

The redefinition of tengerite-(Y), $Y_2(CO_3)_3 \cdot 2-3H_2O$, and its crystal structure

RITSURO MIYAWAKI

Government Industrial Research Institute, Nagoya, Kita, Nagoya 462, Japan

JUNKO KURIYAMA,* IZUMI NAKAI

Department of Chemistry, University of Tsukuba, Ibaraki 305, Japan

ABSTRACT

Tengerite-(Y) is redefined as a hydrous yttrium carbonate mineral with an ideal formula $Y_2(CO_3)_3 \cdot nH_2O$ ($n = 2-3$), on the basis of reexamination of the type specimen, type locality specimens, and synthetic samples. Ca, although previously reported in the literature, is found not to be an essential component of tengerite-(Y). Tengerite-(Y) is orthorhombic, with space group $Bb2_1m$. The crystal structure of tengerite-(Y) was solved and refined to $R = 0.045$ for 765 independent reflections using a hydrothermally synthesized single crystal. Refined lattice parameters are $a = 6.078(4)$, $b = 9.157(2)$, and $c = 15.114(6)$ Å, $Z = 4$. The structure can be described as a sheet structure built up from ninefold-coordinated Y polyhedra and CO_3 trigonal planar groups. The corrugated sheets are connected by other CO_3 groups to form a three-dimensional framework. The structure of tengerite-(Y) is not related to that of lanthanite-(La) despite their compositional similarity. It is suggested that tengerite-(Y) has a close structural relationship to kimuraite-(Y) and lokkaite-(Y), whereas lanthanite-(La) is related to calkingsite-(Ce).

INTRODUCTION

Tengerite was first described as "carbonated yttrium earth" by Svanberg and Tenger (1838), and the mineral name tengerite was introduced by Dana (1868). Svanberg and Tenger (1838) reported that the phase occurred as white pulverulent or fibrous coatings on gadolinite from Ytterby, northeast of Stockholm, Sweden. Although the mineral was described as an yttrium carbonate, no quantitative chemical analysis was made and, of course, no X-ray diffraction analysis was provided. The original definition of tengerite was tenuous, and subsequently several later specimens were erroneously reported as tengerite. The chemical analysis of tengerite from Barringer Hill (Genth, 1889; Hidden, 1905) indicated the presence of considerable amounts of Be. Iimori (1938) gave the chemical formula $Y_3Ca(OH)_3(CO_3)_4 \cdot 3H_2O$ for tengerite from Iisaka, Fukushima, Japan. Stepanov (1961) described a rare-earth carbonate mineral from Kazakhstan as tengerite. Vormo et al. (1966) reported a rare-earth carbonate mineral from Pyörönmaa, Finland, and provisionally named the mineral tengerite. However, "tengerite" samples from Kazakhstan and Pyörönmaa were later found to be new mineral species, namely kamphaugite-(Y) (Raade and Brastad, 1993) and lokkaite-(Y) (Perttunen, 1971). The equivocal definitions of tengerite result from the poor quality of its specimens, which occur as thin crystalline to powdery coatings. Additionally, in almost all cases it is closely associated with other minerals

from which it cannot be easily separated. Such natural occurrences have made it difficult to analyze the chemical composition and crystal structure of tengerite.

Nagashima and Wakita (1968) and Wakita and Nagashima (1972) synthesized a hydrous yttrium carbonate by precipitation from a homogeneous solution of yttrium trichloroacetate. Chemical analysis of their synthetic carbonate yielded the chemical formula $Y_2(CO_3)_3 \cdot nH_2O$ ($n = 2-3$). Its X-ray powder diffraction pattern agreed with those of tengerite samples from Iisaka, Japan, and Rosås, Norway (JCPDS 16-698, now replaced by 27-91), and its IR spectrum was very close to that of the Japanese tengerite. From these facts they concluded that the synthetic product $Y_2(CO_3)_3 \cdot nH_2O$ and natural tengerite may have the same crystal structure. Tareen et al. (1980) have reported the hydrothermal synthesis of single crystals of $Y_2(CO_3)_3 \cdot nH_2O$ ($n = 2-3$), which were practically identical with the substance reported by Nagashima and Wakita (1968).

Perttunen (1971) undertook a reinvestigation of tengerite. He reported that the X-ray powder patterns of tengerite specimens from Pyörönmaa and Lövböle, Finland, Rosås, Norway (Neumann and Bryn, 1958), and Iisaka, Japan (Nagashima and Wakita, 1968), represented one mineral species, whereas that of "tengerite" from Kazakhstan (Stepanov, 1961) showed quite a different pattern from the others. Furthermore, Perttunen (1971) pointed out that Ca seemed to be an unessential constituent in tengerite, according to his X-ray powder diffraction study of synthetic hydrous yttrium carbonate and chemical analysis with reference to the work by Nagashi-

* Present address: Naka Works, Hitachi Ltd., Ibaraki 312, Japan.

