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KAMPHAUGITE-(Y) FROM THE GOUDINI CARBONATITE, SOUTH AFRICA

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Abstract

Kamphaugite-(Y) crystallized as minute white spheroids in cavities of a quartz–barite vein in the Goudini volcanic carbonatite complex, South Africa. The maximum grain-size of individual plates forming these spheroids is 0.003 mm. The mineral is tetragonal with $\omega = 1.661(2)$, a density of 3.18(1) g/cm^3, a Mohs hardness of about 2, a cleavage or parting parallel to {001}, with cell dimensions a 7.402(3), c 21.778(1) Å , V 1192.9 Å^3. Results of a chemical analysis gives the average composition on the basis of 4 C atoms per formula unit as $(\mathrm{Ca}_{1.84}\mathrm{REE}_x)(\mathrm{Y}_{1.46}\mathrm{REE}_{0.54-x})(\mathrm{CO}_3)_4(\mathrm{OH})_{1.65}\bullet 2\mathrm{H}_2\mathrm{O}$ plus interstitial H_2O. Concentrations of all rare-earth elements were determined by ICP–MS. There is a strong enrichment of the middle and heavy REE and a small negative Ce anomaly. The spheroids are zoned and show systematic compositional variations related to a depletion of REE during growth. Twenty-three reflections of the X-ray powder pattern were indexed; the unit-cell dimensions of kamphaugite-(Y) from various localities were determined for comparison. Attention is drawn to intensity variations in the powder patterns and apparent variations in cell dimensions, probably resulting from submicroscopic mosaics caused by displacements of lattice arrays. The IR and Raman spectra of the Goudini mineral are in accordance with the chemical and X-ray results. Kamphaugite-(Y) is clearly a secondary mineral at Goudini. The primary source of yttrium and the rare earths has not yet been found.

Keywords: kamphaugite-(Y), rare-earth geochemistry, carbonatite, X-ray powder diffraction, unit-cell dimensions, yttrium, epithermal mineralization, Goudini complex, Northwest province, South Africa.

Sommaire

La kamphaugite-(Y) a cristallisé en sphérules de taille infime dans des cavités d’une veine à quartz–barite dans le complexe carbonatitique volcanique de Goudini, en Afrique du Sud. La taille maximale des plaquettes individuelles de ces sphérules est 0.003 mm. Il s’agit d’un minéral tétragonal ayant ω égal à 1.661(2), une densité de 3.18(1) g/cm^3, une dureté de Mohs d’environ 2, un clivage ou plan de séparation parallèle à {001}, et une maille élémentaire mesurant a 7.402(3), c 21.778(1) Å , V 1192.9 Å^3. Les résultats de l’analyse chimique donnent la composition moyenne suivante, calculée sur une base de 4 atomes de C par formule unitaire: $(\mathrm{Ca}_{1.84}\mathrm{TR}_x)(\mathrm{Y}_{1.46}\mathrm{TR}_{0.54-x})(\mathrm{CO}_3)_4(\mathrm{OH})_{1.65}\bullet 2\mathrm{H}_2\mathrm{O}$, avec en plus H_2O interstitiel. Le niveau de concentration de chacune des terres rares (TR) a été déterminé par la technique ICP–MS. Il y a un fort enrichissement en terres rares moyennes et lourdes, ainsi qu’une légère anomalie négative en Ce. Les sphérules sont zonées, et témoignent d’un appauvrissement en terres rares au cours de la croissance. Vingt-trois réflexions du spectre de diffraction X ont été indexées; les paramètres réticulaires de la kamphaugite-(Y) provenant des diverses localités ont été déterminés pour fins de comparaison. Il y a des variations importantes en intensité parmi les spectres de diffraction et des variations en paramètres réticulaires, témoignant probablement de la présence de mosaïques submicroscopiques causée par le déplacement de réseaux d’atomes. Les spectres IR et de Raman concordent avec les données chimiques et diffractométriques. La kamphaugite-(Y) est clairement une phase secondaire à Goudini. On n’y a pas encore trouvé la source de l’yttrium et des terres rares.

(Traduit par la Rédaction)

Mots-clés: kamphaugite-(Y), géochimie des terres rares, carbonatite, diffraction X sur poudre, maille élémentaire, yttrium, minéralisation épithermale, complexe de Goudini, province du Northwest, Afrique du Sud.

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INTRODUCTION

An "unidentified yttrium carbonate", now recognized as kamphaugite-(Y), was discovered during field work on the Goudini carbonatite complex in 1957. A brief description was published (Verwoerd 1963), but the mineral was never adequately described owing to paucity of material. On the basis of the preliminary chemical and X-ray data, Perttunen (1971) concluded that it is the same as the so-called "tengerite" from Kazakhstan (misidentified but well described by Stepanov 1961). A third occurrence with an almost identical X-ray powder-diffraction pattern was discovered in the Evans–Lou pegmatite, Quebec, Canada, and labeled "Unknown 21" (Hogarth 1972). Twenty years elapsed before Raade & Brastad (1993) obtained sufficiently well-crystallized material from another locality, Hørtekollen in Norway, for the mineral to be named and characterized. A determination of the structure was performed at the same time (Rømming *et al.* 1993).

Apparently, kamphaugite-(Y) always occurs in minor amounts of minute crystals except at Hørtekollen, but it can no longer be regarded as rare. It is a supergene mineral now known from at least 16 localities all over the world, and new ones are continuously being added to the list. The localities (in order of description) are: 1) Verkhne Espe, Tarbagatai Range, Kazakhstan (Stepanov 1961, Anthony *et al.* 2003), 2) Goudini, Northwest Province, South Africa (Verwoerd 1963), 3) Evans–Lou, Quebec, Canada (Hogarth 1972), 4) Tommot, Yakutia, Russia (Nekrasov *et al.* 1992), 5) Hørtekollen, Oslo, Norway (Raade & Brastad 1993), 6) Høydalen, Tørdal, Telemark, Norway (Raade *et al.* 1993) , 7) Tangen, Kragerø, Norway (Raade & Brastad 1993), 8) Mt. Ploskaya, Keivy massif, Kola Peninsula, Russia (Voloshin *et al.* 1996, Anthony *et al.* 2003), 9) Cala Francese, La Maddalena island, Sardinia, Italy (Gamboni & Gamboni 1998), 10) Rössing, Swakopmund, Namibia (Petersen *et al.* 2001), 11) Paratoo, Olary, South Australia (Wallwork *et al.* 2002), 12) Gronci–Ellis, Mt. Desert, Hancock, Maine, U.S.A. (Anthony *et al.* 2003), 13) Szarvaskö, Bükk Mountains, Hungary (Fehér *et al.* 2003), 14) Feriolo, Verbania, Italy (Guastoni *et al.* 2005), 15) Hirono, Kameoka, Kyoto, Japan (Tsuruta *et al.* 2006), and 16) La Cabrera, Madrid, Spain (González del Tánago *et al.* 2006).

Thirteen of the sixteen occurrences of kamphaugite-(Y) are associated with granitic rocks or pegmatites. This is not surprising in view of the fact that Y and HREE commonly are enriched in such rocks. The three exceptions are Hørtekollen (the type locality), which is a contact-metasomatic skarn, Paratoo, a supergene copper deposit, and Goudini, a volcanic carbonatite complex. Carbonatites are generally enriched in LREE and other trace elements, not Y. The Goudini occurrence thus appears to be geochemically anomalous. However, churchite-(Y), $(Y,Er)PO_4{\bullet}2H_2O$ has been described from the weathering zone of the Sandkopsdrif carbonatite in Western Cape Province, South Africa (Verwoerd 1986).

By 1979, quantitative chemical data based on additional samples from Goudini were available. Assuming the presence of both H_2O and OH to balance charges, the simplest possible formula was calculated to be $Ca(Y,REE)(CO_3)_2OH{\bullet}H_2O$, which eventually proved to be correct. The purpose of this paper is therefore to present previously unpublished data on the Goudini mineral that have been accumulated since 1963, and to review the literature on kamphaugite-(Y).

LOCATION

The geological setting of the Goudini occurrence is briefly described in an accompanying paper (Verwoerd 2008). The volcanic activity that preceded mineralization is now better understood than before.

The unidentified mineral was found in one of several inconspicuous quartz–barite veins in the soil-covered flat south of Goudinikop. The veins can be traced for distances up to 70 m and probably do not exceed half a meter in width. The exact locality (25°07'58" S, 26°11'10" E) is shown as a thin dotted line on the published geological map (Verwoerd 1967). The low outcrop was subsequently destroyed by pitting but may still be located from rubble containing cleavage fragments of colorless barite.

During 1987–1988, geochemical prospecting was carried out in the area by Anglo American Exploration Ltd. A circular yttrium anomaly about 800 m in diameter was delineated, roughly coinciding with a radioactive zone associated with the barite veins (Adrian *et al.* 1989). These authors reported tentative identifications of several secondary rare-earth carbonate minerals (ancylite, burbankite or donnayite, synchysite, doverite), but not the Ca–Y carbonate described here. Thus it is not known whether kamphaugite-(Y) at Goudini is restricted to a single vein of barite or not.

