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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

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ABSTRACT

Kimuraite, ideally $CaY_2(CO_3)_4 \cdot 6H_2O$, occurs as a fissure mineral in alkali basalt exposed at Kirigo, Hizen-cho, Higashi Matsuura-gun, Saga Prefecture, Japan, and vicinity, in association with lokkaite-(Y) and lanthanite-(Nd). It is orthorhombic, space group *Imm*2, *Immm*, *I*222, or $I2_12_12_1$; $a = 9.2545(8)$, $b = 23.976(4)$, $c = 6.0433(7)$ Å, $V = 1340.9(3)$ Å^3, Z = 4. Kimuraite is light purplish to pinkish white with a vitreous to silky luster. The hardness (Mohs) is 2½ on {010}, the density is 2.98 g/cm^3 (calc.), and there is a perfect cleavage on {010}. Optically it is biaxial negative, $2V = 70(5)°$, $r < v$, weak. Refractive indices are $\alpha = 1.584(2)$, $\beta = 1.612(2)$, $\gamma = 1.626(2)$; $\mathbf{a} = X$, $\mathbf{b} = Y$, and $\mathbf{c} = Z$. The strongest lines in the X-ray powder pattern are [d $(I/I_0)(hKl)$] 12.06(100)(020), 6.02(40)(040), 5.93(20)(011), 4.87(10)(031), 4.64(10)(200), 4.01(20)(060), 3.76(30)(051), 2.93(10)(251,022), 2.05(12)(0·11·1). Complete chemical analysis of the associated lokkaite gave a new chemical formula, $CaY_4(CO_3)_7 \cdot 9H_2O$.

INTRODUCTION

In 1982 one of the authors (S.I.) collected a few fragile fissure minerals in alkali olivine basalt exposed at Kirigo, Hizen-cho, Higashi Matsuura-gun, Saga Prefecture, Japan, and sent them to K.S. for identification. The latter recognized their unusual nature, i.e., solubility in acid with effervescence and fluorescence under ultraviolet light. Preliminary chemical analyses and X-ray powder studies by S.M. and A.K. showed them to be lanthanite, lokkaite, and a new hydrous carbonate of Y-group rare-earth elements and Ca. The authors' combined studies suggested that a simple hydration of lokkaite results in the formation of the assemblage of lanthanite and the previously undescribed mineral.

This new mineral has been named kimuraite in honor of Dr. Kenjiro Kimura (1896–), Emeritus Professor at the University of Tokyo, in recognition of his outstanding contributions to the geochemistry and mineral chemistry of rare-earth minerals. The mineral and name have been approved by the Commission on New Minerals and Mineral Names, IMA. Type material has been preserved at National Science Museum, Tokyo and Sakurai Museum, Tokyo.

OCCURRENCE

The locality is an exposure of alkali olivine basalt of the first-stage trachybasalt in the Higashi Matsuura District (Aoki, 1959), which unconformably overlies early Pleistocene sedimentary rocks and pre-Tertiary granodiorite. The basalt is a lava flow with nearly horizontal flowage structures. The new mineral occurs in the upper horizon of the flow. The exposures of kimuraite-bearing basalt are distributed over 5 km around the first locality. The basalt has a gray homogeneous groundmass with olive-green olivine phenocrysts reaching 2 mm across. The rare-earth-element carbonates are exclusively found in minor fissures developed nearly parallel to the flowage structure. The fissures are of various sizes up to 10 cm long and 5 mm wide.

Kimuraite occurs as spherulitic aggregates of scales 4 cm long and 2 cm wide. It is closely associated with coarser-grained lanthanite, which commonly has rectangular outlines up to 2 mm on an edge. These two minerals are in most cases underlain by lokkaite, which forms snow-white spherulitic aggregates on fissure walls. There are also mineral-free and calcite- and/or aragonite-bearing fissures without rare-earth-element carbonates. In addition to the fissures, tiny druses including olivine grains are developed. The fissures with rare-earth-element carbonates have no alteration haloes around them.