TABLE 1. List of tenerite specimens and synthetic samples examined and results of identification

Sample	Locality	Source	Identified mineral species
1	Ytterby	Naturhistoriska Riksmuseet, g10820	mixture of lokkaite-(Y) and lanthanite
1'	Ytterby	Naturhistoriska Riksmuseet, g10820	mixture of kimuraite-(Y) and lokkaite-(Y)
2	Ytterby	Naturhistoriska Riksmuseet, g10821	calcite
3	Ytterby	Naturhistoriska Riksmuseet, L.K.4133	kimuraite-(Y)
4	Ytterby	Naturhistoriska Riksmuseet, 84:0211	mixture of bastnäsite-(Ce) and low quartz
5	Ytterby	Smithsonian Institution, NMNH R13924	mineral X
6	Ytterby	Smithsonian Institution, NMNH C2248	kimuraite-(Y)
7	Canada	Smithsonian Institution, NMNH 97286	lokkaite-(Y)
8	Åskagen	Chalmers University of Technology	mineral X
9	Iisaka	University of Tsukuba, Nagashima Collection	mixture of mineral X and synchysite
10	Iisaka	Sakurai Museum	mixture of mineral X and synchysite
11	synthetic	$Y_2(CO_3)_3 \cdot nH_2O$ (hydrothermal, test tube vessel)	synthetic equivalent of mineral X
12	synthetic	$Y_2(CO_3)_3 \cdot nH_2O$ (hydrothermal, Pyrex tube)	synthetic equivalent of mineral X
13	synthetic	$Y_2(CO_3)_3 \cdot nH_2O$ (gel method)	synthetic equivalent of mineral X

Note: Mineral X is defined as tenerite-(Y) in this study.

ma and Wakita (1968). Recently, Raade and Brastad (1993) have described a new rare-earth mineral, kamphaugite-(Y) $[Ca_2Y_2(CO_3)_4(OH)_2 \cdot 2-3H_2O]$, found in Norway, and reported that it is identical with the mineral from Kazakhstan.

In the present study, a total of ten natural specimens labeled as tenerite and synthetic crystals of $Y_2(CO_3)_3 \cdot nH_2O$ samples were examined by X-ray powder diffraction, chemical analyses, and IR spectroscopy to redefine tenerite. Single-crystal X-ray crystal structure analysis of tenerite-(Y) was carried out to determine the amount of H_2O in the chemical formula, n , and to examine the possible presence of Ca in the structure. The structural relationships between tenerite-(Y) and other rare-earth carbonates, such as lanthanite-(La) and kimuraite-(Y), were also clarified.

This redefinition has been approved in advance of publication by the Commission on New Minerals and Mineral Names, IMA. Two neotype specimens were established for tenerite-(Y): one at the Smithsonian Institution NMNH, R13924 from the type locality, Ytterby, Sweden, and one in the Nagashima Collection at the University of Tsukuba from Iisaka, Japan, now deposited in the National Science Museum of Japan (NSM-M25981).

REDEFINITION

Specimens

Specimens examined in the present study are listed in Table 1. Sample 1 is regarded as the type specimen (B. Lindqvist, personal communication). It is A. F. Svanberg's (and C. Tenger's) original material, which, according to notes of J. J. Berzelius, arrived at his museum in 1838. Sample 9 is a part of the sample analyzed by Iimori (1938).

Synthesis

Synthetic samples were prepared by the following three methods. One is a hydrothermal synthesis reported by Tareen et al. (1980). Concentrated formic acid as a carbonate source and an $Y(OH)_3$ gel, which was obtained by hydrolysis of an YCl_3 solution with aqueous ammonia, were sealed in a Pt capsule and placed in a test-tube type

stellite vessel. The synthesis was carried out at 200 °C under a pressure of 340 kg/cm² for 90 h. The second method is a synthesis using a Pyrex glass tube. About 10–100 mg of starting rare-earth (Y or La) carbonate was placed in a Pyrex tube, with a capacity of 3 mL, together with 0.5 mL of H_2O as solvent. The tube was kept at 130–180 °C in an electric oven for two weeks. The third is a gel method using agar or silica gel as a crystal-growth medium. Three layers, a carbonate-ion source layer, a diffusion layer, and a rare-earth ion source layer, were prepared in a glass test tube. Rare-earth (Y or La) chloride was used for the rare-earth ion source, and ammonium carbonate or sodium hydrogen carbonate was used for the carbonate ion source. The synthesis was carried out at room temperature for 1–3 months. Single crystals of $Y_2(CO_3)_3 \cdot nH_2O$ (sample 11) suitable for crystal structure analysis were obtained from the hydrothermal method.

X-ray powder diffraction analysis

X-ray powder diffraction data of the specimens were obtained with a Gandolfi camera using Ni-filtered $CuK\alpha$ radiation, and some are listed in Table 2. The results indicated that the white crust on gadolinite-(Y) of sample 1, the type specimen, was a mixture of lokkaite and lanthanite, and the thin coating on gadolinite-(Y) (sample 1') gave a powder pattern that was a mixture of kimuraite and lokkaite. Two other specimens, samples 3 and 6 from the type locality, also contained thin white coatings on gadolinite-(Y), and they gave powder patterns similar to that of kimuraite-(Y). Sample 2 was calcite, and sample 4 was a mixture of bastnäsite-(Ce) and quartz. Sample 7, from Canada, gave a diffraction pattern that was identical to that of lokkaite-(Y). Diffraction patterns of samples 5, 8, 9, and 10 were identical to that of synthetic $Y_2(CO_3)_3 \cdot nH_2O$ (sample 11), and the minerals are tentatively denoted as mineral X in Table 1.

