

Kozoite-(Nd), Nd(CO₃)(OH), a new mineral in an alkali olivine basalt from Hizen-cho, Saga Prefecture, Japan

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ABSTRACT

Kozoite-(Nd), Nd(CO₃)(OH), occurs in cavities and fissures of alkali olivine basalt exposed at Niikoba, Hizen-cho, Higashi Matsuura-gun, Saga Prefecture, Japan, in association with lanthanite-(Nd) and kimuraite-(Y). The crystal structure was refined by the Rietveld method in space group *Pmcn*; $a = 4.9829(1)$, $b = 8.5188(2)$, $c = 7.2570(2)$ Å, $Z = 4$ using powder diffraction data obtained by a combination of a Gandolfi camera and monochromatic synchrotron radiation. Kozoite-(Nd) is pale pinkish-purple to white with a vitreous to powdery luster. The calculated density is 4.77 g/cm³. It has high birefringence, $\alpha = 1.698(2)$, $\gamma = 1.780(5)$. The four strongest lines in the X-ray powder patterns [$d(\text{Å})$, l/l_0 , hkl] are (4.29, 100, 110); (2.93, 89, 102); (2.33, 78, 131) and (2.06, 78, 221). Kozoite-(Nd) is the first naturally occurring RE(CO₃)(OH) end-member in the ancylite group.

INTRODUCTION

In 1997, one of the authors (K.T.) collected a pale pink mineral in alkali olivine basalt at Niikoba, Hizen-cho Higashi Matsuura-gun, Saga Prefecture, Japan, and sent them to R.M. for identification. It was recognized as a member of the ancylite mineral group; however, this sample was extremely poor in Ca and Sr, and free from Pb in comparison with other members of ancylite group (Miyawaki et al. 1998). Ancylite group minerals are generally rare, but in some carbonatites they may occur in ore quantities. The mineral and mineral name were approved by the International Mineralogical Association, Commission on New Minerals and Mineral Names. The mineral is named after the late Kozo Nagashima (1925–1985), a chemist, and pioneer in the study of chemistry of rare earth minerals in Japan, in recognition of his contributions to the mineralogy, chemistry and crystallography of rare earth minerals. The type specimen has been deposited at the National Science Museum, Tokyo (NSM-M27940).

OCCURRENCE

Kozoite-(Nd) occurs in alkali olivine basalt at Niikoba, Hizen-cho, Higashi Matsuura-gun, Saga Prefecture, Japan. The alkali olivine basalt is the last-stage lava of the volcanic sequence, which unconformably overlies early Pleistocene sedimentary rocks and pre-Tertiary granodiorite (Nagashima et al. 1986). Kozoite-(Nd) probably formed from postmagmatic hydrothermal activity. In many cases, a pale pinkish-purple to white aggregate of minute kozoite-(Nd) crystals coats platy crystals of lanthanite-(Nd) and/or lanthanite-(La). Kozoite-(Nd) is usually associated with hyalite-type amorphous silica. Kimuraite-(Y) is sometimes found in this association. The shape

of aggregates of kozoite-(Nd) is usually platy, which corresponds to the crystal habit of lanthanite-(Nd) with {010} and {101} (Fig. 1a).

PHYSICAL AND OPTICAL PROPERTIES

Crystals of kozoite-(Nd) exhibit the rhombic-dipyramidal habit (Fig. 1b). Crystals do not exceed 10 μm in size, so their forms could only be observed by SEM and could not be measured. Their morphology differs from that of lanthanite, which is generally tabular. Kozoite-(Nd) is pale pinkish purple to white in color with a vitreous to dull luster. No fluorescence was observed under short or long wave UV light. It has high birefringence: $\alpha = 1.698(2)$ and $\gamma = 1.780(5)$. Due to the small dimensions of the crystals, other optical properties, hardness, cleavage and density could not be measured. The calculated density is 4.77 g/cm³. This mineral is readily soluble with effervescence in dilute hydrochloric acid.