CRYSTAL MORPHOLOGY

At Goudini, kamphaugite-(Y) forms white spheroids and hemispherical aggregates of two different sizes implanted on the walls of drusy cavities measuring up to a few cm across. The smaller, more delicate spheroids range from 0.08 to 0.5 mm in diameter. The larger hemispheroids reach diameters of 2–3 mm and are commonly found to be hollow crusts (Fig. 1)

Under high magnification, the surface of the spheroids is seen to consist of overlapping platy crystals reminiscent of *Tagetes erecta* (Compositae) flower petals (Fig. 2A). There is quite a variety of shapes and sizes. Individual plates are seldom thicker than 1 μm and measure no more than 12 μm on edge, nearly one hundred times smaller than the crystals from Hørtekollen available to Rømming *et al.* (1993). Isolated groups of euhedral tabular crystals up to 10 µm thick are in some cases seen embedded in the platy matrix (Fig. 2B). The possibility that this is another mineral that is indistinguishable from kamphaugite-(Y) by energy-dispersive spectrometry, *e.g.*, lokkaite, $CaY_4CO_3)_7\bullet 9H_2O$, kimuraite, $CaY_2(CO_3)_4\bullet 6H_2O$, or moydite, $(Ca,Y)B(OH)_4(CO_3)$, must be considered. However, it appears unlikely in view of the lack of evidence for such admixtures in the Goudini samples that were X-rayed, chemically analyzed and subjected to vibrational spectrometry. The thicker plates could have crystallized early while the nucleation rate was relatively slow, to be overwhelmed by smaller ones when nucleation rate became rapid. Under high magnification, the latter in some cases show peculiar skeletal structures that may also be ascribed to rapid crystallization (Fig. 3D).

The crystal forms of the tabular and platy crystals cannot be deduced unequivocally from the SEM images, but at least they are consistent with tetragonal symmetry and predominance of {001}. When crushed for optical investigation under the petrographic microscope, the spheroids generally break into diverging wedges that are solid, *i.e.*, without the voids between plates that are so evident on the surface. The plates of the interior therefore appear to be elongate in one direction and arranged in subparallel radiating fashion. This explains what Stepanov (1961) interpreted as "elongated prisms with straight extinction". The wedges exhibit wavy concentric growth-zones within the spheroids. The same type of concentric zoning is well shown on a back-scattered electron image of an equatorial section of a kamphaugite-(Y) spheroid from La Cabrera (González del Tánago *et al.* 2006, Fig. 2) and was studied in detail by electron-microprobe analysis (see below). Stepanov (1961) described this phenomenon as "alternating light and dark strips subparallel to concentric layers of the mineral, resembling rippled water surfaces." Some fragments, however, exhibit a criss-cross structure as expected of platy crystals with all possible orientations, as seen in the SEM photographs.

FIG. 1. Hand specimen of geode with yellow powdery micro-crystals of barite (white rim) and ferruginous chalcedony encrusted by white kamphaugite-(Y) hemispheroids. Coarse glassy barite at the top center. Scale bar in cm.

Voloshin *et al.* (1996) described a peculiar kind of zoning in which a single square crystal plate of kamphaugite-(Y) is surrounded by four sectors having different orientations, each sector in turn being rimmed by kamphaugite-(Y) showing polysynthetic twins resembling those of albite; this is possible because space group $P4_12_12$ allows {001} to be a twin plane.

PHYSICAL PROPERTIES

Optical and other properties of kamphaugite-(Y) reported in the literature are compared in Table 1 with those of kamphaugite-(Y) from Goudini. Deviations from the values recorded for the type locality can be ascribed more to difficulties of measurement than to actual variation. Single crystals or crystal fragments are generally not available, so that the indices of refraction, for example, had to be determined by the immersion method in white light on subparallel aggregates or mosaics. Anomalous biaxial interference-figures were observed at four out of six localities (Table 1), but it is doubtful whether they are real. Petersen *et al.* (2001) obtained a "perfect" uniaxial interference-figure on

TABLE 1. PHYSICAL PROPERTIES OF KAMPHAUGITE-(Y)

	Goudini	Hørte-kollen	Tommot	Kazakh-stan	Kola	Rössing	Szar-vaskö
Color	white	white	white, yellowish	white, yellowish	white	white, colorless	white
Luster	silky	vitreous		vitreous to silky			
ω	1.661(2)	1.663(2)	*1.758	1.642	1.675	1.664(2)	
ε	?	1.627(2)	*1.672	1.620	1.622	1.631(2)	
ω – ε		0.036	*0.086	0.022	0.053	0.033	
2*V* (–) (anomalous)	*57°	~15°	biaxial		17°	0°	
D_{meas}	3.18(1)	3.19(5)	*3.96(4)	*2.85	3.14(5)		
H (Mohs)	~2	2–3	*4-4.5	~2			
Cleavage or parting	{001}	absent	{001}				
Habit	platy	platy	platy	*elongate prisms	lamellar twins	platy	thick tabular
Form of aggre-gate	spheroids and hemi-spheroids	spher-ules	oolitic, reniform crusts	spheru-litic crusts		"pom-pons"	globu-lar
Dimensions**							
spheroids	0.08–3.00		0.1–0.5	3–5		~1	0.5
crystals	0.012	~1			~0.1		0.01-0.02

* These values seem out of line and therefore questionable.
** Dimensions are quoted in mm. Data from other localities: spheroids 1–4 mm (Maddalena), spheroids 0.5–0.8 mm and crystals 0.03 mm (Feriolo).

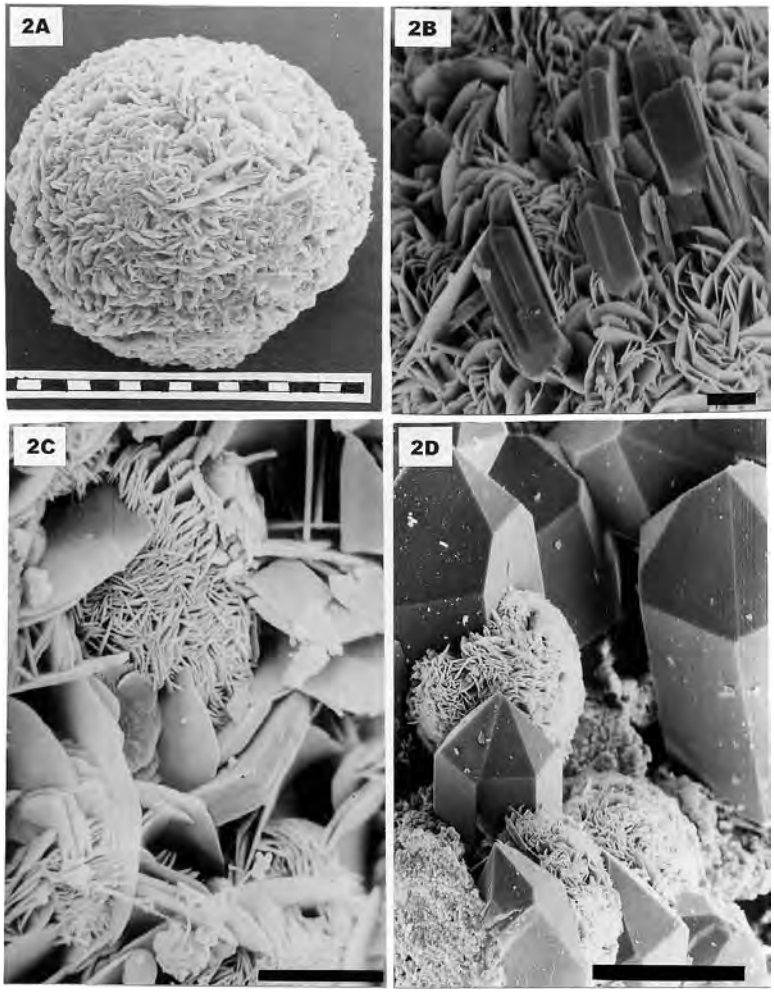

FIG. 2. SEM photographs of kamphaugite-(Y) from Goudini. A. Spheroid 0.15 mm in diameter covered with {001} kamphaugite-(Y) plates in random orientation. Scale bar in units of 10 µm. B. Isolated tabular crystals showing basal parting or cleavage embedded in platy kamphaugite-(Y) aggregate. Scale bar 10 µm. C. Large variation in grain size between two generations of kamphaugite-(Y). Scale bar 10 µm. D. Kamphaugite-(Y) spheroids implanted on doubly terminated quartz microcrystals. Scale bar 100 µm.

platy crystals from Røssing. In the case of Goudini, ω was measured for the ray vibrating parallel to the length of wedge-like splinters, and ε perpendicular thereto. However, the orientation of the plate-like crystals in the aggregate is unknown, and no reliable value of ε could be obtained, coupled with a spurious $2V$ angle, probably the result of overlapping crystals. The best data are undoubtedly those of Hørtekollen and Rössing in view of the larger grain-size. Fluorescence effects have not been observed.

Cleavage or parting can be clearly seen on SEM images of thicker plates of Goudini kamphaugite-(Y) (Figs. 2B, 3B). This is in accordance with the crystal structure, consisting of Ca- and Y-polyhedra arranged in corrugated sheets parallel to {001} according to Rømming *et al.* (1993). It is rather surprising that Raade & Brastad (1993) saw no evidence of this. Hardness was roughly estimated from crushing behavior. Density was measured by flotation in a mixture of bromoform and di-iodomethane.