Redefinition

We have found that the museum specimens labeled tenerite consist of at least five different rare-earth carbonates, including lanthanite (the predominant rare-earth

TABLE 2. X-ray powder diffraction data

<i>hkl</i>	Sample 11 synthetic				Sample 5 Ytterby		Sample 9 Iisaka	
	d_{calc}	$I/I_{0(\text{calc})}$	d_{obs}	I/I_0	d_{obs}	I/I_0	d_{obs}	I/I_0
							14.03	4
							10.65	2
							9.03	6
002	7.56	83	7.53	9	7.66	8	7.60	8
101	5.64	100	5.64	9	5.70	10	5.66	10
111	4.80	3	4.82	2			5.31	4
020	4.58	79	4.58	10	4.62	10	4.60	10
							4.47	4
103	3.88	95	3.89	9	3.91	10	3.90	10
004	3.78	17	3.77	4	3.82	4	3.79	4
113	3.57	25						
121	3.55	44	3.55	7	3.59	8	3.58	8
							3.45	8
							3.23	6
200	3.04	6	3.03	2	3.05	4		
123	2.96	64	2.96	8	2.98	8	2.97	8
024	2.91	12	2.92	4			2.93	4
210	2.88	1						
202	2.82	1						
							2.74	8
105	2.71	3			2.71	4		
212	2.70	5						
131	2.68	14	2.69	5			2.69	6
115	2.60	10	2.60	4	2.62	2	2.60	4
220	2.53	36	2.54	6	2.55	6	2.54	8
006	2.52	7						
222	2.40	14	2.40	4	2.42	4	2.41	4
204	2.37	17	2.37	4	2.39	4	2.38	4
125	2.33	11	2.33	3	2.34	2	2.34	2
214	2.29	8						
040	2.29	8	2.29	4	2.30	4	2.30	4
							2.25	2
026	2.21	15	2.21	4	2.22	4	2.21	4
141	2.12	26	2.12	5				
224	2.10	10	2.11	4	2.13	6br	2.13	6
232	2.07	3	2.07	2				
107	2.04	27	2.04	5				
135	2.03	3			2.05	4	2.04	6
301	2.01	12	2.01	4	2.03	2		
							1.991	6
143	1.972	36	1.971	6	1.985	6	1.975	6
044	1.958	13			1.953	4		
206	1.939	23	1.939	5			1.943	6
							1.884	8
303	1.880	14	1.877	4	1.890	2		
127	1.859	16	1.859	4	1.868	2	1.863	4
321	1.839	13						
240	1.829	21	1.830	6	1.841	4	1.824	6br
226	1.786	26	1.784	6	1.796	4	1.791	6
242	1.777	3						
145	1.748	2			1.752	4		
323	1.739	19	1.741	5			1.745	6
046	1.694	20	1.695	5	1.708	4	1.700	6
244	1.646	5	1.648	3	1.661	2		
109	1.619	6	1.618	3	1.629	2	1.616	6
129	1.526	8			1.531	4br	1.526	6
147	1.521	8	1.523	5br				
400	1.520	3						
0,0,10	1.511	1						
341	1.510	2						
246	1.480	6						
161	1.473	4	1.479	4br	1.490	2		

Note: br = broad.

element could not be specified), lokkaite-(Y), kimuraite-(Y), bastnäsäsite-(Ce), and a mineral species that has a diffraction pattern identical to synthetic $Y_2(CO_3)_3 \cdot nH_2O$. Our identification results are summarized in Table 1. Our semiquantitative analysis of the type specimens, samples

1 and 1', revealed that both are rare-earth carbonates dominated by Y and are mixtures of lokkaite-(Y) and lanthanite (sample 1) and kimuraite-(Y) and lokkaite-(Y) (sample 1').

Of the six Ytterby specimens, only one (sample 5) pro-

TABLE 3. Chemical compositions of tenerite from Ytterby, Iisaka, and synthetic samples

	Sample 5 Ytterby		Sample 9 Iisaka		Sample 10 Iisaka		Sample 12 synthetic		Sample 13 synthetic	
	Wt%	No. atoms (basis M = 2)*	Wt%	No. atoms (basis M = 2)*	Wt%	No. atoms (basis O = 9)	Wt%	No. atoms (basis O = 9)	Wt%	No. atoms (basis O = 9)
La ₂ O ₃	0.2	0.007	n.d.	—	0.17	0.004				
Ce ₂ O ₃	1.5	0.045	0.1	0.003	0.17	0.004				
Pr ₂ O ₃	0.6	0.017	0.2	0.006	0.09	0.002				
Nd ₂ O ₃	5.1	0.147	1.4	0.038	0.52	0.013				
Sm ₂ O ₃	4.4	0.122	1.6	0.042	0.39	0.009				
Eu ₂ O ₃	n.d.	—	0.5	0.012	0.01	—				
Gd ₂ O ₃	6.1	0.163	4.5	0.112	1.00	0.023				
Tb ₂ O ₃	0.7	0.018	0.9	0.023	0.22	0.005				
Dy ₂ O ₃	6.2	0.160	7.6	0.183	1.92	0.042				
Ho ₂ O ₃	0.7	0.017	1.3	0.030	0.47	0.010				
Er ₂ O ₃	1.4	0.035	3.2	0.075	1.46	0.032				
Tm ₂ O ₃	0.6	0.014	0.3	0.008	0.19	0.004				
Yb ₂ O ₃	0.7	0.017	0.9	0.021	1.16	0.024				
Lu ₂ O ₃	0.1	0.003	0.1	0.003	0.16	0.003				
Y ₂ O ₃	26.5	1.135	33.9	1.356	46.46	1.70	59.00	2.08	54.50**	1.96
ΣREE ₂ O ₃	54.8	1.900	56.5	1.912	54.39	1.87				
CaO	1.2	0.100	1.1	0.088	1.79	0.13				
CO ₂	26.9**	2.950	28.8**	2.956	32.35	3.03	32.54	2.94	32.90	3.03
H ₂ O	17.1**	9.162	13.6**	6.818	13.40	3.07	11.17	2.47	12.60	2.84
Total	100		100		101.93		102.71		100	

* M = REE + Ca.