CHEMICAL COMPOSITION

Preliminary chemical analysis using SEM-EDS (JEOL JSM-5400) indicated that the mineral consisted of yttrium and lanthanides, small amounts of Ca, and, sometimes, trace amounts of Sr. No other element with atomic number greater than ten was detected. Quantitative analyses were carried out using a JEOL JXA-8800M WDS electron microprobe analyzer (15kV and 10 nA). The analyses were made for six grains. Fluorine was not detected with the WDS. Carbon and hydrogen were determined by CNH-elementary analysis (Elementar Analysensysteme GmbH vario EL). The analysis was carried out three times for each sample using weights of approximately 5 mg.

The results of the analyses are given in Table 1. The empirical formula on the basis of the two cations per formula unit is: (Nd_{0.85}La_{0.61}Pr_{0.18}Sm_{0.14}Gd_{0.08}Eu_{0.05}Ca_{0.04}Y_{0.03}Ce_{0.01}Dy_{0.01})C_{2.24}H_{2.82}

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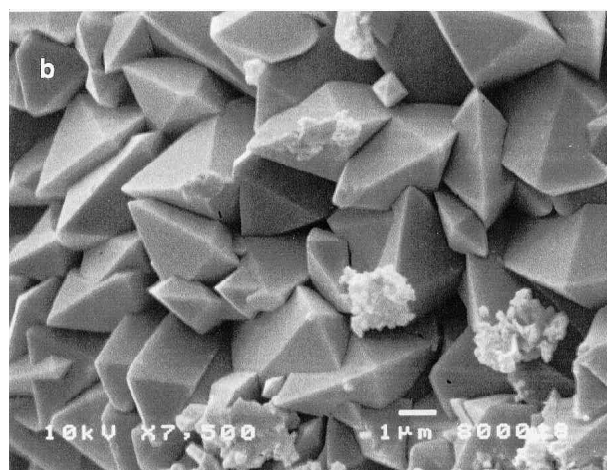
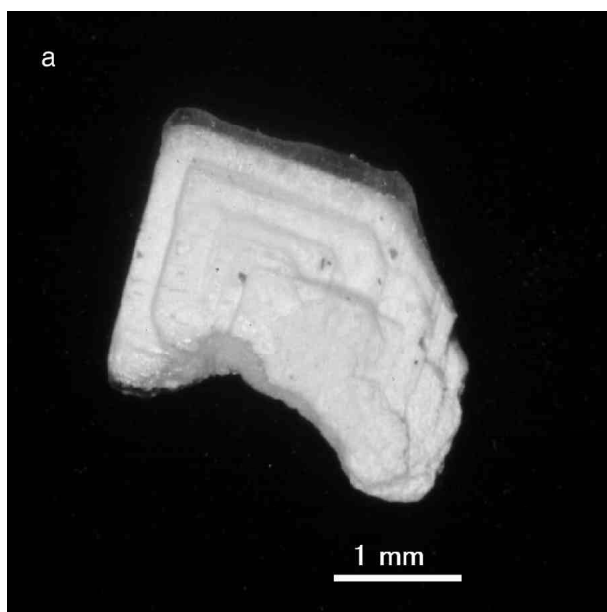


FIGURE 1. Photomicrographs of kozoite-(Nd). (a) An aggregate having pseudofaces corresponding to lanthanite-(Nd). (b) Scanning electron microscope image of the kozoite-(Nd) crystals with rhombic-dipyramidal habit.

$O_{8.88}$. The simplified formula is $(Nd,La,Ca)(CO_3)[(OH),(H_2O)]$, and the ideal formula is $Nd(CO_3)(OH)$, which requires Nd_2O_3 76.04, CO_2 19.89, and H_2O 4.07 wt%.

The lanthanide distribution pattern of kozoite-(Nd) shows a negative Ce anomaly, which was also found in lanthanite-(Nd), kimuraite-(Y) and lokkaite-(Y) (Nagashima et al. 1986) from the same alkali olivine basalt (Fig. 2). The rare earth minerals from Higashi Matsuura district can be classified into two groups based upon their lanthanide patterns: (1) kozoite-(Nd) and lanthanite-(Nd) and (2) kimuraite-(Y) and lokkaite-(Y). The minerals in the latter group have yttrium as the predominant rare earth and they are relatively abundant in heavy rare earths, whose ionic radii are close to that of yttrium.