CHEMICAL COMPOSITION

Methods

Spheroids of Goudini kamphaugite-(Y) were analyzed by the author using the MAC electron microprobe at the Geophysical Laboratory in Washington, D.C., in 1978. A synthetic $YNbO_4$ standard was used for Y. For Ca and the lanthanide elements, the four synthetic CaAl silicate glass standards of Drake & Weill (1972), in which the elements are combined in a way to eliminate most interferences, were used. Owing to sample

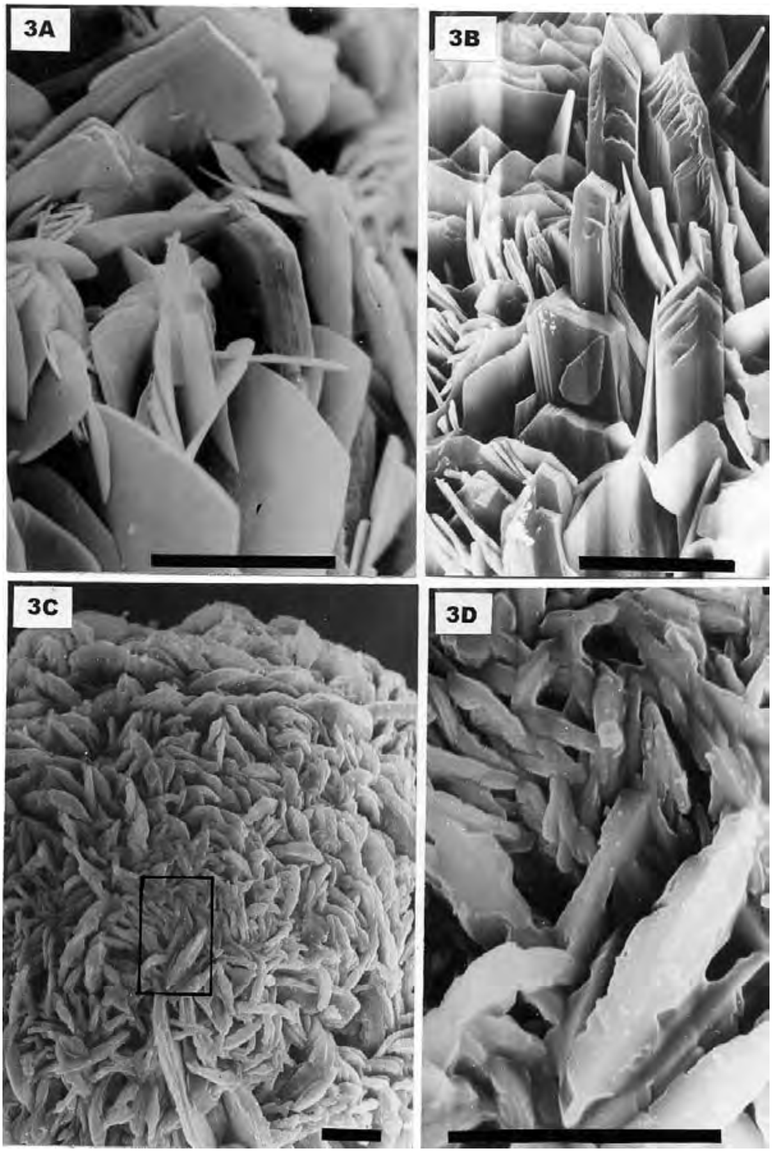

FIG. 3. SEM photographs of kamphaugite-(Y) from Goudini (cont'd.). A. Edges of thin kamphaugite-(Y) basal plates showing possible tetragonal crystal forms. Scale bar 10 µm. B. Traces of cleavage or skeletal crystallization in kamphaugite-(Y). Scale bar 10 µm. C. Distorted, thickened, thinned and indented kamphaugite-(Y) plates as a result of rapid crystallization or natural corrosion. Scale bar 10 µm. D. Close-up showing the same features as C. Scale bar 10 µm.

deterioration under the electron beam, low intensities and short counting-times had to be employed. A beam diameter of 20 μm, 15 kV excitation, a specimen current of 0.02 μA and 20 second counts proved satisfactory for the major cations Ca, Y, Gd, Dy, Er and Yb. For the minor elements, 60-s counts were taken, and the beam shifted at 10-second intervals, each analysis therefore covering a square of approximately 100^2 μm. Data were corrected using a MAGIC IV program after appropriate corrections for overlap between Ho$L\alpha_1$ and Gd$L\beta_1$, Er$L\alpha_1$ and Tb$L\beta_1$, Tm$L\alpha_1$ and Dy$L\beta_1$ in the unknown were made according to the suggestion by Snetsinger *et al.* (1968) for analyzing the sample for V in the presence of Ti.

The analysis (except Ca) was repeated in 2005 using ICP–MS, the first for kamphaugite-(Y), because the method is generally considered superior for Y and the REE. It was carried out at the University of Cape Town using a Perkin–Elmer ELAN 6000 instrument and artificial multi-element standards. Two separate dissolutions of about 5 mg hand-picked material each (the mineral dissolves in dilute HCl with effervescence), were run three times, and the results averaged.

Carbon and hydrogen were determined in triplicate using a modified Perkin–Elmer 240 elemental analyzer at the CSIR National Chemical Laboratory in 1979. In this case, hand-picked samples of about 2 mg were heated to 950°C for a maximum time in the ignition zone, and tested against standard extra pure $CaCO_3$ for complete recovery of CO_2.

Results

The two ICP–MS analyses showed excellent reproducibility, with little difference in results between samples (Table 2). The results include minor Ba and Sr contents and traces of Th, U and Pb. In view of the close association between kamphaugite-(Y) and barite at Goudini, it was decided to calculate the empirical formula after subtracting BaO, SrO and an equivalent amount of sulfate as impurities, and to adjust Y and the REE upward accordingly. A similar recalculation of the data of Nekrasov *et al.* (1992) was made for kamphaugite-(Y) from Tommot, and included in Table 3. Raade & Brastad (1993) had to apply a considerably larger correction for impurities to their Hørtekollen analysis. The results obtained by X-ray-fluorescence analysis of kamphaugite-(Y) from Kazakhstan by Stepanov (1961) are not used here; only Y and the REE were determined, and according to the author the samples contained no more than 60% of kamphaugite-(Y).

Electron-microprobe analyses of the Goudini kamphaugite-(Y) were averaged (55 determinations of the major elements Ca, Y, Gd, Dy, Er, Yb and 13 of the minor elements on six spheroids). The results compare quite well with the ICP–MS data (Table 3); only Ce is seriously overestimated. Apparently, the electron-microprobe approach tends to overestimate small amounts of the LREE, as is evident from a comparison of the chondrite-normalized REE plot of Goudini kamphaugite-(Y) (Fig. 4) with those of other localities

TABLE 2. RESULTS OF ICP-MS ANALYSES OF KAMPHAUGITE-(Y) FROM GOUDINI

	1	% rsd	2	% rsd	Average
La	5.01	6.64	3.97	5.00	4.49
Ce	18.9	5.79	18.7	5.93	18.80
Pr	35.4	2.59	45.1	1.31	40.25
Nd	95.7	0.76	1242	1.05	1099.5
Sm	5861	0.88	6645	1.87	6253.0
Eu	4798	0.73	4894	0.23	4846.0
Gd	22516	2.17	22939	0.82	22727.5
Tb	5918	1.60	5901	1.53	5909.50
Dy	47311	0.24	46636	0.53	46973.5
Ho	9576	1.20	9407	1.52	9491.5
Er	24608	1.27	24638	0.51	24623.0
Tm	2835	1.14	2866	0.08	2850.5
Yb	12972	0.58	13877	1.13	13424.5
Lu	1287	1.23	1368	0.33	1327.5
Sr	320	0.44	343	2.85	331.5
Y	211657	1.01	211996	0.95	211826.5
Ba	5202	1.10	2298	2.18	3750.0
Pb	3.42	0.80	3.57	2.66	3.5
Th	198	1.07	215	0.65	206.5
U	6.38	1.56	6.92	4.41	6.7

Values are quoted in ppm; rsd: relative standard deviation (sd/average concentration × 100). The analyses were made at the Department of Earth Sciences, University of Cape Town.