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* Deceased on January 6, 1985.

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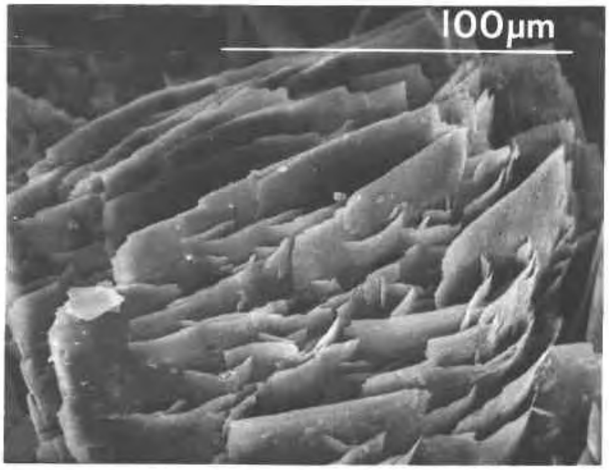

Fig. 1. SEM photograph of kimuraite. Scale bar is 100 μm.

OPTICAL AND PHYSICAL PROPERTIES

Kimuraite is light purplish to pinkish white in color, reflecting the presence of rare-earth elements such as Nd. The luster is vitreous to silky on the cleavage plane. The hardness measured on the cleavage plane, which is perfect along {010}, is 2½. The calculated density is 2.98 g/cm³, which is appreciably higher than the measured density, 2.6(1) g/cm³. The difference is ascribed to the porous state of the mineral. The SEM photograph (Fig. 1) indicates that the cluster of kimuraite is a loose aggregate of tabular crystals. It is optically biaxial and negative; $2V = 70(5)°$; dispersion $r < v$, weak. The refractive indices, measured by the immersion method, are $\alpha = 1.584(2)$, $\beta = 1.612(2)$, $\gamma = 1.626(2)$. The optical orientation is $\mathbf{a} = X$, $\mathbf{b} = Y$, and $\mathbf{c} = Z$. It is strongly fluorescent under short- and long-wave ultraviolet light, showing reddish purple and purple colors, respectively. It is readily soluble with effervescence in dilute hydrochloric acid.

CHEMICAL COMPOSITION

Kimuraite was chemically analyzed with an Inductively Coupled Plasma–Atomic Emission Spectrometer (ICP-AES). Water and CO_2 were determined by conventional analysis. In the preparation of standard solutions for the ICP-AES analysis, special care was taken to prevent spectral interferences (Iwasaki, Fuwa, and Haraguchi, ms.). In order to minimize the variation of the nebulization efficiency owing to the difference of the viscosities of the solutions, the acid contents in each standard solution were adjusted to 1.2 *N* HCl to match the digested sample solution. A 6.55-mg sample was dissolved in 40 mL of 1.2 *N* HCl. The measurements were repeated three times for each element. The data were then averaged and corrected for the spectral interferences. The results of chemical analyses given in Table 1 yield the empirical formula $Ca_{0.99}REE_{2.02}C_{3.99}O_{12} \cdot 6.12H_2O$, calculated on the basis of O = 12 for the anhydrous part. This leads to the ideal formula $CaY_2(CO_3)_4 \cdot 6H_2O$ with Z = 4, where Y signifies the dominance of Y-group rare-earth elements. If specification of rare-earth elements is needed, the mineral should be termed kimuraite-(Y).

Table 1. Chemical analysis of kimuraite

	wt%	No. atoms (O=12)
La_2O_3	0.50	0.018
Ce_2O_3	0.02	0.001
Pr_2O_3	0.37	0.015
Nd_2O_3	2.97	0.107
Sm_2O_3	0.95	0.033
Eu_2O_3	0.39	0.013
Gd_2O_3	2.49	0.083
Tb_2O_3	0.36	0.012
Dy_2O_3	2.44	0.079
Ho_2O_3	0.62	0.020
Er_2O_3	1.69	0.053
Tm_2O_3	0.17	0.005
Yb_2O_3	0.56	0.017
Lu_2O_3	0.06	0.002
Y_2O_3	29.41	1.57
(ΣRE_2O_3	43.00	2.02)
CaO	9.23	0.99
CO_2	29.13	3.99
H_2O	18.32	12.24
Total	99.68	

Number of atoms is based on 12 oxygen atoms in the anhydrous part.