TABLE 1. Chemical composition of kozoite-(Nd) from Saga, Japan

	wt%			No. cations
	Average	Range		
La_2O_3	21.39	19.09–27.25	La	0.61
Ce_2O_3	0.26	0.11–0.44	Ce	0.01
Pr_2O_3	6.25	5.54–7.62	Pr	0.18
Nd_2O_3	30.66	29.01–33.70	Nd	0.85
Sm_2O_3	5.39	4.69–6.47	Sm	0.14
Eu_2O_3	1.84	1.55–2.15	Eu	0.05
Gd_2O_3	2.99	2.20–3.67	Gd	0.08
Tb_2O_3	0.11	0.00–0.35	Tb	0.00
Dy_2O_3	0.24	0.04–0.54	Dy	0.01
Y_2O_3	0.70	0.13–1.20	Y	0.03
CaO	0.49	0.00–1.47	Ca	0.04
SrO	bld	bld	Sr	bld
CO_2^*	21.10	21.10	C	2.24
H_2O^*	5.44	5.44	H	2.82
Total	96.86			

Note: bld = below limits of detection.

* Bulk $[\Sigma(RE^{3+} + M^{2+}) = 2]$ where $\Sigma RE^{3+} = 1.96$.

CRYSTALLOGRAPHY

Powder X-ray diffraction data were obtained using a 114.6 mm Gandolfi camera using monochromatic X-ray ($\lambda = 2.1597 \text{ \AA}$) from a synchrotron light source. The diffraction data were measured at BL-39XU of the SPring-8, Japan Synchrotron Radiation Research Institute (JASRI), Hyogo, Japan using a Si(111) double crystal monochromator and the data were recorded on an Imaging Plate. Procedural details are given by Nakai et al. (unpublished manuscript). No single-crystal work could be carried out because of the small size and aggregation of crystals. The crystal structure was successfully refined with the orthorhombic ancylite structure [*Pm**cn*] (Dal Negro et al. 1975) by the Rietveld method using RIETAN (Izumi 1993), and the refinement converged to $R_{wp} = 6.09$, $R_p = 3.99$, $R_R = 17.91$, $R_e = 2.77$, $S = 2.1997$, $d = 0.2303$, $R_1 = 8.06$, and $R_F = 4.16$ (Fig. 3). The powder diffraction data and refined lattice parameters are listed in Table 2. The final atomic coordinates with displacement parameters and interatomic distances are given in Tables 3 and 4, respectively.

INFRARED SPECTRA AND THERMAL BEHAVIOR

The infrared absorption spectrum was obtained by an FT-IR spectrometer (JASCO FT/IR-230) using the KBr method in transmission mode. The spectrum (Fig. 4) exhibits absorption bands at 3450 cm^{-1} due to the OH group, and at 1370, 1440, and 1500 cm^{-1} , due to the carbonate group. A weak absorption at 1650 cm^{-1} due to H-O-H bending was also observed.

The DTA-TG curves were recorded using a Rigaku TG-DTA/GC-MS thermal analyzer in He gas from room temperature to $900 \text{ }^\circ\text{C}$ at a heating rate of $20 \text{ }^\circ\text{C}/\text{min}$. The exhaust gas was simultaneously analyzed by a gas chromatograph-mass (GC-MS) analyzer. Kozoite-(Nd) shows two endothermic peaks accompanying weight loss at 485 and $716 \text{ }^\circ\text{C}$ (Fig. 5a). CO_2 and H_2O were detected for the first weight loss at $485 \text{ }^\circ\text{C}$, whereas only CO_2 was detected for the second weight loss at $716 \text{ }^\circ\text{C}$ (Fig. 5b). The weight loss for the first step is 16.07 wt%, of which 11.98 and 4.09 wt% could be attributed to CO_2 and H_2O , respectively, based on the GC-MS results. The weight

TABLE 2. Powder X-ray diffraction data and lattice parameters of kozoite-(Nd)