** Calculated.

duced a diffraction pattern corresponding to synthetic Y₂(CO₃)₃·nH₂O. Specimens from Åskagen, Sweden, (sample 8) and Iisaka (samples 9 and 10) also gave the same diffraction patterns. These patterns agree well with that for the Norwegian tenerite reported in JCPDS 27-91. The other Ytterby specimens gave patterns representing various mixtures, including lokkaite-(Y), lanthanite, kimiraitite-(Y), calcite, bastnäsite-(Ce), and quartz.

We found that the hydrous yttrium carbonate minerals from Ytterby, Sweden (sample 5), Åskagen (sample 8), Iisaka, Japan (samples 9 and 10), Rosås, Norway (JCPDS 27-91), and Pyörönmaa, Finland (Perttunen, 1971), belong to one mineral species, which is identical to synthetic Y₂(CO₃)₃·nH₂O (sample 11). Consequently, it is reasonable to redefine this species as tenerite-(Y). The observed and calculated X-ray powder diffraction data for the synthetic substance given in Table 2 should be regarded as the standard diffraction data of tenerite-(Y).

CHEMICAL COMPOSITION

Quantitative analyses of rare-earth elements and Ca were carried out for the two neotype materials (samples 5 and 9) using a Rigaku 3270E X-ray fluorescence analyzer at Osaka Analytical Center, Rigaku Industrial Corporation. A 120-μg sample was carefully picked under a microscope and was dissolved with 120 μL of 1N HNO₃. A 100-μL sample of the solution was then dropped on filter paper (Rigaku drip paper Microcarry 3379C1). The calibration-curve method combined with the fundamental parameter method using standard solutions was applied to the determination. Corrections were made for overlap of other analytical lines. Anions compensating for the plus charges of the cations were attributed to the

CO₃²⁻ ion; i.e., REE₂(CO₃)₃ and CaCO₃. The H₂O content was calculated by difference. The results are given in Table 3. The resulting cation ratios are reliable, but their absolute values and the H₂O content may not be, because we used an extremely small sample, and we did not directly determine the CO₂ and H₂O contents.

Complete quantitative analyses of natural (sample 10) and synthetic (samples 12, 13) samples were based on analysis for C and H, and on inductively coupled plasma atomic emission spectroscopic (ICP-AES) analysis for the remaining cations. The results are listed in Table 3. The analyses gave the following empirical formulae for samples 10, 12, and 13: Ca_{0.13}REE_{1.87}C_{3.03}O₉·3.07H₂O, Y_{2.08}C_{2.94}O₉·2.47H₂O, and Y_{1.96}C_{3.03}O₉·2.84H₂O, respectively. The number of H₂O molecules ranges from 2 to 3, confirming the values reported for synthetic tenerite-(Y) (Nagashima and Wakita, 1968).

OPTICAL PROPERTIES

Optical properties were measured using a fine powder of sample 5. Tenerite-(Y) is biaxial, $n_x = 1.587$ and $n_z = 1.616$. The calculated value of n for synthetic Y₂(CO₃)₃·2H₂O ($D_{\text{calc}} = 3.110 \text{ g/cm}^3$) is 1.620 based on the Gladstone-Dale relationship (Mandarino, 1976).

INFRARED SPECTRA

IR spectra were measured on a Jasco IR-700 spectrometer using the KBr method. The spectrum of synthetic tenerite-(Y) indicates characteristic absorptions of carbonate ions at 1510(s), 1463(s), 1425(s), 867(m), 850(m), 840(m), 765(m), 700(m), 690(m) cm⁻¹ (s = strong, m = medium). A broad medium-intensity band resulting from H₂O stretching vibrations appears in the frequency range

TABLE 4. Atomic positional and thermal parameters

Atom	x	y	z	B	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Y	0.4984(5)	0	0.34223(5)	0.93*	0.0065(1)	0.00243(5)	0.00110(2)	-0.0004(2)	-0.0010(1)	0.0006(1)
C1	0.256(1)	0.257(3)	0.1957(5)	0.70(11)						
C2	0.276(3)	0.064(2)	0.5	1.18*	0.007(4)	0.003(1)	0.0016(6)	-0.001(2)	0	0
O1	0.332(2)	0.129(1)	0.2201(7)	0.75(16)						
O2	0.1068(10)	0.253(3)	0.1343(4)	0.82(8)						
O3	0.311(2)	0.375(1)	0.2292(7)	0.79(17)						
O4	0.473(2)	0.012(2)	0.5	1.18(20)						
O5	0.186(2)	0.097(2)	0.421(1)	2.08*	0.002(2)	0.011(2)	0.0026(5)	0.000(1)	0.0006(8)	-0.0024(9)
O6	0.183(3)	0.414(2)	0.411(1)	2.28(35)						

Note: estimated standard deviations in parentheses.

* B_{eq} is calculated from $\frac{1}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2)$. The anisotropic temperature factor form is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

of 3500–3000 cm^{-1} , and the H_2O deformation band is a shoulder at 1650(m) cm^{-1} . Similar absorptions are observed in the spectra of the neotype material (sample 5) and kimuraite-(Y). They are typical of hydrous carbonates.

