text{ cm}^{-1}$) causes high uncertainties in the thermal parameters, and the anisotropic refinement is therefore not reported here. Although the chemical analysis clearly indicates three water molecules per 4CO₃, only two were detected by the structure determination. Difference Fourier calculations gave no indication of hydrogen atoms

Table 2. Atomic parameters for kamphaugite-(Y).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ²)
Y(1)*	0.99024(10)	0.76810(9)	0.56887(3)	0.0087(2)
Ca(1)**	0.9975(2)	0.2618(2)	0.5633(1)	0.0074(4)
C(1)	0.6734(11)	0.5487(11)	0.5767(4)	0.013(2)
C(2)	0.3251(10)	0.9596(11)	0.5864(4)	0.009(2)
O(1)	0.8126(7)	1.0108(8)	0.5357(3)	0.012(1)
O(2)	0.0146(9)	0.3030(8)	0.2776(3)	0.019(1)
O(11)	0.6910(8)	0.7035(9)	0.6021(3)	0.015(1)
O(12)	0.5441(9)	0.4521(9)	0.5873(3)	0.025(2)
O(13)	0.8047(8)	0.5036(9)	0.5387(3)	0.022(2)
O(21)	0.4672(9)	1.0420(8)	0.6029(3)	0.022(2)
O(22)	0.2867(9)	0.8083(8)	0.6096(3)	0.018(1)
O(23)	0.2109(8)	1.0255(8)	0.5468(3)	0.016(1)

* Population factors: 0.90(1) Y, 0.10(1) Gd

** Population factors: 0.93(1) Ca, 0.07(1) Y

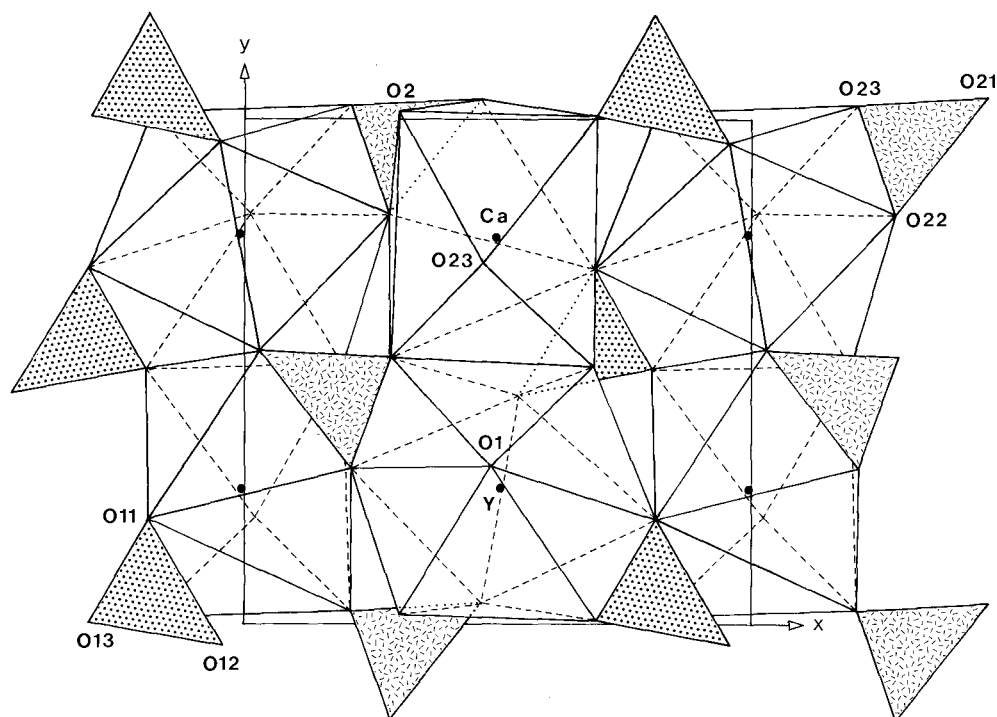


Fig. 1. Crystal structure of kamphaugite-(Y) projected onto (001), showing the corrugated sheet (approximately between $z=1/2$ and $3/4$). Note that one face of the Ca-polyhedra, O(1)-O(11)-O(13), appears as a line in this projection.

nor could any additional water molecule be found. Final atomic parameters are listed in Table 2 and bond distances in Table 3. Tables of observed and calculated structure factors are available from the authors or from the Editorial office.

