Eur. J. Mineral.
1993, **5**, 679-683

Kamphaugite-(Y), a new hydrous Ca-(Y,REE)-carbonate mineral

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Abstract: Kamphaugite-(Y) occurs as white to colourless platy crystals (< 1 mm across) in cavities of a magnetite-helvite skarn deposit at Hørtekollen, Oslo region, Norway. It has been previously reported in the literature with insufficient data from the USSR, South Africa and Canada. The chemical composition is $Ca_2(Y,REE)_2(CO_3)_4(OH)_2 \cdot 3H_2O$. It is tetragonal, $P4_12_12$, $a = 7.434(1)$, $c = 21.793(3)$ Å; $Z = 4$. The strongest reflections of the powder pattern for $FeK\alpha_1$ are [d in Å, (I_{obs}), (hkl)]: 6.140 (100) (102), 4.381 (80) (104), 3.516 (60) (202), 2.831 (50) (214) and 2.631 (90) (220). The mineral from Hørtekollen is anomalously biaxial with $2V(-) \approx 15°$; $\alpha = 1.627$, $\beta \approx \gamma = 1.663$ (± 0.002). The density is 3.19 ± 0.05 g/cm^3 (meas.) and 3.24 g/cm^3 (calc.). Mohs' hardness is about 2–3. Comparison is made with related REE-bearing carbonate minerals.

Key-words: new mineral, kamphaugite-(Y), tengerite, Ca-Y-REE-carbonate, Norway.

Introduction

The Ca-Y-carbonate mineral described in the present study has already been reported in the literature from three different localities, but with insufficient data for a complete characterization. It was first described and identified as 'tengerite' by Stepanov (1961) from a locality in Kazakhstan, USSR. Mineev (1974) used the term 'calciotengerite' for the same mineral. Its X-ray powder pattern is similar to that of an unnamed Ca-Y-carbonate from Transvaal, South Africa (Verwoerd, 1963). The third locality is in the Evans-Lou pegmatite, Quebec, Canada (Hogarth, 1972).

Three Norwegian occurrences of the mineral are known. It was initially found as a fine-grained alteration product of kuliokite-(Y) from the Høydalen granite pegmatite, Tørdal (Raade *et al.*, 1993). The discovery of considerably better crystallized material in the Hørtekollen deposit enabled us to describe this mineral as a new species. The third locality, the Tangen pegmatite quarry near Kragerø, was found by Ole T. Ljøstad during the revision of this paper. Here the mineral occurs as well-crystallized rosettes along cracks in quartz and feldspar.

The mineral is named kamphaugite-(Y) after Erling Kamphaug (1931–), a mineral collector who supplied us with the first specimens for investigation. Two other collectors, Hans Vidar Ellingsen and Hermann Fylling, were also involved in this new mineral find at the Hørtekollen locality. The mineral and its name were approved by the Commission on New Minerals and Mineral Names of the I.M.A. Type material is preserved in the Mineralogical-Geological Museum, University of Oslo, under catalogue no. 14769.

Previous work

The mineral described by Stepanov (1961) occurs as a secondary replacement product after gagarinite, $NaCaY(F,Cl)_6$, in metasomatically altered alkali granites from the Kazakh SSR. X-ray spectrometric analyses of three samples show Ca, Y, Yb as the main elements and variable contents of the REE, but with the Y group predominating. Refractive indices are 1.620 and 1.642 for a white sample and 1.611 and 1.636 for a yellow sample. The density is given as 2.85 g/cm^3. The X-ray powder pattern was tentatively indexed on a tetragonal cell with $a = 8.375$, $c = 8.72$ Å. DTA curves of two samples show endothermal peaks at 130–200, 490–500, 580 and 710–760 °C.

The South African mineral was discovered in a quartz-barite vein within the carbonatized

0935-1221/93/0005-0679 $ 1.25

Goudini volcano (Verwoerd, 1963). It occurs as less than 1 mm white spheroids on ferruginous opal, and effervesces in dilute acids. Optical emission spectrograms show Ca and Y as the main constituents with minor Yb, Er, Dy and Gd. One of the refractive indices is 1.64 and the birefringence is approximately 0.02. An unindexed powder pattern is tabulated which closely resembles that of the Kazakh mineral.

Hogarth (1972) has reported an unknown mineral, designated UN-21, as white crusts on loose fragments in the pit of the Evans-Lou pegmatite. It was noted to have a similar X-ray pattern to the 'tengerite' of Stepanov (1961) and the unidentified carbonate of Verwoerd (1963), but with the 2.73 Å reflection greatly strengthened. No other data have been published on this mineral.