TABLE 3. CHEMICAL COMPOSITION OF KAMPHAUGITE-(Y)

	Goudini[1] ICP-MS	Goudini EMPA	Hørtekollen[2] EMPA	Kola EMPA	Tommot[3] EMPA	Rössing[4] EMPA	La Cabrera[5] EMPA	Szarvasko[6] EMPA	Idealized[7]
CaO	16.95	16.95	18.4	18.19	19.28	15.11	17.80	20.07	19.14
Y_2O_3	27.09	27.99	30.5	28.64	24.40	27.12	33.80	29.72	38.53
La_2O_3	<0.01	0.00					0.05	0.10	
Ce_2O_3	<0.01	0.10					0.24	0.93	
Pr_2O_3	<0.01	0.01					0.10	0.33	
Nd_2O_3	0.13	0.11	1.4		0.73	1.47	0.51	2.13	
Sm_2O_3	0.74	0.84	0.8		0.93	0.03	0.55	1.55	
Eu_2O_3	0.56	0.60					0.14	0.53	
Gd_2O_3	2.64	2.47	1.6	0.32	2.66	3.57	1.98	3.26	
Tb_2O_3	0.68	0.54		0.24		0.81	0.76	0.63	
Dy_2O_3	5.43	5.37	2.1	1.63	5.11	5.58	3.91	4.91	
Ho_2O_3	1.10	1.24		0.67		1.27	0.64	0.99	
Er_2O_3	2.84	3.29	1.2	2.86	3.83	2.59	2.24	2.74	
Tm_2O_3	0.33	0.29			0.26	0.37	0.17	0.50	
Yb_2O_3	1.54	1.73	1.1	3.43	2.01	1.07	1.07	1.65	
Lu_2O_3	0.15	0.00			0.04		0.70	0.43	
CO_2	28.90	28.90	29.6			27.7			30.04
H_2O	9.29	9.29	12.1			7.93			12.29
Total	98.37	99.72	98.8			97.20			100.00

Notes: 1: Sr and Ba are subtracted as impurities (0.7% barite, this paper); 2: Be is subtracted as an impurity (6% helvite according to Raade & Brastad 1993); 3: Fe, Ce, Ca and P are subtracted as impurities (0.12% hematite, 0.23% monazite, 1.14% apatite) from results of EMP analyses 1-3 in Nekrasov *et al.* (1992); 4: In addition, Petersen *et al.* (2001) reported 0.11% Na_2O and 0.81% F [Na in kamphaugite-(Y) from Australia is also mentioned by Wallwork *et al.* (2002)]; 5: In addition, González del Tánago *et al.* (2006) reported 0.04% SiO_2, 0.12% P_2O_5, 0.14% ThO_2, 0.15% UO_2 and 0.29% F; 6: Analytical results are suspect. With CO_2 = 29.53%, the total is 100%, and the amount of H_2O is nil; 7: Calculated from formula $Ca_2Y_2(CO_3)_4(OH)_2{\cdot}3H_2O$ (Raade & Brastad 1993). For purposes of comparison, the single-crystal formula of Rømming *et al.* (1993) is less relevant. Methods: ICP–MS: Inductively coupled plasma – mass spectrometry (except CaO, CO_2, H_2O), EMPA: electron-microprobe analysis (except CO_2, H_2O).

(González del Tánago *et al.* 2006, Fig. 4), regardless of which chondrite values are used. As expected, the curve shows a strong enrichment of the MREE and HREE in conformity with solid solution for Y. Plots from some localities exhibit deviations from a smooth convex shape, probably the result of inaccuracy. The Goudini plot shows a small negative Ce anomaly. This may be doubted because the La in solution (diluted 200,000 times) is close to its detection limit, but the anomaly does remain even if La content is assumed to be zero. Selective depletion of Ce with respect to the other LREE can be explained by the fact that only Ce is known to assume a higher oxidation state (Ce^{4+}) in minerals, *e.g.*, cerianite, CeO_2. Tetravalent Ce would not be accommodated at either the Y or Ca sites of kamphaugite-(Y) and would be removed in solution. The small anomaly might therefore be indicative of strongly oxidizing near-surface conditions during crystallization of the barite – quartz – kamphaugite-(Y) assemblage.

Tables 3 and 4 demonstrate considerable variability in the composition of kamphaugite-(Y) from different localities, with Rössing having the highest, and Hørtekollen as well as Kola the lowest total rare-earth contents. Calculated empirical formulae (Table 4) show a deficiency of Ca with respect to the theoretical number of two ions in all cases except Tommot. On the basis of their structure refinement, Rømming *et al.* (1993) discussed the possibility that some REE and Y might substitute for Ca, but found the evidence to be ambiguous. Mean Y–O and Ca–O bond distances in kamphaugite-(Y) are virtually the same (2.442 and 2.449 Å, respectively) and ionic radii for coordination numbers 8 and 9 are close to each other (1.10 and 1.12 Å respectively: Shannon & Prewitt 1969). The data from only seven localities (Table 4) are not sufficient to establish any possible correlation involving Ca, Y and REE. However, a large number of spot analyses by microprobe are available to test the possibility of systematic chemical variations in the Goudini kamphaugite-(Y). From Figure 5, it is clear that both Y and Ca are negatively correlated with REE, the former more steeply than the latter. Among the four most abundant REE, similar distributions are shown by Gd and

TABLE 4. NUMBER OF IONS AND H_2O MOLECULES PER FORMULA UNIT IN KAMPHAUGITE-(Y)

	1	2	3	4	5	6	7	8
Ca	1.78	1.82	1.84	1.86	1.90	1.95	2.02	2
Y	1.56	1.65	1.46	1.76	1.49	1.61	1.27	~1.5
La				<0.01				
Ce				0.01				
Pr				<0.01				
Nd	0.06		0.005	0.02		0.05	0.03	
Sm	0.08	0.03	0.03	0.02		0.03	0.03	
Eu			0.02	<0.01				
Gd	0.12	0.13	0.09	0.06	0.01	0.05	0.09	
Tb	0.02	0.02	0.02	0.02	0.01			
Dy	0.20	0.12	0.18	0.12	0.05	0.07	0.16	
Ho	0.04	0.07	0.04	0.02	0.02	0.03		
Er	0.08	0.08	0.09	0.07	0.09	0.04	0.12	
Tm	0.02	0.02	0.01	<0.01			0.01	
Yb	0.04	0.03	0.05	0.03	0.10	0.03	0.06	
Lu		0.03	0.005	0.02				
CO_3	4	4	4	4*	4*	4	4*	4
OH	2.00	2.18	1.65	2.00	1.11	1.54	1.35	2
H_2O	2.00	?	2.31	2.38	4.02	3.22	2.83	2
ΣREE	0.66	0.53	0.54	0.39	0.28	0.27	0.50	~0.5
D_{calc}	3.46		3.35	3.36	3.10	3.24	3.24	3.33

Columns: 1: Rössing (Na, F included with Ca, OH), 2: Hirono (F included with OH), 3: Goudini, 4: La Cabrera (recalculated for C = 4), 5: Kola, 6: Hørtekollen, 7: Tommot, 8: Idealized (Rømming *et al.* 1993). * The amount of CO_2 is estimated, not determined. Compositions are recalculated on the basis of 4 C atoms per formula unit (*apfu*). Density is calculated from unit-cell data (Table 6).

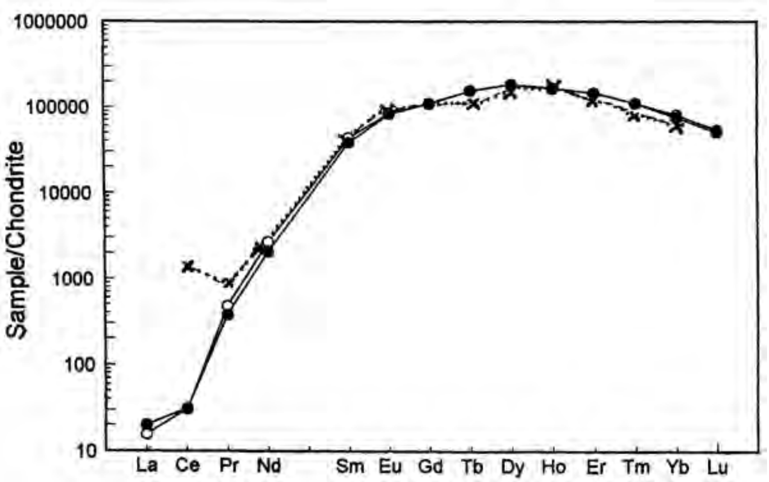

FIG. 4. Chondrite-normalized plot of REE in Goudini kamphaugite-(Y). Chondrite values from Sun & McDonough (1989).

Dy, whereas Er and Yb vary between the same narrow limits as Ca and probably cluster around a constant value. The conclusion seems justified that the REE with smaller ionic radii occupy only the Y positions in the structure, whereas those with larger ionic radii occupy Y positions preferentially, but also the slightly larger Ca positions. Trivalent ions in Ca positions will cause charge imbalance which can be compensated by vacancies, *e.g.*, $3Ca^{2+} \rightleftharpoons 2\ Gd^{3+}$.