Description of the structure

The structure was solved in space group $P4_12_12$. The cell content is $8[\text{CaY}(\text{CO}_3)_2(\text{OH})\cdot\text{H}_2\text{O}]$. There are two non-equivalent carbon sites in the structure. All atoms are in general positions with multiplicity 8. The Ca atom is in irregular 8-coordination with a long bond distance Ca-O(21) of 2.781 Å. The Y atom is in 9-coordination, two of the bonds being distinctly longer than the others (Table 3).

The triangular carbonate groups and the Ca- and Y-polyhedra form corrugated sheets parallel to (001). A basal projection of a single sheet is shown in Fig. 1 and an (100) projection of the full cell in Fig. 2. Each Y-polyhedron is connected within the sheets to two Ca-polyhedra through

Table 3. Bond distances (Å).

C(1)-O(11)	1.28(1)	C(2)-O(21)	1.27(1)
C(1)-O(12)	1.22(1)	C(2)-O(22)	1.26(1)
C(1)-O(13)	1.32(1)	C(2)-O(23)	1.31(1)
mean	1.27	mean	1.28
Y(1)-O(1)	2.350(6)	Ca(1)-O(1)	2.395(6)
Y(1)-O(1)	2.309(6)	Ca(1)-O(2)	2.517(7)
Y(1)-O(2)	2.593(7)	Ca(1)-O(11)	2.356(7)
Y(1)-O(11)	2.388(7)	Ca(1)-O(13)	2.361(7)
Y(1)-O(12)	2.473(7)	Ca(1)-O(21)	2.781(7)
Y(1)-O(13)	2.491(7)	Ca(1)-O(22)	2.348(7)
Y(1)-O(21)	2.415(7)	Ca(1)-O(23)	2.395(7)
Y(1)-O(22)	2.395(7)	Ca(1)-O(23)	2.438(6)
Y(1)-O(23)	2.566(6)	mean	2.449
mean	2.442		

common corners, O(11) and O(22), to one Ca-polyhedron by edge-sharing along O(23)-O(1) and to one Ca-polyhedron by face-sharing on O(2)-O(21)-O(13). The Ca-polyhedron is connected within the sheets to four Y-polyhedra in a similar fashion (Fig. 1).

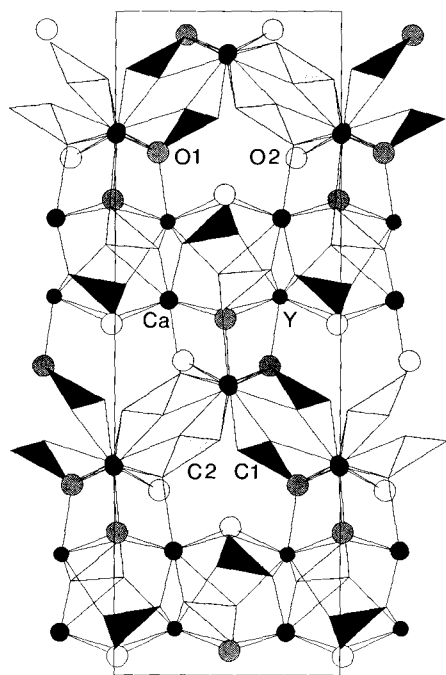


Fig. 2. Crystal structure of kamphaugite-(Y) projected onto (100). The y -axis is horizontal and the z -axis is vertical, the origin is at the centre of the drawing. Carbonate groups are shown as triangles. The two oxygen atoms O(1) and O(2) that are not bonded to the carbonate groups are drawn as spheres; O(1) is the donor atom of a hydroxyl group and O(2) belongs to a water molecule. The 8-coordination of Ca and the 9-coordination of Y are clearly visible. Channels parallel to x (and y) are seen as open spaces between the corrugated (001) sheets at z -parameters 0, 1/4, 1/2 and 3/4.