Type locality

With the present description of the new mineral, the Hørtekollen occurrence at Lier, Buskerud, Norway, becomes the type locality of kamphaugite-(Y). It is a contact-metasomatic skarn deposit in the Oslo region, mined in the last century on a small scale for magnetite and described in some detail by Goldschmidt (1911). Mineralization occurs at the contact between an isolated raft of Silurian sediments, about 20 m long, and a Permian biotite granite, the Finnemarka granite. The principal skarn minerals are helvite, grossular, fluorite, quartz and alkali feldspar, with subordinate biotite, pyroxene, amphibole, wollastonite, rhodonite, epidote, tourmaline, calcite, molybdenite, sphalerite and galena. The new mineral occurs as a late-stage phase in cavities which, apart from crystals of helvite and other skarn minerals, may also contain allanite, chabazite, heulandite, apatite, scorodite, hemimorphite and montmorillonite. The mineralogy and paragenetic sequence of this interesting deposit have not been completely explored. It has been protected by law since 1984 and mineral collecting is now prohibited.

Mineral description

Kamphaugite-(Y) occurs as platy crystals with a roughly square outline, rarely up to 1 mm across. In some cases the outline is eight-sided, but the faces are rough and could not be measured. The crystals are platy on {001} and typically form divergent or rose-like aggregates, sometimes growing to small spherules. It is moderately abundant and, due to its thin-platy habit, the total amount of material at hand may amount to only a few mg. It is white to colourless; small spherules may be weakly yellow to brown. The streak is white. The mineral is transparent and has a vitreous lustre. No fluorescence in ultra-violet light was detected. Cleavage or parting were not observed. It is brittle with an uneven fracture. The Mohs' hardness is about 2–3. Density was measured as $3.19 \pm 0.05\,g/cm^3$ using heavy liquids. Kamphaugite-(Y) from Hørtekollen is anomalously biaxial with $2V(-) \approx 15°$. The refractive indices were measured in white light by the immersion method (± 0.002): $\alpha = 1.627$, $\beta \approx \gamma = 1.663$. Axial dispersion was not observed. The acute bisectrix is perpendicular to the plates, i.e. $X = c$.

X-ray crystallography

Single-crystal diffractometry shows the mineral to be tetragonal with possible space groups $P4_12_12$ or $P4_32_12$. The crystal structure was solved in space group $P4_12_12$ to $R = 0.067$ (Rømming *et al.*, 1993). The cell parameters are $a = 7.434(1)$, $c = 21.793(3)$ Å, $V = 1204.4(3)$ Å^3.

Observed and calculated X-ray powder patterns are given in Table 1. The experimental pattern was obtained with a 9 cm Debye-Scherrer camera using Fe$K\alpha_1$ radiation. No internal standard was used, but the data have been corrected to conform with the results of the single-crystal study by adding 0.18° to the 2θ values. We had to resort to this unconventional procedure because of the minimal amount of material available to us. Besides, we have previously experienced an excellent agreement between sets of cell parameters obtained independently from powder and single-crystal data (e.g. Table 1 in Rømming & Raade, 1989). Unit-cell data refined from the powder data are $a = 7.437(2)$, $c = 21.79(1)$ Å, $V = 1205.2(7)$ Å^3.

Chemical composition

Five chemical analyses were carried out with a Cameca Camebax electron microprobe operated at 15 kV and 10 nA. The following standards were used: wollastonite (Ca), pure oxide glasses (Y, Yb, Er, Gd, Dy) and mixed oxide glasses (Nd, Sm). The REE glass standards of Drake & Weill (1972)

Table 1. X-ray powder diffraction data for kamphaugite-(Y).