González del Tánago *et al.* (2006) reported similar observations on kamphaugite-(Y) from La Cabrera, but the ratio (Y + Ca)/REE is different (Fig. 6). The slope of the regression line transferred from their Figure 3 is 1.231, which is close to $2(Y^{3+} + Ca^{2+}) = 5/3\ (REE^{3+})$. In the case of Goudini, the slope is 3.50, and the ratio, approximately $2(Y^{3+} + Ca^{2+}) = 3/5\ (REE^{3+})$. Thus the Goudini mineral has a narrower range of variation in REE content and a wider range of Ca and Y per formula

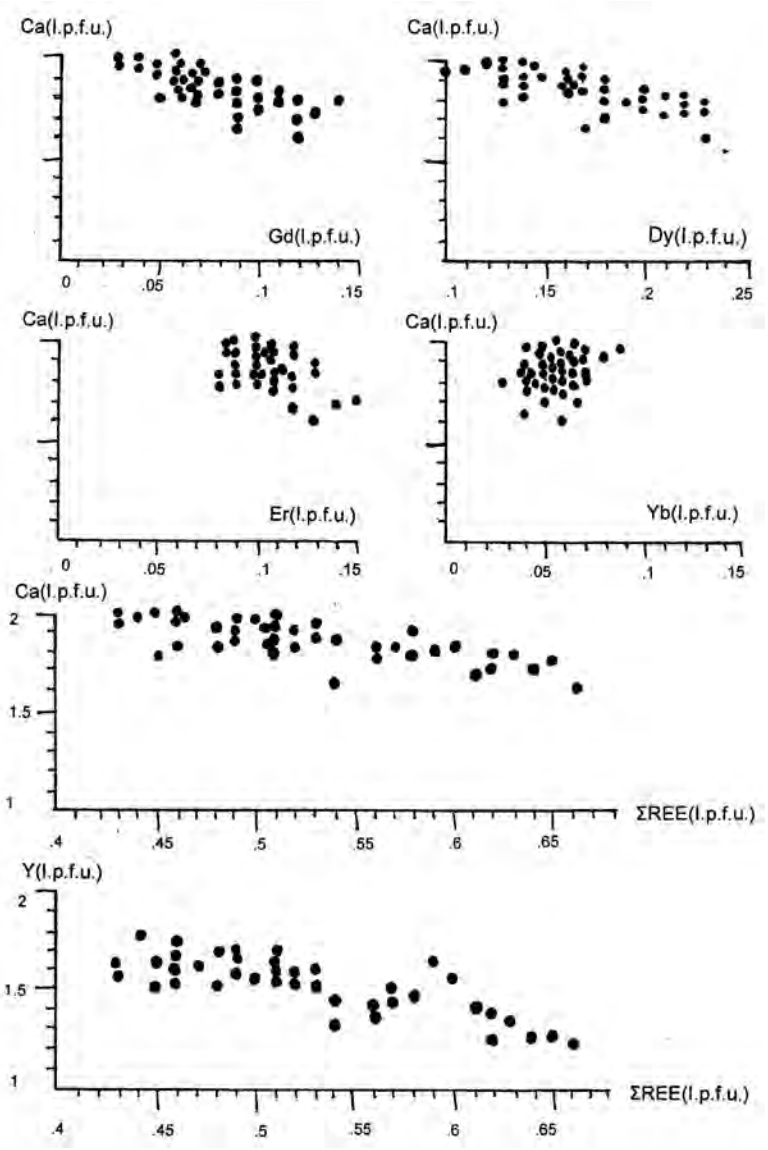

FIG. 5. Variation in chemical composition of Goudini kamphaugite-(Y) based on results of 43 electron-microprobe analyses; i.p.f.u.: number of ions per formula unit.

unit than the La Cabrera mineral; it must also tolerate greater charge imbalance. But the partial overlap of the two fields indicates that in large part the two samples of kamphaugite have exactly the same composition in terms of Ca, Y and ΣREE.

The internal compositional variations of kamphaugite-(Y) from Goudini are not random. The reason is to be found in the concentric zoning of the spheroids already described. Two examples are shown in Figure 7. There was a gradual depletion of REE (especially Gd and Dy) coupled with progressive increase of Y and Ca from core to rim during growth of the spheroids. González del Tánago *et al.* (2006) claimed that the brighter zones on their BSE image of a spheroid from La Cabrera are richer in REE relative to Y, but this implies oscillatory instead of progressive zoning. The possibility that the dark zones have a different origin will now be considered.

A discrepancy in H_2O content exists between the empirical formula of the Hørtekollen mineral derived from chemical analysis ($3H_2O$ per $4CO_3$) and the structural determination, which implies only $2H_2O$. Channels in the structure are not large enough to accommodate extra molecules of H_2O (Rømming *et al.* 1993). Evidence from the Høydalen occurrence also indicates that the H_2O content of kamphaugite-(Y) is variable (Raade *et al.* 1993). The H_2O content of the Goudini mineral and the measured density are closer to the theoretical values of the structural formula than kamphaugite-(Y) from elsewhere (Table 4). It should be remembered that only the structure determination was performed on a single-crystal fragment. All other studies of kamphaugite-(Y) (including average chemical composition as well as DTA, IR and Raman spectroscopy) pertain to aggregates. The SEM photographs (Figs. 1, 2) clearly show how irregular the outer surfaces of such aggregates can be. If the internal growth-zones of the kamphaugite-(Y) spheroids represent such surfaces, it seems very likely that variable amounts of non-essential H_2O will be occluded between crystals. The generalized formula of Rømming *et al.* (1993) should therefore be accepted as correct.

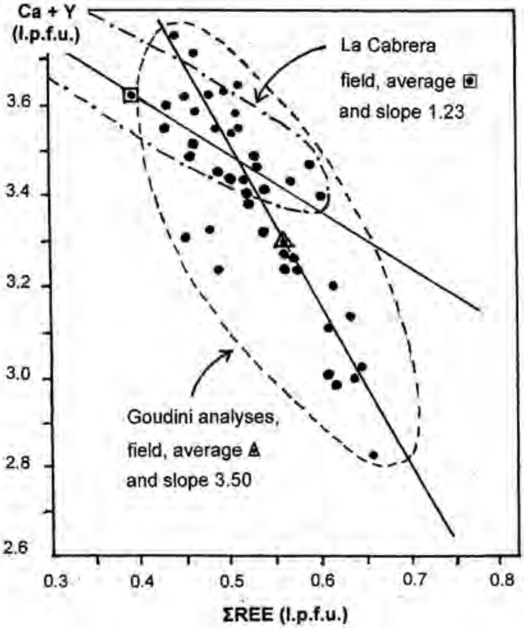

FIG. 6. Substitution of ΣREE^{3+} for ($Y^{3+} + Ca^{2+}$) in Goudini kamphaugite-(Y), (n = 43) compared with data of La Cabrera (n = 51) after recalculation on the basis of C = 4 (González del Tánago *et al.* 2006).

According to these findings the empirical formula of the Goudini kamphaugite-(Y) is: $(Ca_{1.84}REE_x)(Y_{1.46}REE_{0.54-x})(CO_3)_4(OH)_{1.65}•2H_2O$, with extra H_2O.

X-RAY POWDER DIFFRACTION

X-ray powder patterns were obtained using a Debye–Scherrer camera 57.3 mm in diameter and Co*K*α radiation, with the sample mounted in a rubber ball. The preliminary measurements reported earlier (Verwoerd 1963) were made without correction for film shrinkage. They were therefore repeated, averaged and increased by a factor of 1.0034. The data are in very good agreement with the values calculated from the unit-cell dimensions of kamphaugite-(Y) from the type locality (Hørtekollen), and have been indexed accordingly (Table 5). One rather weak reflection (*d* = 2.317 Å) could not be indexed and presumably belongs to an unidentified impurity.

Fairly extensive powder-diffraction data from five localities plus limited data (strongest lines only) from two more are now available. In addition, Raade *et al.* (1993) commented that kamphaugite-(Y) from Høydalen has a clearly visible {004} reflection not observable in powders from the type locality, and an enhanced {008} reflection. Hogarth (1972) was the first to notice such unexpected variations in intensity; he found the {008} reflection "greatly strengthened" at Evans–Lou but misidentified the index as {013}. If only basal reflections were involved, the obvious explanation would have been preferred orientation of platy fragments of the crystal. Raade *et al.* (1993) discounted this possibility, and their argument is strengthened by Féher *et al.* (2003), who used a Gandolfi camera, designed to eliminate preferred orientation effects. The results showed the {004} reflection of kamphaugite-(Y) from Szarvaskö as weak and {008} as rather strong or moderate, comparable to that at Høydalen. However, it is not clear why the authors of both papers ascribe the phenomenon to a low H_2O content in the mineral.