Kimuraite has an unusual distribution pattern of lanthanides (Fig. 2), in which Ce is anomalously poorer than both La and Pr, as compared to the Oddo-Harkins' rule (Oddo, 1914; Harkins, 1917). Furthermore, the low-Ce anomaly was observed in the chemical composition of the associated lanthanite-(Nd) (Table 2, Fig. 3). A similar Ce anomaly was reported from Brazil (Cesbron et al., 1979; Roberts et al., 1980) for lanthanite-(Nd) formed in a sedimentary environment.

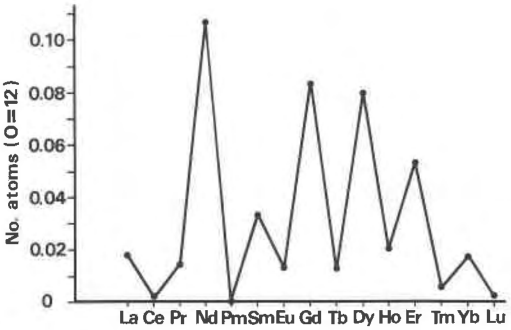

Fig. 2. Distribution pattern of lanthanides in kimuraite, indicating a Ce anomaly.

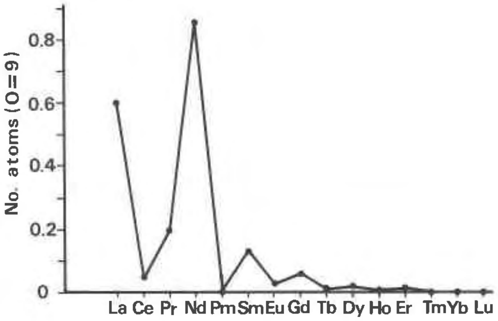

Fig. 3. Distribution pattern of lanthanides in lanthanite-(Nd). Ce is less abundant than La and Pr.

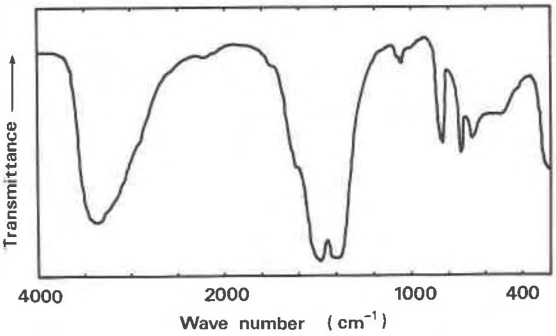

Fig. 4. Infrared absorption spectrum of kimuraite.

X-RAY CRYSTALLOGRAPHY

X-ray single-crystal study including Weissenberg, precession, and four-circle diffractometer methods showed kimuraite to be orthorhombic. The diffraction patterns indicate the space group to be *Imm*2, *Immm*, *I*222, or $I2_12_12_1$. A least-squares technique applied to the diffraction angles of 25 strong reflections in the range of $40° < 2\theta < 50°$ measured by an automated four-circle diffractometer produced the refined cell parameters a = 9.2545(8), b = 23.976(4), c = 6.0433(7) Å, V = 1340.9(3) Å^3.

X-ray powder data (Table 3) were obtained using an X-ray powder diffractometer, Ni-filtered Cu*Kα* radiation, a scan rate of ½°/min, and Si (NBS, SRM640a) and mica (NBS, SRM675) as internal standards. A preferred orientation effect due to the perfect {010} cleavage may be present.