The sheets are interconnected through the oxygen atoms O(1) and O(23), which are bonded to $2Y+1Ca$ and to $1Y+2Ca$, respectively. Accordingly, each Y-polyhedron is connected to one Y-polyhedron in the adjacent sheet by edge-sharing along O(1)-O(1) and to one Ca-polyhedron by edge-sharing along O(1)-O(23). Similarly, each Ca-polyhedron has a common edge O(23)-O(23) with another Ca-polyhedron and a common edge O(1)-O(23) with a Y-polyhedron in the adjacent sheet. Channels parallel to the x - and y -axes are present between the corrugated sheets at $z=0, 1/4, 1/2$ and $3/4$ (Fig. 2). The relatively few bonds between the sheets would imply a perfect cleavage on {001}, although this could not be observed with certainty because of the thin platy {001} nature of the crystals (Raade & Brastad, 1993).

For a better comprehension of the structure, it is possible to make a transparency of the (001) projection (Fig. 1). The transparency is then placed over the original to match exactly, then turned 90° around one of the 4_1 -axes (at the mid-points of the cell edges). If kept a few cm above the original, an image is obtained of the sheet below or above, according to whether the movement is clock- or anticlockwise, respectively.

Bond valences and hydrogen bonding

A bond-valence summation is presented in Table 4. The valencies of Y, C(1) and C(2) are close to the theoretical values. The Ca site shows a significantly higher value of 2.298 v.u., which indicates some substitution of REE and/or Y for Ca.

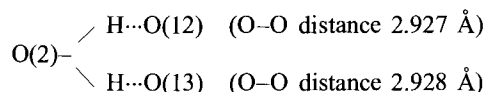
Bond summations for the oxygen atoms show that O(1) is the donor atom for a hydroxyl group, and that O(2) must belong to a water molecule.

Table 4. Bond-valence table (valence units).

	Y(1)	Ca(1)	C(1)	C(2)	Σ
O(1)	0.409	0.315			1.181
	0.457				
O(2)	0.212	0.226			0.438
O(11)	0.369	0.349	1.346		2.064
O(12)	0.293		1.583		1.876
O(13)	0.279	0.345	1.208		1.832
O(21)	0.343	0.111		1.383	1.837
O(22)	0.362	0.357		1.421	2.140
O(23)	0.228	0.315		1.241	2.064
		0.280			
Σ	2.952	2.298	4.137	4.045	13.432

Empirical bond-valence parameters from Brown & Altermatt (1985).

There are three oxygen atoms – O(12), O(13) and O(21) – with bond valences around 1.8 v.u., indicating that they are acceptor atoms in the hydrogen bonding. From steric and bond-length considerations, it may be concluded that the hydroxyl is bonded O(1)-H...O(21) (O–O distance 2.965 Å) and the water molecule is bonded



The bond from the hydroxyl group lies within the sheet, whereas the water molecule has one hydrogen bond to O(12) within the sheet and the other to O(13) across to the adjacent sheet.

Water content of kamphaugite-(Y)

From the chemical analysis, a formula with $3\text{H}_2\text{O}$ per 4CO_3 has been proposed by Raade & Brastad (1993). Nevertheless, only $2\text{H}_2\text{O}$ is implied from the structural investigation. If the fully hydrated kamphaugite-(Y) has a cell content of $4[\text{Ca}_2\text{Y}_2(\text{CO}_3)_4(\text{OH})_2\cdot 3\text{H}_2\text{O}]$, it follows that the four extra water molecules compared to the unit-cell content $8[\text{CaY}(\text{CO}_3)_2(\text{OH})\cdot\text{H}_2\text{O}]$, as determined from X-ray refinement, should have a multiplicity of 4 and thus be situated in a special position. This fixes the z -parameter to 0, $1/4$, $1/2$ and $3/4$. It is evident from Fig. 2 that there are channels in the structure between the corrugated sheets at such z -coordinates. However, these are not large enough to accommodate extra water molecules. Calculations show that an oxygen atom situated at $1/2$, $1/2$, $1/2$ is only 1.96 Å apart from its nearest neighbour O(12). Three other atoms – O(2), O(13) and C(1) – are closer than 2.8 Å.

It is presently not possible for us to explain the discrepancy in water content as obtained from chemical analysis and structure determination. It should be noted that a similar situation has been described for tengerite by Miyawaki *et al.* (1986). These authors found $\text{Y}_2(\text{CO}_3)_3\cdot 2\text{H}_2\text{O}$ from the structure determination, while the chemical analyses gave up to $2\text{H}_2\text{O}$. They attribute the difference to the presence of zeolitic water in tengerite, but do not give further details on the precise position of the extra water molecules.