<i>h k l</i>	<i>l</i>	<i>d</i> (obs)	<i>d</i> (calc)	<i>h k l</i>	<i>l</i>	<i>d</i> (obs)	<i>d</i> (calc)
0 1 1	47	5.50	5.52	3 2 1			
1 1 0	100	4.29	4.30	3 0 2	20	1.509	{ 1.513
0 2 0	54	4.24	4.26	2 3 3	26	1.479	1.510
1 1 1	72	3.69	3.70	2 0 4	13	1.465	1.481
0 2 1	48	3.66	3.67	2 1 4	16	1.444	1.467
0 0 2	14	3.62	3.63	3 3 0	11	1.433	1.445
0 1 2	52	3.33	3.34	3 2 2	16	1.421	1.434
1 2 1	27	2.95	2.96	0 6 0	16	1.419	1.423
1 0 2	89	2.93	2.93	3 3 1	21	1.405	1.420
1 1 2	12	2.76	2.77	0 5 3	10	1.391	1.407
0 2 2	15	2.76	2.76	2 2 4	12	1.385	1.393
0 3 1	59	2.640	2.644	0 4 4	17	1.379	1.387
2 0 0	41	2.488	2.492	2 5 1			{ 1.381
1 3 0	13	2.464	2.467	1 1 5	13	1.373	1.381
1 2 2	26	2.412	2.416	0 2 5			{ 1.375
1 3 1	78	2.333	2.336	3 1 3	11	1.350	1.374
0 1 3	39	2.323	2.327	2 4 3	11	1.344	1.352
2 1 1	10	2.266	2.271	1 4 4	11	1.329	1.345
0 3 2	11	2.234	2.236	0 6 2	12	1.321	1.331
2 2 0	24	2.148	2.151	2 5 2	26	1.310	1.322
0 4 0	29	2.127	2.130	3 2 3	24	1.303	1.311
1 1 3	16	2.105	{ 2.108	3 4 1	14	1.288	1.304
0 2 3			2.103	1 6 2	25	1.277	1.289
2 2 1	78	2.060	2.062	1 3 5	18	1.250	1.278
0 4 1	37	2.041	2.044	4 0 0	18	1.245	1.251
2 1 2	75	1.994	1.997	2 6 0	23	1.233	1.246
1 2 3	29	1.935	1.938	3 0 4	13	1.224	1.234
1 4 1	28	1.889	1.891	2 5 3	18	1.214	1.225
2 2 2	14	1.846	1.850	3 1 4	21	1.212	1.216
0 3 3	27	1.839	1.841	1 5 4			1.213
2 3 1	25	1.811	1.813	2 2 5			{ 1.205
0 1 4	10	1.771	1.774	0 7 1	19	1.203	1.203
1 4 2	20	1.721	1.723	0 4 5			1.200
2 1 3	17	1.698	1.701	4 2 0	13	1.195	1.199
1 1 4	21	1.669	1.672	3 5 0	15	1.189	1.196
0 5 1	12	1.656	1.659	1 7 0	14	1.182	1.189
3 1 0	21	1.628	1.630	4 2 1	16	1.179	1.182
2 4 0	13	1.617	1.619	3 5 1	13	1.173	1.180
1 5 0	21	1.610	1.612	1 7 1	21	1.167	1.174
2 2 3	16	1.606	1.607	0 7 2	18	1.153	1.167
3 1 1	13	1.589	1.591	3 4 3	15(sh)	1.151	1.154
2 4 1	24	1.578	1.580				1.152
1 5 1	12	1.572	1.574				
0 5 2	15	1.541	1.542				
1 4 3	14	1.520	1.522				

Note: $a = 4.9829(1)$, $b = 8.5188(2)$, $c = 7.2570(2)$ Å. (sh) = shoulder.