Table 2. Chemical analysis of lanthanite-(Nd) from Hizen-cho, Saga Prefecture, Japan

	wt%	No. atoms (O=9)
La_2O_3	15.77	0.596
Ce_2O_3	1.11	0.042
Pr_2O_3	5.18	0.193
Nd_2O_3	23.42	0.856
Sm_2O_3	3.69	0.130
Eu_2O_3	0.80	0.028
Gd_2O_3	1.74	0.059
Tb_2O_3	0.10	0.003
Dy_2O_3	0.34	0.011
Ho_2O_3	0.02	0.001
Er_2O_3	0.03	0.001
Tm_2O_3	n.d.	—
Yb_2O_3	n.d.	—
Lu_2O_3	n.d.	—
Y_2O_3	0.48	0.026
(ΣRE_2O_3	52.68	1.946)
CO_2	21.38	3.04
H_2O	23.37	15.96
Total	97.43	

INFRARED SPECTRA AND THERMAL BEHAVIOR

An infrared absorption spectrum (Fig. 4) was obtained with a HITACHI 260-50 infrared spectrophotometer using the KBr method. The presence of water molecules in kimuraite is shown by the broad band of H_2O stretching vibrations in the frequency range 3500–3000 cm^{-1} and by the H_2O deformation band, which appears as a shoulder at 1630 cm^{-1}. The broad bands in the region 1500–1400 cm^{-1}, weak absorptions at 1090 and 1062 cm^{-1}, and medium ones at 856, 842, 748, and 685 cm^{-1} are attributed to the CO_3^{2-} absorption bands.

The DTA and TGA curves are given in Figure 5. The former has a strong endothermic peak at 160°C, corresponding to the loss of water. There are apparently four small endothermic peaks in the range of 500–750°C, which are interpreted to represent the loss of CO_2. The weight-loss steps on a synchronized-recording TGA curve correspond well with the endothermic changes in the DTA diagram. The TGA diagram shows two steps of the weight loss. One in the range of 60–400°C corresponds to the loss of water, and the other, in the range of 400–750°C to the loss of CO_2. This is consistent with the results of the chemical analysis.

The infrared spectra of kimuraite after thermal treatment (Fig. 6) confirm the interpretation of the results of the DTA and TGA studies. The infrared spectrum of the sample heated at 300°C has no H_2O absorption, and the spectrum of the sample heated at 550°C shows a significant decrease in the intensities of the CO_3^{2-} absorptions. The sample heated at 1000°C gives the absorption peaks of rare-earth oxides. The weak CO_3^{2-} absorption band in the range of 1600–1400 cm^{-1} is due to $CaCO_3$, which was formed by the carbonation of CaO.

NEW DATA ON LOKKAITE

Lokkaite was originally reported as tengerite by Vorma et al. (1966) from the Pyörönmaa pegmatite at Kangasala in southwestern Finland. The mineral occurs as isolated white radial disclike aggregates on the surfaces of and in fissures in albite. Later, it was shown to be a new mineral