CRYSTAL STRUCTURE

Experimental

The crystals, hydrothermally synthesized using formic acid, have well-developed faces showing orthorhombic morphology with mmm symmetry. A transparent single-crystal fragment having dimensions of approximately $0.050 \times 0.075 \times 0.125$ mm was cut from the synthetic crystal and was used for the subsequent X-ray diffraction study. Oscillation and Weissenberg photographs verified that the Laue symmetry is orthorhombic and that the possible space groups are $Bb2_1m$, $Bbnn$, or $Bbm2$. The lattice parameters were determined utilizing a Rigaku AFC-5 four-circle automated diffractometer using graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71068$ Å). The lattice parameters, obtained by least-squares refinement of the 2θ values of 25 strong reflections, are $a = 6.078(4)$, $b = 9.157(2)$, $c = 15.114(6)$ Å, $V = 841.2(7)$ Å³.

A 2θ - ω scan technique, at a scan rate of $2^\circ/\text{min}$, was used to measure the diffraction intensities in one-eighth of a reciprocal sphere up to $\sin \theta/\lambda = 0.904$. The intensity measurement was repeated twice for a reflection with $\sigma(|F_o|)/|F_o|$ larger than 0.05. The intensities of three standard reflections, measured every 50 observations, did not show any fluctuation larger than 3%. The data were corrected for Lorentz and polarization factors. An absorption correction was made using the ACACA program (Wuensch and Prewitt, 1965) in a late stage of the structure determination ($\mu_{\text{MoK}\alpha} = 142.6$). A total of 1397 independent reflections were obtained, of which 765 reflections have $|F_o| \geq 3\sigma(|F_o|)$ and were used in the subsequent crystal structure analysis.

Structure determination and refinement

Patterson synthesis clearly demonstrated that the true space group is $Bb2_1m$. An initial model of the structure was determined by direct methods using the program Multan-80 (Main et al., 1980). The results suggested ap-

proximate positions of an Y atom and four O atoms, which were confirmed by the Patterson map. Refinement and difference Fourier synthesis resulted in locating two additional O atoms and two C atoms. The atomic parameters were refined by least squares utilizing the program RFIN2 (Finger, 1969), employing scattering factors taken from Cromer and Mann (1968) and anomalous dispersion factors from the International Tables for X-ray crystallography (Ibers and Hamilton, 1974). Final cycles with anisotropic temperature factors for Y, C2, and O5 yield $R = 0.045$ ($R_w = 0.050$) for the unrejected reflections and $R = 0.151$ ($R_w = 0.051$) for all reflections. No residual electron density greater than $0.9 \text{ e}/\text{Å}^3$ was observed in the final difference Fourier map. Final atomic positional and thermal parameters are reported in Table 4. Observed and calculated structure factors are given in Table 5.¹

Description of the structure

The crystal structure of tenerite-(Y) is illustrated in Figure 1. The structure is constructed from corrugated (001) sheets of ninefold-coordinated Y polyhedra in which the Y polyhedra share edges O1-O2 and O2-O3 with the carbonate ion of C1 wedged between the corner-sharing polyhedra. The sheets are linked together at O4 corners by the other carbonate ion of C2 to form a three-dimensional framework. The interatomic distances and bond angles were calculated using UMBADTEA (Finger and Prince, 1975) and are listed in Table 6. The Y atom is coordinated by eight O atoms of the carbonate groups and a H_2O molecule, with Y-O distances ranging from 2.34(2) to 2.53(1) Å. The trigonal planar carbonate ions are slightly distorted. In each carbonate group, O-C-O angles subtended by the edges O1-O2 (115.3°), O2-O3 (119.8°), and O4-O5 (117.6°) shared with the Y polyhedra are smaller than 120° , whereas the angles subtended by the nonshared edges O1-O3 (124.8°) and O5-O5 (124.4°) are greater than 120° .

¹ Table 5 may be obtained by ordering Document AM-93-519 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

The number of H₂O molecules in tenerite-(Y)

Because positions of H atoms could not be detected in the difference Fourier map, the bond valences were calculated according to the procedure of Donnay and Allmann (1970) to reveal H₂O molecule sites. The O6 atom, which does not belong to the carbonate groups, is assigned to a H₂O molecule on the basis of the bond valence sum (0.37 vu). The values of the bond valence sums of O5 (1.59 vu) and O6 together with their relatively short O5-O6 distances, 2.91(3) and 2.81(3) Å, indicate that these O atoms are involved in H bonding. A correction of the bond valence sums for H bonds after Donnay and Allmann (1970) gave more ideal values, 1.89 and 0.07 for O5 and O6, respectively, and confirmed the presence of H bonds. The H bonds are illustrated by light broken lines in Figure 1a. Bond valence sums for other atoms (Y = 2.99; C1 = 3.98; C2 = 3.98; O1 = 1.84; O2 = 1.95; O3 = 2.14; O4 = 2.12 vu) are in good agreement with the expected formal valence.

The chemical formula of tenerite-(Y) determined by the present structure analysis is Y₂(CO₃)₃·2H₂O. The number of H₂O molecules, two, is smaller than the values determined by the chemical analyses for natural and synthetic tenerite-(Y), which range between 2 and 3 (see Table 3). Perttunen (1971) reported that much of the H₂O can be lost without any apparent changes in the structure, based on checks of the X-ray powder diffraction patterns of a wet sample and a sample dried at 110 °C. The difference between the number of H₂O molecules derived from the present structure analysis and that determined by the chemical analysis suggests the presence of zeolitic H₂O in tenerite-(Y), as proposed by Nagashima and Wakita (1968). The zeolitic H₂O molecules may be situated in cavities between the corrugated sheets.