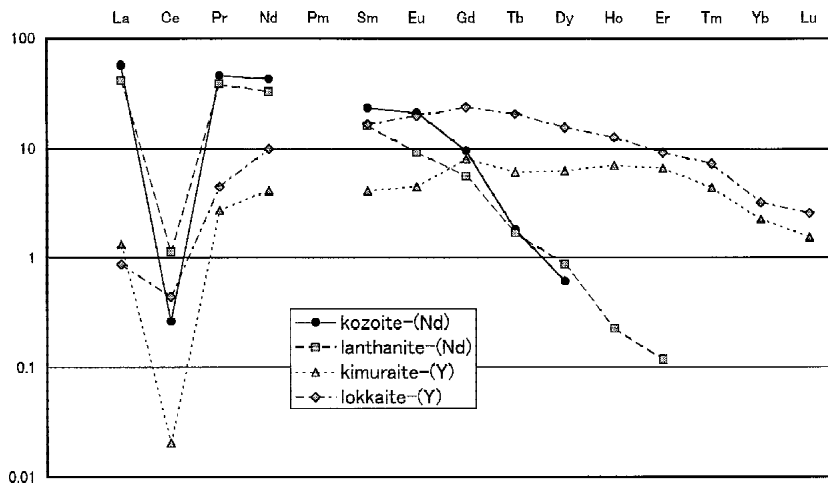


FIGURE 2. Chondrite-normalized lanthanide distribution patterns of kozoite-(Nd), lanthanite-(Nd), kimuraite-(Y) and lokkaite-(Y) from Saga Prefecture, Japan. Data for lanthanite-(Nd), kimuraite-(Y), and lokkaite-(Y) are from Nagashima et al. (1986).

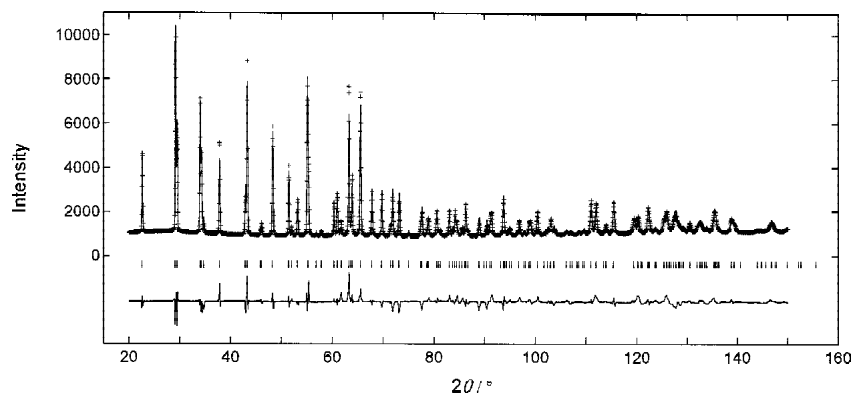


FIGURE 3. Result of Rietveld analysis for kozoite-(Nd). Observed and calculated diffraction profiles (top) are given as plus signs and as a line, respectively. Short bars indicate Bragg angles, and the pattern at the bottom indicates the difference between the observed and calculated intensities.

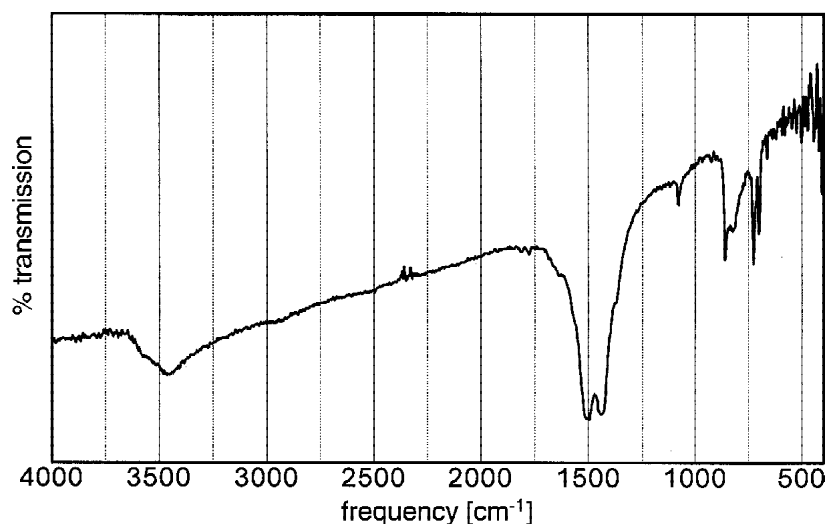


FIGURE 4. Infrared absorption spectrum of kozoite-(Nd) in a KBr pellet.