Table 3. X-ray powder-diffraction data for kimuraite

h k l	$d_{calc.}$	$d_{obs.}$	I/I_o
0 2 0	11.99	12.06	100
1 1 0	8.63	8.66	2
0 4 0	5.99	6.02	40
0 1 1	5.86	5.93	20
1 0 1	5.06	5.11	1
0 3 1	4.82	4.87	10
2 0 0	4.63	4.64	10
2 2 0	4.32	4.33	3
0 6 0	4.00	4.01	20
1 4 1	3.87	3.87	5
0 5 1	3.76	3.76	30
2 4 0	3.66	3.68	1
2 1 1	3.63	3.64	6
2 3 1	3.34	3.35	7
1 6 1	3.14	3.16	6
2 6 0	3.02	3.03	4 sh
0 0 2	3.02		
0 8 0	3.00	3.01	8
0 2 2	2.93	2.93	10
2 5 1	2.92		
3 2 1	2.68	2.69	5
1 8 1	2.58	2.59	5
2 0 2	2.53	2.55	8
2 8 0	2.52	2.52	6
2 7 1	2.51		
2 2 2	2.48	2.48	4 sh
0 9 1	2.44	2.44	3
0 6 2	2.41	2.42	4 sh
0 10 0	2.40	2.41	6
2 4 2	2.33	2.35	1
4 0 0	2.31	2.32	1
4 2 0	2.27	2.27	1
1 7 2	2.20	2.23	1
4 4 0	2.16	2.16	4 sh
2 9 1	2.16		
4 1 1	2.15	2.15	4 sh
3 1 2	2.15		
2 10 0	2.13	2.13	8
0 8 2	2.13		
4 3 1	2.09	2.09	7
0 11 1	2.05	2.05	12
3 8 1	2.03	2.02	2 br
0 1 3	2.01	2.01	1 br
4 6 0	2.00		
4 5 1	1.970	1.972	4 br
0 3 3	1.953	1.948	4 br
2 8 2	1.933	1.934	4
0 10 2	1.878	1.881	9
2 11 1	1.875	1.876	8 sh
0 5 3	1.857	1.858	2 br
4 0 2	1.837	1.836	6
4 8 0	1.831	1.832	6
4 2 2	1.816	1.818	4 sh
5 0 1	1.770	1.773	2
1 6 3	1.766	1.766	3
0 13 1	1.764		
5 2 1	1.751	1.754	3
2 10 2	1.740	1.741	4
0 7 3	1.736		
2 13 1	1.648	1.648	2 br
0 15 1	1.545	1.547	2 br
0 16 0	1.498	1.502	2 br
6 3 1	1.469	1.469	2 br
1 3 4	1.466	1.465	2 br
2 15 1	1.466		
0 4 4	1.465		
6 0 2	1.374	1.376	1 br
0 8 4	1.349	1.343	1

sh : shoulder, br : broad.

with the chemical formula $Ca_{0.23}REE_{1.58}(CO_{2.87})_3 \cdot 1.58H_2O$ and named lokkaite by Perttunen (1971). Although he mentioned that the essential difference between lokkaite and tengerite is not in the degree of hydration, significant contamination of his samples by tengerite precluded an adequate analysis of lokkaite. Since pure specimens are available from the Japanese locality, we have carried out an X-ray powder study and a complete chemical analysis of this mineral.

X-ray powder data for lokkaite using Si and mica internal standards are given in Table 4. The original data for lokkaite from the Pyörönmaa pegmatite are included for comparison and to prove the identity of the two phases. The refined unit-cell dimensions, produced by the pro-

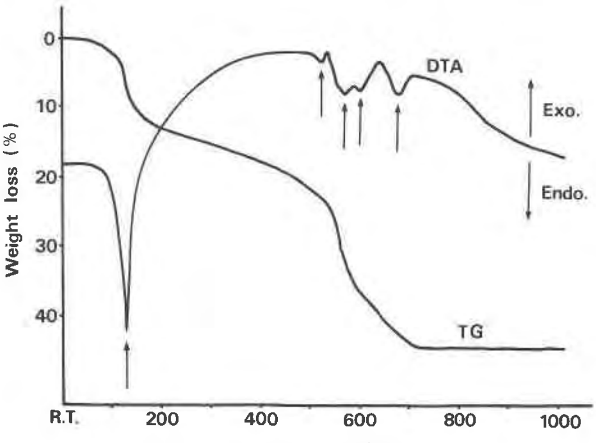

Fig. 5. DTA and TGA curves of kimuraite under atmospheric pressure.