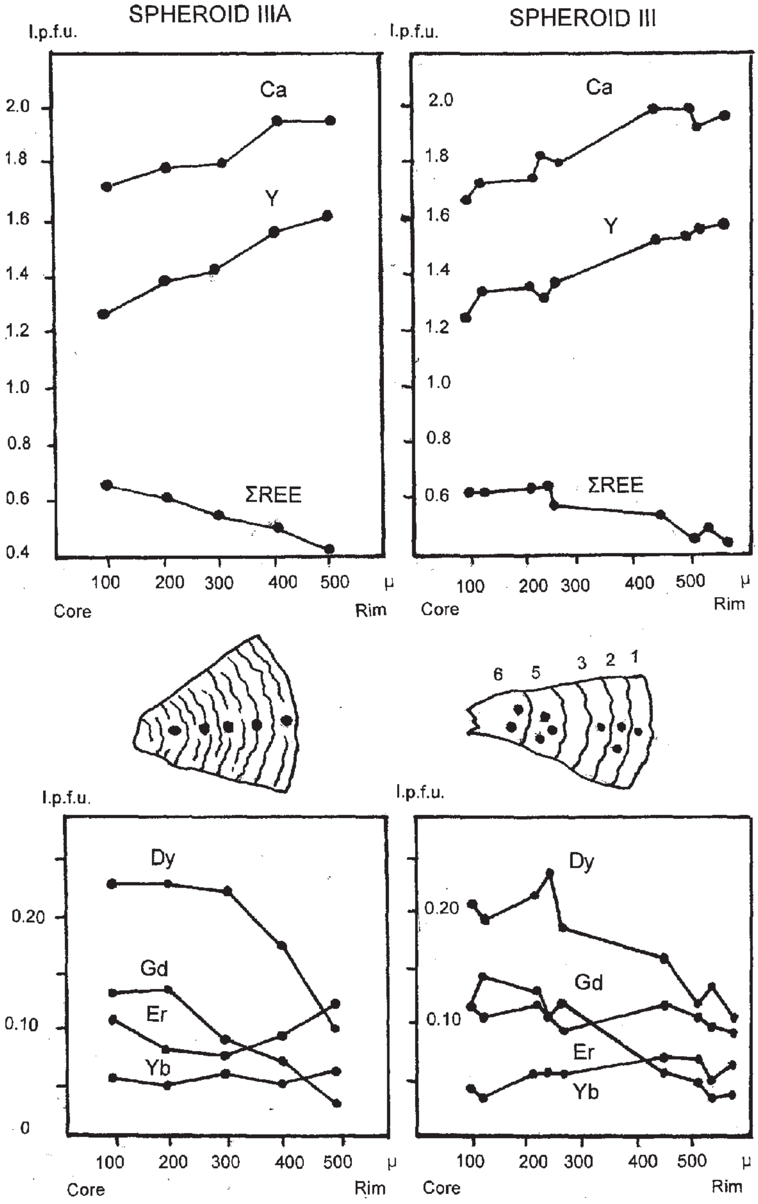

FIG. 7. Two fragments of spheroid of Goudini kamphaugite-(Y) analyzed by electron microprobe, one with clearly defined zones of ~60 μm analyzed separately (III) and one with vague zones analysed at regular 100 μm intervals from rim to core (IIIA).

Attention may be drawn to several other variations in intensity in the powder patterns of kamphaugite-(Y) of greater magnitude than those usually encountered with the powder method: reduction of {322} and {228} at Hørtekollen, exaggeration of {216} at Kola, exaggeration of {202} at Tommot, and reduction of {102} and {104} at both Kazakhstan and Evans–Lou (Fig. 8). Among the most important factors affecting the intensity of X-ray diffraction are the number of atoms per unit volume and departures from an ideal lattice (the "structure factor"). Attempts to find a correlation between intensities of reflections and Ca, Y or REE content of kamphaugite-(Y) were not successful. But perhaps it is the relative degree of order and disorder with which the various atoms occupy lattice positions, rather than their relative numbers, that count. Regarding lattice imperfections, the observation of Nekrasov *et al.* (1992) of "subparallel microblocks of 100 Å to 500 Å in size" in particles of kamphaugite-(Y) from Tommot is highly significant. Such structural mosaics, through the displacement of lattice arrays, will control the phase relations of the reflections and thereby determine their amplitudes (Klug & Alexander 1954).

The unit-cell dimensions of the Goudini kamphaugite-(Y) were derived from the XRD powder pattern and refined by least squares using the CELREF Version 3 program. Since there are differences among the cell dimensions reported in the literature for kamphaugite-(Y), it was decided to subject all available data to the same procedure. Some of the results (Table 6) are not very precise owing to difficulties of measurement depending on the quality of the photographs and absence of high-angle reflections. Nevertheless, real differences in *a*, *c* and *V* appear to exist because there is little overlap of error bars (Fig. 9). Both *a* and *c* increase by about 1% between Goudini and Feriolo samples at the low end and Szarvaskö at the high end, resulting in a volume increase of 3.7%. No correlation was found between any of these quantities and the chemical variability of kamphaugite-(Y), except that small unit-cell volumes (Rössing, Goudini) seem to be associated with large deficiencies of Ca. In fact, linear relationships possibly exist between cell volume, calculated density and Ca deficiency (Figs. 10A, B), but the data (from Tables 4 and 6) are not sufficient to be confident about this. Perhaps minor deviations from the ideal structure can be held responsible for differences in unit-cell dimensions as in the case of variations in X-ray intensity.

TABLE 5. X-RAY POWDER-DIFFRACTION DATA FOR KAMPHAUGITE-(Y) FROM GOUDINI

h k l	I_{calc}	d_{calc}	d_{obs}	I_{obs}	*h k l*	I_{calc}	d_{calc}	d_{obs}	I_{obs}
1 0 1	0.72	7.0359			3 2 2	1.81	2.0258	2.022	5
1 0 2	9.99	6.1409	6.07	10	3 2 4	1.58	1.9283		
0 0 4	1.22	5.4482	5.45	2	2 2 8	3.19	1.8914	1.885	10b
1 0 3	1.43	5.1956			2 0 10	2.50	1.8800		
1 1 1	1.23	5.1100			3 1 7	1.48	1.8760		
1 0 4	5.44	4.3944	4.40	8	4 0 0	2.18	1.8585		
1 1 3	1.74	4.2586			1 1 11	1.35	1.8538		
1 0 5	0.77	3.7599			4 0 1	1.35	1.8517		
2 0 2	3.31	3.5179	3.517	6	3 2 6	1.01	1.7930	1.806	1
1 1 5	0.83	3.3552	3.316	3	3 1 8	0.53	1.7798		
2 1 1	0.98	3.2865			4 1 2	0.53	1.7788		
1 0 6	1.05	3.2634			4 1 4	0.62	1.7117		
2 1 2	2.34	3.1798	3.188	3	3 2 8	1.06	1.6440	1.651	2
1 0 7	0.76	2.8716	2.888	7	4 2 2	1.06	1.6432		
2 1 4	4.85	2.8379			2 1 12	0.44	1.5937		
2 0 5	3.00	2.8282			4 0 8	0.93	1.5352	1.529	2
0 0 8	2.20	2.7241	2.726	3	4 2 6	0.44	1.5115		
2 2 0	4.33	2.6283	2.628	7	3 0 12	0.28	1.4648	1.464	1
2 1 6	3.14	2.4523	2.466	2b	5 0 4	0.45	1.4343		
2 2 4	0.52	2.3672			5 0 6	0.26	1.3759	1.374	1
3 1 1	0.93	2.3372			4 2 10	0.93	1.3216		
			2.317	1	1 1 16	0.59	1.3185		
3 0 4	0.97	2.2556			3 0 14	0.59	1.3181		
2 2 5	0.64	2.2507			4 3 9	0.05	1.2670	1.267	1
3 1 3	0.44	2.2366	2.235	4	5 0 10	0.29	1.2282		
1 1 9	0.56	2.1993			4 1 13	0.29	1.2277		
2 0 8	0.56	2.1972			2 2 16	0.24	1.2093	1.213	1
1 0 10	0.60	2.0912	2.085	1				1.161	1
3 0 6	0.72	2.0469							

Note: d_{calc} and I_{calc} from JCPDS 79–1669 (1998) based on the unit cell and the structure determination of kamphaugite-(Y) from the type locality (Rømming *et al.* 1993). With few exceptions, only reflections with I_{calc} > 0.5 on a scale of 1 to 10 (*i.e.*, 5%) are listed; b: broad line. The *d* values are expressed in Å.

VIBRATIONAL SPECTROSCOPY

Infrared spectra of the Goudini mineral were obtained with a few mg of sample dispersed in KBr, using both Digilab and Perkin–Elmer FT–IR spectrophotometers in Washington and the Chemistry Department at Stellenbosch, respectively. The Perkins–Elmer spectrum shows better resolution (12.5 cm^{-1}) and is reproduced here (Fig. 11).

Essentially the same IR spectrum for kamphaugite-(Y) from the Tommot rare-earth deposit has been published by Nekrasov *et al.* (1992). For kamphaugite-(Y) from Kazakhstan, Stepanov (1961) reported two absorption bands identical in depth and width at 3 000 and 3 500 cm^{-1} indicating in his opinion almost equal contents of hydroxyl and H_2O; however, such an interpretation is too simplistic.

The main absorption bands of the Goudini mineral have wavenumbers in the ν_3 C–O stretch range (1497.8 and 1406.6 cm^{-1}), and the ν_2 C–O out-of-plane bend (871.6 cm^{-1}), whereas the ν_4 C–O in-plane bend (750.4 cm^{-1}) can also be recognized. Rømming *et al.* (1993) found that the triangular carbonate groups in the structure are asymmetrical, with unequal C–O bond distances; this explains the quadruple splitting of the ν_3 stretch band (Fig. 11). The fourth normal vibration of the CO_3^{2-} group (ν_1) is not IR-active (Nakamoto 1997).