hkl	Hørtekollen, Norway[1]				Kazakhstan[2]		Transvaal[3]	
	I_{calc}	d_{calc} (Å)	d_{obs} (Å)	I_{obs}	d_{obs} (Å)	I_{obs}	d_{obs} (Å)	I_{obs}
102	100	6.142	6.140	100	6.0	6	6.09	10
004	17	5.447						
103	18	5.196						
111	16	5.112						
104	71	4.395	4.381	80	4.30	5	4.36	8
113	23	4.260						
105	11	3.760						
202	45	3.519	3.516	60	3.426	6	3.50	6
115	12	3.355						
211	13	3.288					3.31	3
106	14	3.263	3.263	5				
212	34	3.181	3.178	10	3.198	4	3.19	3
107	11	2.871						
214	70	2.839	2.831*	50	2.895	8	2.87	7
008	32	2.724	2.723	20	2.734	4	2.71	4
220	63	2.629	2.631	90	2.638	10	2.63	7
216	48	2.453	2.450	20	2.450	3	2.46	2
311	13	2.338	2.335	5			2.33	1
304	14	2.256	2.259	5	2.283	3	2.23	2
					2.234	4		
119	9	2.199						
1010	9	2.091			2.102	4	2.08	1
306	10	2.047						
322	29	2.027	2.027	10	2.012	6	2.02	3
324	26	1.929	1.929	20	1.956	2		
228	51	1.892	1.891	30				
2010	39	1.880	1.882	20	1.871	10	1.88	9
400	34	1.859	1.861	20				
326	17	1.794						
414	10	1.712	1.712	5				
					1.672	4		
422	18	1.644	1.644	10	1.639	4	1.65	2
408	17	1.536	1.536	10	1.518	4	1.52	2
					1.451	4	1.46	2
					1.316	4		
					1.226	3		

[1] I_{calc} (≥ 9): computed from the crystal structure (Rømming *et al.*, 1993) with the program LAZY PULVERIX (Yvon *et al.*, 1977) for Fe$K\alpha_1$ radiation and Debye-Scherrer camera.
d_{calc}: computed from the refined unit-cell data *a* 7.437(2), *c* 21.79(1) Å.
d_{obs}: from 9 cm Debye-Scherrer camera with Fe$K\alpha_1$ radiation.
I_{obs}: visually estimated.
[2] Stepanov (1961).
[3] Verwoerd (1963).
* not used in cell refinement.

were analysed as unknowns to check the accuracy of the analyses, which was found to be very good (less than 10 % relative deviation on the low side). A small amount of F was detected with the microprobe, but was not analysed (< 0.5 wt.%). The sample was moved during analysis to minimize decomposition under the electron beam. H_2O and CO_2 were determined on 864.4 μg of hand-picked material with a Perkin-Elmer 240 CHN analyser. 0.8 wt.% BeO was determined by AAS in a HCl solution made from a 105.3 μg aliquot of the same lot, indicating contamination with 6 % helvite

Table 2. Chemical composition of kamphaugite-(Y) in wt.%.

	1		2
CaO	18.4	(0.2)	19.14
Y_2O_3	30.5	(0.3)	38.53
Nd_2O_3	1.4	(0.3)	
Sm_2O_3	0.8	(0.3)	
Gd_2O_3	1.6	(0.3)	
Dy_2O_3	2.1	(0.4)	
Er_2O_3	1.2	(0.1)	
Yb_2O_3	1.1	(0.3)	
CO_2	29.6		30.04
H_2O	12.1		12.29
	98.8		100.00

1. Mean of 5 electron-microprobe analyses (with standard deviations). CO_2 and H_2O determined with a CHN analyser.
2. Theoretical composition of $Ca_2Y_2(CO_3)_4(OH)_2{\cdot}3H_2O$.

which was then subtracted, and the H_2O and CO_2 values were recalculated accordingly (two analyses of helvite from Hørtekollen with a mean value of 13.17 wt.% BeO were published by Goldschmidt, 1911). The analytical results with standard deviations are given in Table 2. The REE with odd atomic numbers could not be determined with the microprobe, but may sum to about 1 wt.% REE_2O_3.

The empirical formula based on C = 4 is: $Ca_{1.95}(Y_{1.61}REE_{0.27})_{\Sigma 1.88}(CO_3)_{4.00}(OH)_{1.54}{\cdot}3.22H_2O$. The inaccuracy in the REE^{3+} determination is responsible for the low OH^- value. The simplified formula is $Ca_2(Y,REE)_2(CO_3)_4(OH)_2{\cdot}3H_2O$. The mineral dissolves with effervescence in dilute acids.

With $Z=4$, the calculated density is 3.24 g/cm^3, in good agreement with the measured value of 3.19 g/cm^3. The Gladstone-Dale relationship gives (with β set equal to γ) a compatibility index $1\text{-}K_p/K_c = 0.026$, which is in the 'excellent' category (Mandarino, 1981). It was unfortunately not possible to obtain enough material for an infrared spectrum, nor for DTA or TGA runs.