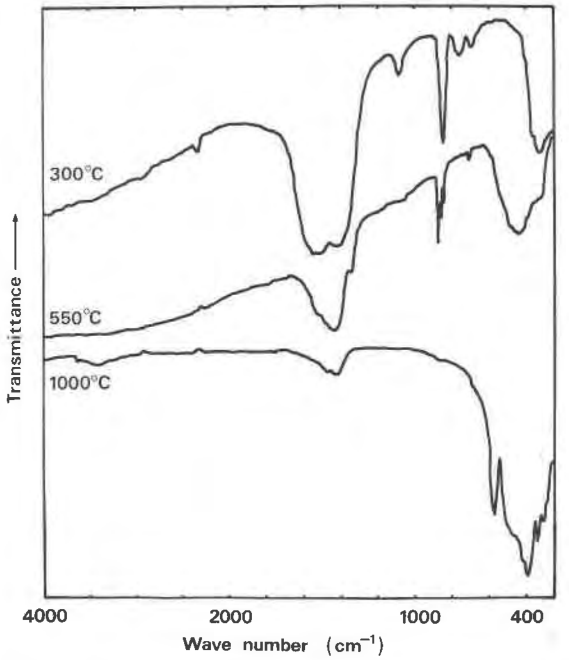

Fig. 6. Infrared absorption spectra of heated kimuraite at 300, 550, and 1000°C.

Table 4. X-ray powder-diffraction data for lokkaites

	Present study			Perttunen (1971)	
$h\ k\ l$	$d_{calc.}$	$d_{obs.}$	I/I_o	$d_{obs.}$	I/I_o
2 0 0	19.67	19.81	25	19.6	35
4 0 0	9.84	9.90	50	9.77	50
6 0 0	6.56	6.56	70	6.51	55
2 1 0	5.83	5.85	50	5.79	45
4 1 0	5.19	5.19	7	5.17	6
0 0 2	4.63	4.62	55	4.59	75
6 1 0	4.47	4.49	10	4.43	10
10 0 0	3.93	3.94	50	3.90	60
8 1 0	3.83	3.84	100	3.81	100
2 1 2	3.63	3.63	25	3.60	20
4 1 2	3.45	3.45	7	3.43	6
6 1 2	3.22	3.23	10		
0 2 0	3.05	3.06	7	3.04	6
10 0 2	3.00	3.01	10	2.987	30
8 1 2	2.95	2.95	40	2.931	40
0 2 2	2.55	2.55	30	2.525	35
16 0 0	2.46	2.46	25	2.443	16
10 2 0	2.41	2.41	15		
16 0 2	2.17	2.17	15	2.158	16
18 1 0	2.06	2.06	40	2.045	35
18 0 2	1.977	1.979	10		
16 2 0	1.915	1.913	15	1.904	10
8 3 0	1.880	1.882	20	1.870	16

gram of Appleman and Evans (1973), are $a = 39.35(2)$, $b = 6.104(4)$, and $c = 9.26(1)$ Å, which are comparable to those of the original material, $a = 39.07$, $b = 6.079$, and $c = 9.19$ Å.

Chemical analysis of Japanese lokkaite was carried out applying the same procedures as for kimuraite (Table 5). The empirical formula, calculated on the basis of O = 21 in the anhydrous part, is $Ca_{1.03}REE_{3.99}C_{7.00}O_{21} \cdot 8.6H_2O$, or ideally $CaY_4(CO_3)_7 \cdot 9H_2O$. Ca is an essential component of lokkaite. This distinguishes lokkaite from tengerite. The empirical formula of the original lokkaite is $Ca_{0.23}\ REE_{1.58}(CO_{2.87})_3 \cdot 1.58H_2O$ or $Ca_{0.56}REE_{3.85}C_{7.32}O_{21} \cdot 3.85H_2O$ on the present basis. Perttunen (1971) mentioned that the X-ray powder pattern of his specimen showed overlapping of tengerite and lokkaite reflections (Table 4). The chemical analysis of cations was therefore made with the electron microprobe (Vorma et al., 1966), but this does not appear to be suitable for the analysis of a hydrous carbonate mineral. The infrared absorption spectrum of Japanese lokkaite is given in Figure 7. It is worth noting that the infrared spectra of lokkaite and kimuraite resemble each other, suggesting a close structural relationship between the two minerals.