The broad peak between 3 000 and 3 600 cm^{-1} is attributed to O–H stretches (ν). As a result of molecular interactions and differing chemical environments that affect the strength of hydrogen bonds, this absorption

TABLE 6. UNIT-CELL DIMENSIONS OF KAMPHAUGITE-(Y)

Locality	*a* (Å)	*c* (Å)	*V* (Å^3)	References
Goudini	7.402(3)	21.778(1)	1192.9	This paper
Feriolo	7.415(2)	21.751(8)	1195.9	Guastoni *et al.* (2005)
Rössing	7.418(5)	21.80(3)	1199.6	Petersen *et al.* (2001)
Hørtekollen	7.434(1)	21.793(3)	1204.4	Rømming *et al.* (1993)
Hørtekollen	7.437(2)	21.79(1)	1205.2	Raade & Brastad (1993)
Tommot	7.44	21.84	1208.9	Nekrasov et al. (1992)
La Cabrera	7.449(4)	21.793(4)	1209.3	González del Tánago *et al.* (2006)
Evans-Lou	7.460(9)	21.824(3)	1214.5	Hogarth (1972), this paper
Kazakhstan	7.461(4)	21.903(1)	1219.3	Stepanov (1961), this paper
Kola	7.471(2)	21.908(1)	1222.7	Voloshin *et al.* (1996), this paper
Szarvasko	7.48(2)	21.961(2)	1236.7	Fehér *et al.* (2003), this paper

Refined from XRD powder-diffraction data, with two exceptions: Rømming *et al.* (1993) used single-crystal XRD measurements, and Nekrasov *et al.* (1992) employed electron-diffraction measurements made of particles in a suspension.

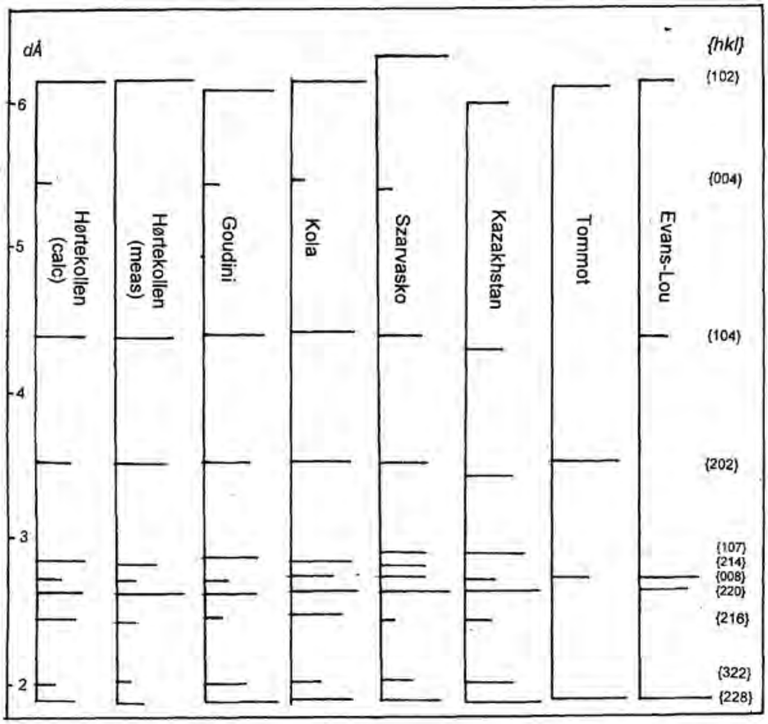

FIG. 8. Spacings and intensities of selected XRD powder-diffraction reflections of kamphaugite-(Y).

band does not differentiate between adsorbed water, water of hydration and hydroxyl groups (Smith 1999). However, the presence of tightly held H_2O molecules in kamphaugite-(Y) is unequivocally shown by the absorption peak at 1654.1 cm^{-1}, due to the scissoring of the two O–H bonds in H–O–H. A sharp absorption peak at 1075.8 cm^{-1} (which is split in two at 1050 and 1100 cm^{-1} in the case of Tommot but not Goudini) may be ascribed to the O–H bending vibration (δ).

Additional information was obtained by Raman spectroscopy, which was performed in the Physics Department of Witwatersrand University; the first spectrum of this mineral is presented here (Fig. 12). As expected, the Raman spectrum shows a sharp peak at 1086.5 cm^{-1}, the ν_1 wave number of the CO_3^{2-} group that is missing from the IR spectrum. The ν_2 vibration of CO_3^{2-} at 871.6 cm^{-1} is not Raman-active, and therefore absent. The other two normal vibrations ν_3 and ν_4 should be present but are weak.

In the O–H symmetric and antisymmetric stretching region, the Raman spectrum reveals the fine structure that is not evident in the IR spectrum. There are four prominent peaks at 3140.0. 3207.5, 3297.5 and 3383.0 cm^{-1}, which fall within the range for H_2O molecules held either by weak hydrogen bonds to the anion, or by weak ionic bonds to the metal, or by both (Nakamoto 1997). The spectrum shows no evidence of H–O–H scissoring at 1700–1600 cm^{-1}. At the low end of the spectrum (200–500 cm^{-1}), the peaks may be ascribed to metal–oxygen bonds. A few minor vibrational features that could not be identified (more prominent as Raman peaks than IR absorption bands) occur between 3 000 and 2 200 cm^{-1}.

Qualitatively, the spectra confirm the results of chemical and X-ray analyses, but unfortunately do not resolve the uncertainty about the H_2O content of kamphaugite-(Y) from Hørtekollen, as discussed by Rømming *et al.* (1993).

THERMAL STUDIES

Sufficient material for DTA and TG studies on the Goudini and Hørtekollen minerals was not available. The DTA curves of kamphaugite-(Y) from Kazakhstan were published by Stepanov (1961), showing four endothermic effects between 130° and 760°C. Slightly different results (Table 7) were obtained on kamphaugite-(Y) from Høydalen (Raade *et al.* 1993) and La Cabrera (González del Tánago *et al.* 2006). Owing to the many variables involved in DTA determinations (*e.g.*, heating rate), the temperature differences are not considered significant. Although a DTA peak at ~550°C is not recorded for material from La Cabrera, there is a step on the corresponding TG curve with a weight loss of 10.8% between 450° and 600°C. The four endothermic effects are interpreted to be successive losses of interstitial H_2O (more tightly held in the case of La Cabrera than at Kazakhstan and probably absent at Høydalen), water of crystallization, OH and CO_2. Stepwise decarbonation involving metastable formation of $CaCO_3$ was postulated by González del Tánago *et al.* 2006).

PARAGENESIS

At Goudini, kamphaugite-(Y) was one of the last minerals to crystallize during late hydrothermal or epithermal mineralization following volcanic activity. It occupies drusy cavities in a quartz–barite vein and does not replace any other mineral. In this particular vein, barite occurs in several forms, both early and late in the sequence: (1) as replacement remnants in chalcedony under the microscope, (2) predominantly as aggregates of transparent colorless crystals of up to several cm in size, and (3) as an ochre-yellow to white powder lining some of the cavities in which kamphaugite-(Y) was deposited (Fig. 1). The SEM photographs reveal that

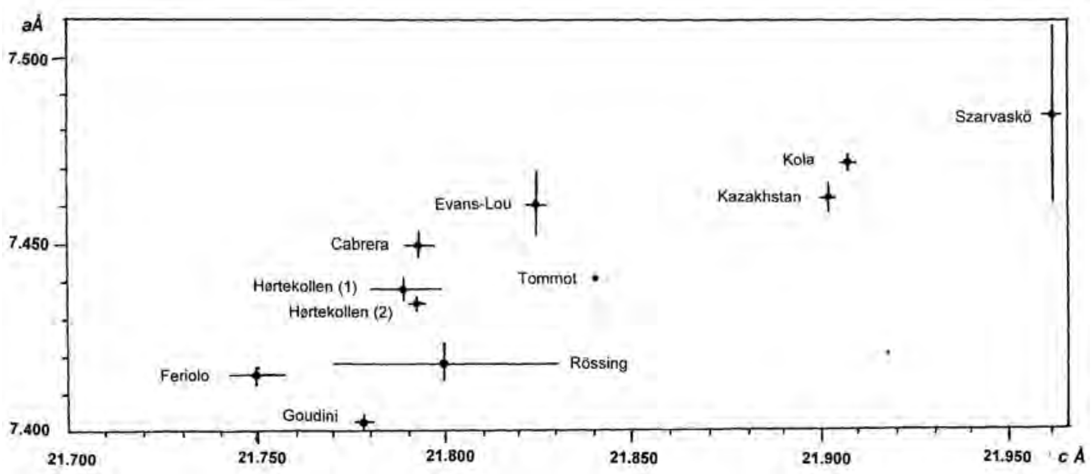

FIG. 9. Variation diagram of unit-cell dimensions of kamphaugite-(Y) from various localities.

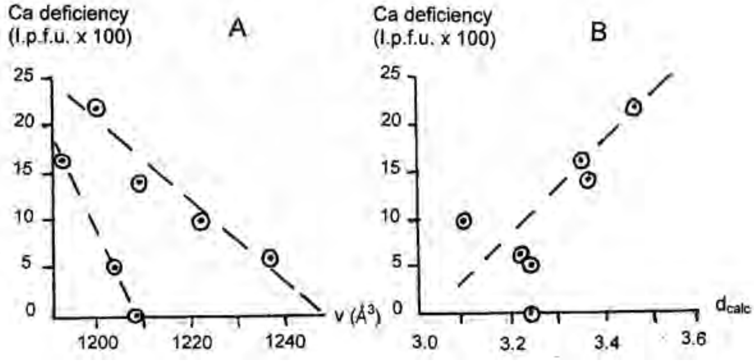

FIG. 10. A. Relationship between Ca deficiency of kamphaugite-(Y) from various localities and unit- cell volume. B. Relationship between Ca deficiency and calculated density.