Ca content in tenerite-(Y)

Small amounts of Ca were found in our chemical analysis of samples 5, 9, and 10 (Table 3). Nagashima and Wakita (1968) and, later, Perttunen (1971) suggested that Ca seems to be a nonessential constituent of tenerite-(Y), though many published analyses of natural tenerite-(Y) samples indicated its presence. Attempts at synthesis of yttrium carbonate containing Ca have been unsuccessful (Nagashima and Wakita, 1968). This was confirmed by our synthesis experiment. In addition, our crystal structure analysis gives the formula Y₂(CO₃)₃·2H₂O, and the crystal structure does not support any mechanism for charge compensation, which would allow the substitution of divalent Ca for trivalent Y, except through a deficiency of carbonate ions, which is not probable.

X-ray powder diffraction patterns of samples 9 and 10 showed the presence of small amounts of impurities, mainly synchysite. Therefore, the Ca content detected in the above analyses is ascribed to impurities. Tenerite-(Y) is known to be an alteration product of rare-earth minerals such as gadolinite-(Y) and yttrialite-(Y); it occurs as fine crystals, closely associated with other min-

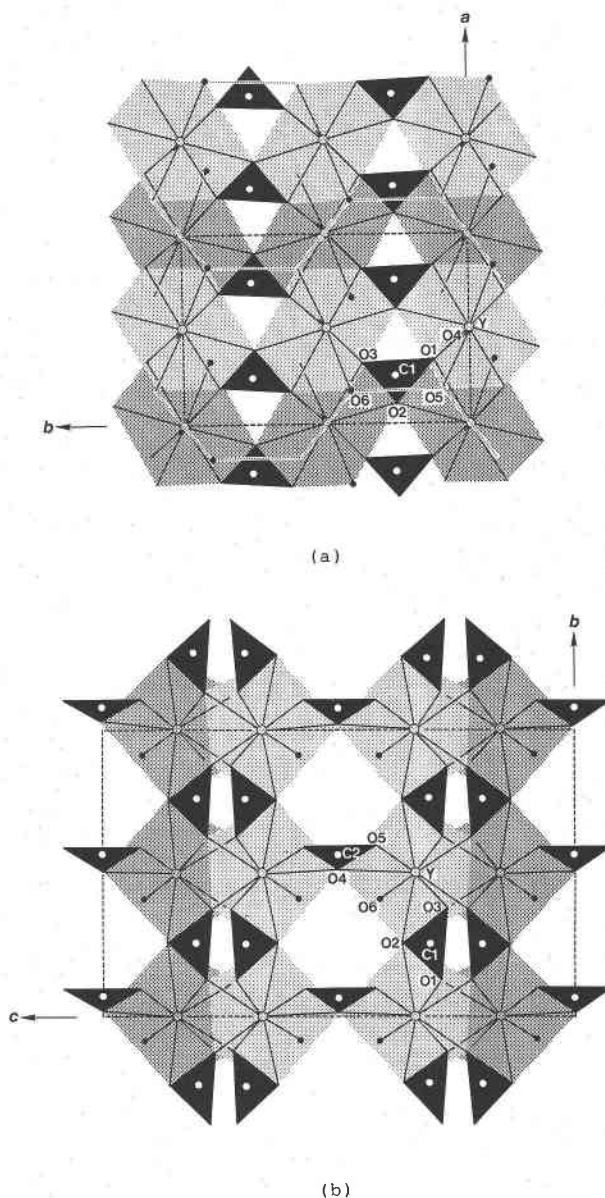


Fig. 1. Crystal structure of tenerite-(Y). (a) A corrugated sheet at $z = 0.25$ projected onto (001); (b) a projection viewed down (100) showing the connection between the sheets.

erals. We presume that the Be content or Ca content of tenerite reported previously must be caused by contamination by associated minerals. Consequently, the ideal chemical formula of tenerite-(Y) should be written as Y₂(CO₃)₃· n H₂O ($n = 2-3$).

Relationship to other hydrous rare-earth carbonate minerals

The chemical composition of lanthanite-(La), La₂(CO₃)₃·8H₂O, is closely related to that of tenerite-(Y); both minerals are hydrous rare-earth carbonate with carbonate to REE ratios of 3:2. Nevertheless, their crystal structures are quite different. In contrast to the corrugated

TABLE 6. Interatomic distances (Å) and bond angles (°) with estimated standard deviations in parentheses