Relationship to other minerals

For a long time, the nomenclature of the group of Ca-Y-carbonates has been ambiguous and several minerals have been concealed under the designation 'tengerite'. This situation was considerably improved by the description of the new minerals lokkaite-(Y), $CaY_4(CO_3)_7{\cdot}9H_2O$ (Perttunen, 1971; Nagashima *et al.*, 1986) and kimuraite-(Y), $CaY_2(CO_3)_4{\cdot}6H_2O$ (Nagashima *et al.*, 1986). The description of kamphaugite-(Y), $Ca_2Y_2(CO_3)_4(OH)_2{\cdot}3H_2O$, adds another species to this group.

The formula of tengerite-(Y) has been established as $Y_2(CO_3)_3{\cdot}2\text{–}3H_2O$ (Nagashima & Wakita, 1968; Wakita & Nagashima, 1972), later confirmed by the structure determination of Miyawaki *et al.* (1986). Tengerite, lokkaite and kimuraite are structurally related, having orthorhombic cells with similar *a* and *b* dimensions. The possible arrangement of different kinds of sheets in these three structures has been compared by Miyawaki & Nakai (1987). The cell dimensions of kamphaugite bear no resemblance to the other minerals of the group, and its structure is different (Rømming *et al.*, 1993).

The so-called tengerite from Iisaka, Japan, has been given the tentative formula
$CaY_3(CO_3)_4(OH)_3{\cdot}3H_2O$ (Iimori, 1938),
which is frequently quoted in the literature. The mineral's X-ray powder data were not given, but a subsequent investigation has shown that they are similar to those of tengerite proper (Nagashima & Wakita, 1968). The calcium content may – at least in part – be due to admixed synchysite, $CaREE(CO_3)_2F$, which has been detected by Miyawaki (pers. comm., 1989). It should be noted that the refractive indices reported for the Iisaka mineral ($\alpha = 1.622$, $\gamma = 1.642$) are very close to the values for 'tengerite' from Kazakhstan (Stepanov, 1961); thus, the presence of kamphaugite-(Y) as a possible minor phase cannot be completely excluded (cf. discussion by Raade *et al.*, 1993).

Discussion

On the basis of X-ray powder data (Table 1) and chemical compositions, there can be no doubt that the minerals reported by Stepanov (1961), Verwoerd (1963) and Hogarth (1972) are identical with the mineral described here as kamphaugite-(Y). However, the tentative tetragonal indexing of Stepanov is not correct, and his density is too low. By comparing the refractive indices, possible variations in composition must be taken into account, especially the water content and the OH/F ratio. There are indications that the water contents of both tengerite and kamphaugite could be variable

(Nagashima & Wakita, 1968; Miyawaki *et al.*, 1986; Rømming *et al.*, 1993).

Kamphaugite-(Y) from Hørtekollen is a low-temperature, late-stage mineral found in cavities; the only younger phase is represented by an occasional coating of montmorillonite. It is unlikely that kamphaugite-(Y) was formed by decomposition of a precursor mineral, and there is no obvious candidate for such. In the other reported occurrences, where kamphaugite-(Y) is clearly a secondary mineral, it forms coatings or fine-grained masses and not aggregates of distinct crystals as in the Hørtekollen deposit.

The anomalous biaxiality of the Hørtekollen mineral has not affected the space-group symmetry as determined by X-ray diffraction. Foord & Mills (1978) have discussed the causes of anomalous optical properties in minerals. Such anomalies may be secondary in nature, originating after crystal growth. Mechanical deformation can be ruled out for the freely growing crystals from Hørtekollen, and a rapid temperature or pressure quench producing internal stresses is not very likely. We are thus left with a primary cause for the anomalous optical angle, which probably originated from strain induced by chemical heterogeneities or structural defects which occurred during crystal growth.

Acknowledgements: We are greatly indebted to H. Austrheim at the Oslo museum for his invaluable assistance with the microprobe analyses, to V. K. Din at the Department of Mineralogy, British Museum (Natural History) for the H_2O and CO_2 determination, and to C. Rømming (Department of Chemistry, University of Oslo) for the single-crystal study. We are also most grateful to R. Kristiansen for contributing his knowledge of literature studies. Last, but not least, we thank E. Kamphaug for providing material for the initial studies.

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Received 7 December 1989
Modified version received 20 February 1991
Accepted 20 December 1991

Publication postponed by the author until completion of the companion paper by Rømming et al. (1993).