Discussion

Yttrium with a coordination as high as 9-fold is typical of carbonate minerals, and is explained by

the low average negative charge of $-2/3$ per oxygen atom in CO_3^{2-} ions (Miyawaki & Nakai, 1987). Minerals chemically related to kamphaugite-(Y) are tengerite $[\text{Y}_2(\text{CO}_3)_3\cdot 2\text{H}_2\text{O}]$, lokkaite $[\text{CaY}_4(\text{CO}_3)_7\cdot 9\text{H}_2\text{O}]$ and kimuraite $[\text{CaY}_2(\text{CO}_3)_4\cdot 6\text{H}_2\text{O}]$. A structural relationship among these three orthorhombic minerals is reflected in their comparable lattice parameters. They are built from different arrangements of corrugated sheets of 9-coordinated Y and carbonate groups, separated by Ca and water in the case of kimuraite and lokkaite (Miyawaki & Nakai, 1987). Kamphaugite has a different kind of corrugated sheet with alternating Ca and Y atoms.

The refined populations of the Ca and Y positions of kamphaugite-(Y) (Table 2) are only of limited usefulness since it was not possible to vary more than two elements at each site. The atomic scattering factor of Gd was chosen because this element is situated about midway in the list of REE and also because of its appreciable content besides Dy in kamphaugite-(Y). The microprobe analytical data (Raade & Brastad, 1993) give the following empirical formula, based on $\text{C}=4$: $\text{Ca}_{1.95}(\text{Y}_{1.61}\text{Nd}_{0.05}\text{Sm}_{0.03}\text{Gd}_{0.05}\text{Dy}_{0.07}\text{Er}_{0.04}\text{Yb}_{0.03})_{\Sigma 1.88}(\text{CO}_3)_{4.00}(\text{OH})_{1.54}\cdot 3.22\text{H}_2\text{O}$.

According to this composition, the mean atomic number for Y plus the six REE with even atomic numbers that could be analysed is 42.7 (recalculated to full occupancy of the Y position; including REE with odd atomic numbers will increase the mean atomic number to a maximum of about 44). This compares fairly well with the mean atomic number of 41.5 for the Y site as obtained from the structure refinement. In the case of the tentatively suggested substitution of Y for Ca, the result obtained from the structure refinement does not correspond that well with the analytical data.

Bond-valence calculations (Table 4) would seem to indicate that virtually no Ca substitutes for Y+REE, but that Ca seems to be substituted by up to 15 at.% REE and/or Y. Such a content is too high compared with the microprobe data, and about twice that obtained for Y substitution in the Ca position from the structure refinement. This might indicate compositional grain to grain variations coupled with some inaccuracy in the analytical data, but a more likely explanation would be that the use of bond-valence summations may not be a reliable method for assessing the degree of substitution.

The difference in water contents obtained by chemical and structural analyses is discussed

above. There are additional indications that the water content of kamphaugite-(Y) may be variable. A DTA run of the Kazakh specimen showed that appreciable amounts of water are lost at 130–200 °C (Stepanov, 1961). On the other hand, it was found by DTG that weight loss of impure kamphaugite-(Y) from Tørdal starts slowly only at ca. 250 °C. The 004 and 008 reflections of the XRD powder diagrams may have strongly variable intensities, as also observed by Hogarth (1972). For the Tørdal kamphaugite-(Y) – which evidently has a lower water content – the 004 reflection is always clearly visible on Debye-Scherrer films and 008 is strongly enhanced, whereas the 004 reflection may or may not be visible on films of the Hørtekollen material (Raade *et al.*, 1993). Preferred orientation can almost certainly be ruled out by the method employed. It should also be noted that the 004 reflection is not reported for the apparently water-rich kamphaugite-(Y) from Kazakhstan (Stepanov, 1961; cf. Raade *et al.*, 1993), although it could be argued that it is not strong enough to be visible on this exposure. An adequate explanation of these features is unfortunately not possible at the present stage of investigation.

Kamphaugite-(Y) from Hørtekollen is anomalously biaxial, an optical property which was explained by Raade *et al.* (1993) as being due to some primary cause such as strain induced by chemical heterogeneities or structural defects occurring during crystal growth. The optical anomaly may possibly be caused by partial ordering of atoms in the structure, e.g. of cations at the Ca and Y sites.

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