Distances (Å)					
Y-O1	2.41(1)	C1-O1	1.31(3)	O6-O5	2.91(3)
O1'	2.53(1)	O2	1.30(1)	O5	2.81(3)
O2	2.37(3)	O3	1.24(2)		
O2'	2.44(3)				
O3	2.36(1)				
O3'	2.45(1)	C2-O4	1.29(2)		
O4	2.392(2)	O5	1.34(2) × 2		
O5	2.42(2)				
O6	2.34(2)				
Angles (°)					
O1-Y-O1'	79.8(3)	O2-Y-O2'	163.1(3)	O3'-Y-O4	114.3(4)
O1-Y-O2	117.8(3)	O2-Y-O3	77.3(4)	O3'-Y-O5	77.7(5)
O1-Y-O2'	76.1(4)	O2-Y-O3'	54.2(3)	O3'-Y-O6	132.4(6)
O1-Y-O3	83.6(4)	O2-Y-O4	83.1(5)	O4-Y-O5	55.8(5)
O1-Y-O3'	64.5(4)	O2-Y-O5	93.7(5)	O4-Y-O6	67.8(5)
O1-Y-O4	135.5(5)	O2-Y-O6	80.5(5)	O5-Y-O6	123.6(6)
O1-Y-O5	82.5(5)	O2'-Y-O3	115.7(3)		
O1-Y-O6	148.7(5)	O2'-Y-O3'	135.7(4)	O1-C1-O2	115.3(21)
O1'-Y-O2	135.7(4)	O2'-Y-O4	80.1(5)	O1-C1-O3	124.8(9)
O1'-Y-O2'	52.7(3)	O2'-Y-O5	77.9(5)	O2-C1-O3	119.8(22)
O1'-Y-O3	64.0(4)	O2'-Y-O6	91.9(6)		
O1'-Y-O3'	132.0(4)	O3-Y-O3'	80.3(3)	O4-C2-O5	117.6(9) × 2
O1'-Y-O4	113.6(4)	O3-Y-O4	140.9(5)	O5-C2-O5	124.4(19)
O1'-Y-O5	130.1(5)	O3-Y-O5	157.5(5)		
O1'-Y-O6	70.1(5)	O3-Y-O6	75.7(5)		

sheets in tengerite-(Y), the crystal structure of lanthanite-(La) (Dal Negro et al., 1977) consists of platy sheets parallel to (010). Furthermore, lanthanite-(La) has a free H₂O molecule between the platy sheets that is not coordinated to any cations. The sheets are connected only by H bonding, accounting for the micaceous {010} cleavage. In the crystal structure of lanthanite-(La), the rare-earth elements occupy two independent tenfold-coordinated sites. One rare-earth atom bonds to six O atoms of carbonate groups and four O atoms of H₂O, and another atom bonds to eight and two O atoms. On the other hand, the Y atom in tengerite-(Y) is coordinated by eight O atoms of carbonate ions and one of H₂O. Therefore, it may be reasonable that the formation of these minerals depends on the ionic radii of the rare-earth element. Our study showed that phases identical with tengerite-(Y) were synthesized from the Y rare-earth source, but not from La. Lanthanite-(La) was obtained only from the La rare-earth source.

Nagashima et al. (1986) reported that there is a correlation between the lattice parameters and the number of

cations of kimuraite-(Y) and lokkaite-(Y) (Perttunen, 1971). The lattice parameters of tengerite-(Y) are also related to kimuraite-(Y) and lokkaite-(Y) (Table 7); the *a* and *b* axes of tengerite-(Y) are very similar to *c* and *a* of kimuraite-(Y) and *b* and *c* of lokkaite-(Y), respectively. The ratio of the remaining axes *c* of tengerite-(Y), *b* of kimuraite-(Y), and *a* of lokkaite-(Y) is 15.114(6):23.976(4):39.35(2) Å = 1.92:3.05:5 ≈ 2:3:5, which corresponds to the ratio of the number of cations in each chemical formula, 2:3:5. This suggests that these minerals have a close structural relationship and can be classified in the same mineral group, on the basis of their crystal structures.

On the other hand, the lattice parameters *a* and *c* of lanthanite-(La) and calkinsite-(Ce) (Pecora and Kerr, 1953) are also closely related (Table 7). Both lanthanite-(La) and calkinsite-(Ce) are hydrous rare-earth carbonate with carbonate to REE ratios of 3:2, REE₂(CO₃)₃·*n*H₂O, and the difference in their chemical formulae is only in the numbers of H₂O molecules; *n* = 8 for lanthanite-(La),

TABLE 7. A comparison of the crystallographic data for tengerite-(Y), kimuraite-(Y), lokkaite-(Y), lanthanite-(La), and calkinsite-(Ce)

	Tengerite-(Y),*	Kimuraite-(Y),**	Lokkaite-(Y),**	Lanthanite-(La),†	Calkinsite-(Ce),‡
	Y ₂ (CO ₃) ₃ ·2-3H ₂ O	CaY ₂ (CO ₃) ₄ ·6H ₂ O	CaY ₄ (CO ₃) ₇ ·9H ₂ O	La ₂ (CO ₃) ₃ ·8H ₂ O	Ce ₂ (CO ₃) ₃ ·4H ₂ O
Space group	<i>Bb2,m</i>	<i>I2mm, Immm, I222, I2,2,2,</i>	<i>Pb2m, Pbm2, Pbcm</i>	<i>Pbnb</i>	<i>P2,22,</i>
Cell dimensions (Å)	<i>a</i> = 6.078(4) <i>b</i> = 9.157(2) <i>c</i> = 15.114(6)	<i>c</i> = 6.0433(7) <i>a</i> = 9.2545(8) <i>b</i> = 23.976(4)	<i>b</i> = 6.104(4) <i>c</i> = 9.26(1) <i>a</i> = 39.35(2)	<i>a</i> = 9.504(4) <i>c</i> = 8.937(5) <i>b</i> = 16.943(6)	<i>a</i> = 9.57(2) <i>c</i> = 8.94(2) <i>b</i> = 12.65(8)
Cations per formula	2	3	5	2	2

* Present study.

** Nagashima et al. (1986).

† Dal Negro et al. (1977).