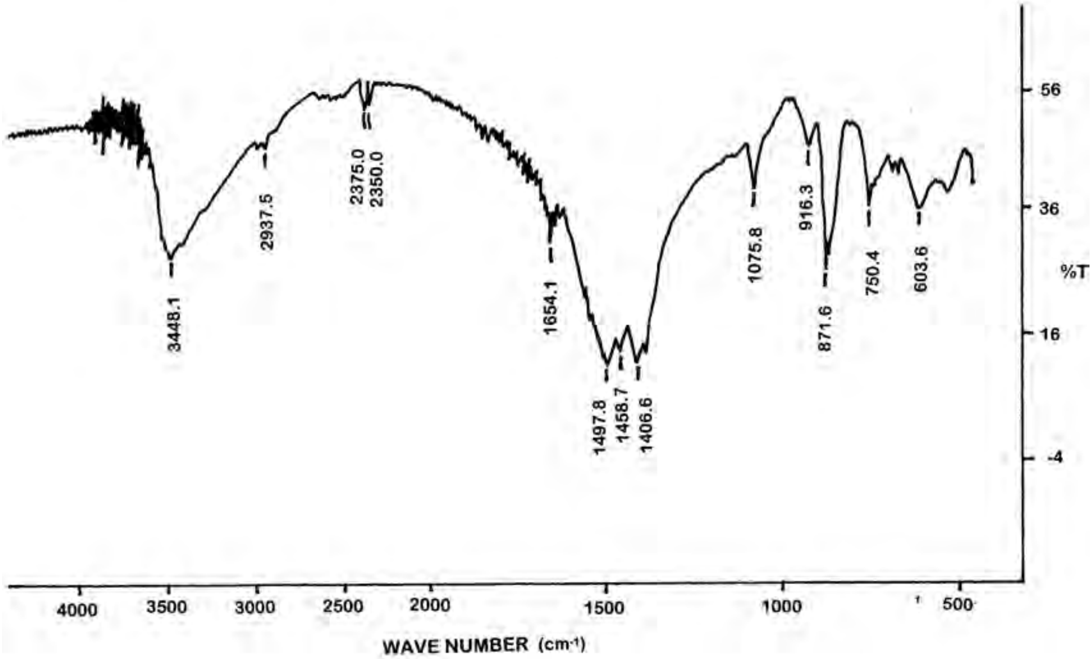

FIG. 11. Infrared absorption spectrum of kamphaugite-(Y) from Goudini.

the powdery coating consists of euhedral barite with a grain size of 1–10 μm.

Some kamphaugite-(Y) spheroids encrust minute quartz crystals in a drusy cavity (Fig. 2D), and some are coated in turn by a thin layer of hyaline quartz. The only other associated minerals, earlier than kamphaugite-(Y), are yellow to red and brown mixtures of "limonite", goethite and ferruginous chalcedony (recrystallized opal). Many pieces of chalcedony are angular fragments of silicified carbonate rock cemented by the coarse-grained barite.

The quartz–barite veins are intimately associated with a ferruginous silicified zone forming an oval ring of intermittent outcrops 600 by 400 m in diameter, which are radioactive. Microscopic evidence favors the view that it is the alteration product of sövitic carbonatite. There are scattered outcrops of sövite in this poorly exposed area. It coincides with an yttrium anomaly 800 m wide, as established by geochemical exploration.

These observations suggest that kamphaugite-(Y) was deposited by hydrothermal solutions that leached Y and REE from an unidentified precursor mineral in carbonatite. The cause of the radioactivity was first thought to be a primary uranium mineral (Verwoerd 1967), but thorianite has since been identified (Adrian *et al.* 1989). A more likely source of the rare elements would be yttropyrochlore or another member of the pyrochlore group, although Nb is not a characteristic trace element at Goudini. The niobium content of the phonolitic nephelinite is not high (110–120 ppm), but well above the level of most volcanic rocks. Yttrium (50–60 ppm) is about double that of normal basalt, and uranium (6–7 ppm) is also relatively high (Verwoerd 2008, Table 1).

Monazite occurs as a primary mineral in the sövite dykes that cut the volcaniclastic sediments of the Goudini volcano (Verwoerd 1967). The interesting question remains, therefore, what caused the decoupling of light and heavy REE, with the latter eventually becoming enriched in the secondary environment together with Y? It appears that the separation took place during the magmatic stage with the LREE becoming immobilized in monazite, whereas the MREE, HREE, Y and U were leached from pyrochlore or some other precursor. Fluids from an epithermal vent would not have interacted with the dykes.

González del Tánago *et al.* (2006) devoted their attention to investigating the conditions of formation of kamphaugite-(Y) at La Cabrera. From stable isotope analyses and textural relations with coexisting minerals, they concluded that crystallization took place from solutions with a meteoric source of carbon at temperatures below 50°C. This could very well apply to kamphaugite-(Y) from Goudini also.

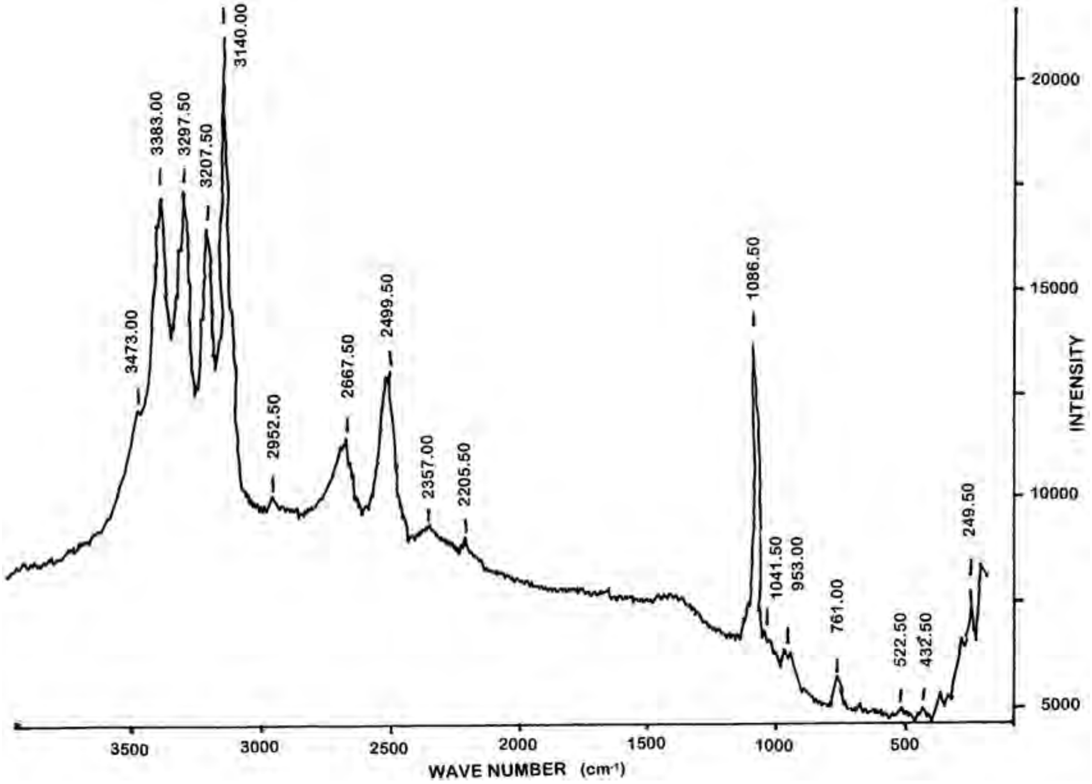

FIG. 12. Raman spectrum of kamphaugite-(Y) from Goudini.

TABLE 7. ENDOTHERMIC EFFECTS ON DTA CURVES OF KAMPHAUGITE-(Y)

	1	2	3	4
Kazakhstan	130°-200°C	490°-500°C	580°C	710°-760°C
Høydalen	n.p.	470°C	540°C	680°C
La Cabrera	342°C	430°C	n.p.	754°C

n.p.: not present.

ACKNOWLEDGEMENTS

The friendship of John Gittins and his discovery of agrellite in the Kipawa complex (Gittins *et al.* 1976) encouraged me to continue my attempt to describe a new mineral; this paper comes nearest to achieving that goal. I thank Anton le Roex for the REE analysis by ICP–MS, F.W.E. Strelow for determining the C and H contents, D. Glenister for the density measurement, D.N. Steenkamp for the SEM microphotographs, E. Förtsch for checking the X-ray-diffraction results, W.J. Engelbrecht for the IR spectrum, Pamela Murphy for the Raman spectrum, Ilia Kubantsev of IMGRE, Moscow, for translating the paper by Stepanov, and J.-A. Gertenbach for refining the unit-cell dimensions, as well as several scientists at the Geophysical Laboratory of the Carnegie Institution and the Smithsonian Institution in Washington D.C. for help during an early stage of the investigation. Two referees, Gunnar Raade and D.D. Hogarth, made very useful suggestions for improving the manuscript.

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