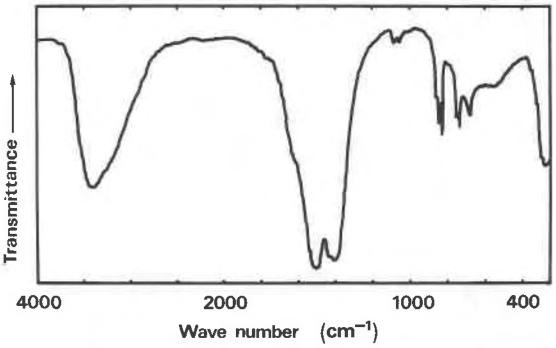

Fig. 7. Infrared absorption spectrum of lokkaite. A marked resemblance to the spectrum of kimuraite is observed.

Table 5. Chemical analyses of lokkaite from Saga Prefecture, Japan, and Kangasala, southwestern Finland

	Present study		Perttunen (1971)	
	wt %	No. atoms (O=21)	Range of results(%)	Mean value
La_2O_3	0.33	0.022	0.2- 0.3	0.2
Ce_2O_3	0.43	0.029	0.6- 1.1	0.7
Pr_2O_3	0.61	0.041	0.2- 0.4	0.3
Nd_2O_3	7.13	0.398	1.1- 1.8	1.3
Sm_2O_3	3.84	0.241	1.6- 2.2	1.8
Eu_2O_3	1.72	0.107		
Gd_2O_3	7.47	0.452	4.1- 5.4	4.6
Tb_2O_3	1.22	0.073	1.1- 1.5	1.2
Dy_2O_3	6.02	0.354	6.2- 8.8	6.8
Ho_2O_3	1.12	0.065		trace
Er_2O_3	2.35	0.135	3.1- 4.4	4.0
Tm_2O_3	0.28	0.016	0.7- 1.2	0.9
Yb_2O_3	0.80	0.045	1.8- 3.0	2.2
Lu_2O_3	0.10	0.005		trace
Y_2O_3	20.64	2.005	29 -29.5	29.0
$(\Sigma RE_2O_3$	54.06	3.99		53.0)
CaO	5.25	1.03	2.6- 3.4	3.2
Fe_2O_3	n.d.	——	0.3- 0.4	0.4
CO_2	28.09	7.00		32.4
$H_2O(-)$	14.13	17.20		5.4
$H_2O(+)$				1.6
Total	101.53			96.0

RELATIONSHIPS TO OTHER MINERALS

Kimuraite is the second mineral in the $CaO\text{-}REE_2O_3\text{-}CO_2\text{-}H_2O$ system, lokkaite being the first. The two minerals show a marked structural resemblance. The cell parameters a and c of kimuraite, 9.2545(8) and 6.0433(7) Å, are very close to c and b of lokkaite, 9.26(1) and 6.104(4) Å, respectively. The ratio of cation numbers in kimuraite and lokkaite, 3:5, corresponds to that of the b dimension of kimuraite and a of Japanese lokkaite, i.e., 23.976: 39.35 = 3:4.92 ≈ 3:5. In addition, the ratio 3:5 is equal to that of the total oxygen atoms in both minerals, suggesting similar packing of the structural constituents. Perttunen (1971) mentioned that lokkaite has a distinct superstructure, the dimensions of the subcell being $a' = ½a$, $b' = b$, and $c' = c$. This was also confirmed in the powder pattern of Japanese lokkaite (Table 4). On the other hand, kimuraite does not show such a feature. This evidence indicates that the structural relationship between the two minerals is not so simple. In order to solve the problem, crystal-structure analyses of the two minerals are being performed by the second author.

An interesting compositional relationship is also found in the mineral assemblage from Kirigo and the neighboring exposures. This is expressed by the equation

$$\underset{\text{lokkaite}}{CaREE_4(CO_3)_7 \cdot 9H_2O} + 5H_2O \rightarrow \underset{\text{lanthanite}}{REE_2(CO_3)_3 \cdot 8H_2O} + \underset{\text{kimuraite}}{CaREE_2(CO_3)_4 \cdot 6H_2O}.$$

This equation accounts for the formation of the lanthanite-kimuraite assemblage by simple hydration of lokkaite, except for the minor discrepancy in the distribution patterns of lanthanides of these minerals.

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