‡ Pecora and Kerr (1953).

and $n = 4$ for calkinites-(Ce). This suggests that calkinites-(Ce) may have a sheet structure similar to that of lanthanite-(La).

Consequently, the five minerals described above may be classified into two mineral groups; i.e., the tenerite group and the lanthanite group. It is worth noting that minerals of the former group consist of Y-group rare-earths, whereas those of the latter consist of Ce-group rare-earths. To clarify the relationship between the ionic radii of rare-earth elements and the crystal structures of the hydrous rare-earth carbonates and to substantiate the structural relations among these minerals, structure analyses of kimuraite-(Y) and lokkaite-(Y) are now in progress.

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REFERENCES CITED

- Cromer, D.T., and Mann, J.B. (1968) X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Crystallographica*, A24, 321–324.
- Dal Negro, A., Rossi, G., and Tazzal, V. (1977) The crystal structure of lanthanite. *American Mineralogist*, 62, 142–146.
- Dana, J.D. (1868) *A system of mineralogy*, 710 p. Wiley, New York.
- Donnay, G., and Allmann, R. (1970) How to recognize O^{2-} , OH^- , and H_2O in crystal structures determined by X-rays. *American Mineralogist*, 55, 1003–1015.
- Finger, L.W. (1969) Determination of cation distribution by least-squares refinement of single crystal X-ray data. *Carnegie Institution of Washington Year Book*, 67, 216–217.
- Finger, L.W., and Prince, E. (1975) National bureau of standards technical note 854, p. 54–55. U.S. Government Printing Office, Washington, DC.
- Genth, F.A. (1889) Contributions to mineralogy, no. 44. *American Journal of Science*, 38, 198–203.
- Hidden, W.E. (1905) Some results of late minerals research in Llano County, Texas. *American Journal of Science*, 19, 425–433.
- Ibers, J.A., and Hamilton, W.C. Eds. (1974) International tables for X-ray crystallography, vol. IV, p. 148–150. Kynoch Press, Birmingham, U.K.
- Iimori, T. (1938) Tenerite found in Iisaka, and its chemical composition. *Scientific Papers of the Institute of Physical and Chemical Research (Tokyo)*, 34, 832–841.
- Main, P., Fiske, S.J., Hull, S.E., Lessinger, L., Germaine, G., Declercq, J.-P., and Woolfson, M.M. (1980) MULTAN-80: A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data. Universities of York, U.K., and Louvain, Belgium.
- Mandarino, J.A. (1976) The Gladstone-Dale relationship. I. Derivation of new constants. *Canadian Mineralogist*, 14, 498–502.
- Nagashima, K., and Wakita, H. (1968) On the composition of tenerite. *Nippon Kagaku Zasshi*, 89, 856–859 (in Japanese).
- Nagashima, K., Miyawaki, R., Takase, J., Nakai, I., Sakurai, K., Matsu- bara, S., Kato, A., and Iwano, S. (1986) Kimuraite, $CaY_2(CO_3)_4 \cdot 6H_2O$, a new mineral from fissures in an alkali olivine basalt from Saga Prefecture, Japan, and new data on lokkaite. *American Mineralogist*, 71, 1024–1029.
- Neumann, H., and Bryn, K.Ø. (1958) X-ray powder patterns for mineral identification. IV. Carbonates, p. 6, 20. I Kommissjon Hos H. Asche- houg, Oslo.
- Pecora, W.T., and Kerr, J.H. (1953) Burbankite and calkinites, two new carbonate minerals from Montana. *American Mineralogist*, 38, 1169–1183.
- Perttunen, V. (1971) Lokkaite, a new hydrous RE-carbonate from Pyö- rönmaa pegmatite in Kangasara, SW-Finland. *Bulletin Commission Géologique de Finlande*, 43, 67–72.
- Raade, G., and Brastad, K. (1993) Kamphaugite-(Y), a new hydrous Ca-(Y,REE)-carbonate mineral. *European Journal of Mineralogy*, in press.
- Stepanov, A.V. (1961) New and rare minerals in alkali granites of Kazakhstan. *Trudy Kazakhskogo Nauchno-Issledova-Tel'skogo Instituta Mineralnogo Syrya*, 5, 147–161 (in Russian).
- Svanberg, A.F., and Tenger, C. (1838) Kolsyrad ytterjord. Årsberättelse om Framstegen i Fysik och Kemi, 16, 206–207 (in Swedish; not seen; extracted from Dana's System of Mineralogy (7th edition), vol. 2, p. 275–276, 1951).
- Tareen, J.A.K., Narayanan Kutty, T.R., and Krishnamurty, K.V. (1980) Hydrothermal growth of $Y_2(CO_3)_3 \cdot nH_2O$ (tenerite) single crystals. *Journal of Crystal Growth*, 49, 761–765.
- Vorma, A., Ojanperä, P., Hoffrén, V., Siivola, J., and Löfgren, A. (1966) On the rare earth minerals from the Pyörönmaa pegmatite in Kangasala, southeastern-Finland. *Bulletin Commission Géologique de Finlande*, 38, 241–274.
- Wakita, H., and Nagashima, K. (1972) Synthesis of tenerite type rare earth carbonates. *Bulletin of the Chemical Society of Japan*, 45, 2476–2479.
- Wuensch, B.J., and Prewitt, C.T. (1965) Correction for X-ray absorption by a crystal of arbitrary shape. *Zeitschrift für Kristallographie*, 122, 24–59.

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