TABLE 3. Final atomic parameters for kozoite-(Nd)

	x	y	z	B(Å ²)
M*	0.25	0.3346(1)	0.6457(3)	0.2
C	0.75	0.188(2)	0.777(2)	0.4
O1	0.75	0.314(1)	0.697(1)	1.0
O2	0.537(1)	0.1131(7)	0.848(1)	1.0
O3	0.25	0.417(1)	0.003(1)	2.0

Notes: The four H atoms were not located in the unit cell.

* The occupancy parameter for the M site was fixed according to the chemical analysis : 0.425Nd + 0.305La + 0.09Pr + 0.07Sm + 0.04Gd + 0.025Eu + 0.005Ce + 0.005Dy + 0.015Y + 0.02Ca.

TABLE 4. Interatomic distances (Å) of kozoite-(Nd)

M-O3	2.38(1)	C-O2	1.21(1) × 2
M-O3	2.68(1)	C-O1	1.33(1)
M-O1	2.526(2) × 2		
M-O2	2.597(6) × 2	mean	1.25
M-O2	2.63(1) × 2		
M-O2	2.785(8) × 2		
mean	2.61		

loss for the second decarbonation step is 9.89 wt%. The estimated amounts for the exhausted CO₂ and H₂O gas, 21.87 and 4.09 wt%, respectively, are comparable with the findings from the elementary analysis (Table 1).

The dehydration temperature of kozoite-(Nd), 485 °C, is much higher than those of kimuraite-(Y), 160 °C (Nagashima et al. 1986), and lanthanite-(Nd), 119 °C (Roberts et al. 1980). This is understandable on structural grounds. In the crystal structure of kozoite-(Nd), the rare earth cations are strongly bonded to hydroxyl and carbonated anions, while the crystal structure of lanthanite-(La) (Dal Negro et al. 1977) consists of La₂(CO₃)₃ layers weakly connected by hydrogen-bonds to interlayer water molecules. These bonding features are reflected in the difference of the dehydration temperatures. This also explains why kozoite-(Nd) is stable against the electron beam in the microprobe analysis, while associated rare earth carbonate minerals, such as kimuraite-(Y) and lanthanite-(Nd), are seriously damaged by the electron beam.

RELATIONSHIP TO OTHER MINERALS

Kozoite-(Nd) is dimorphous with hydroxylbastnäsite-(Nd) (Maksimovic and Pantó 1985), and is isostructural with ancylite-(Ce) and other members of the ancylite group: calcioancylite-(Ce) (Pekov et al. 1997), calcioancylite-(Nd) (Orlandi et al. 1990), ancylite-(Ce) (Dal Negro et al. 1975),

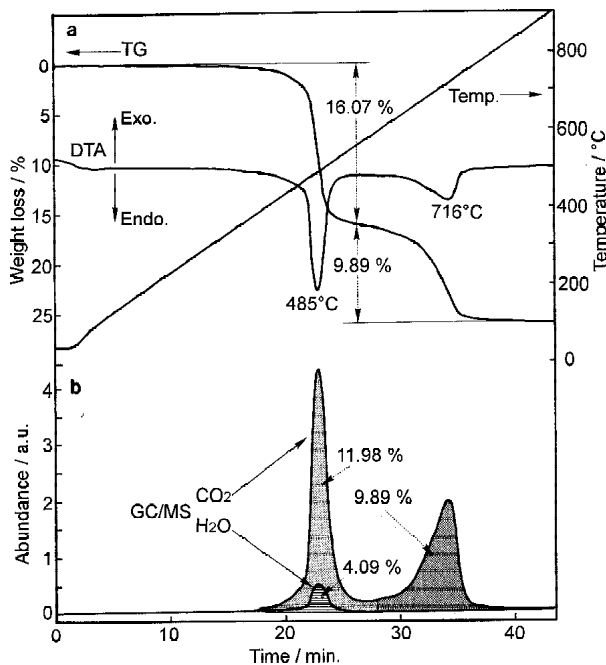


FIGURE 5. (a) DTA and TG curves of kozoite-(Nd). (b) The abundance of exhaust gases simultaneously recorded during the thermal analysis (GC-MS).

ancylite-(La) (Yakovenchuk et al. 1997) and gysinite-(Nd) (Sarp and Bertrand 1985; Chabot and Sarp 1985) (Fig. 6a).

Kozoite-(Nd) is much richer in neodymium and poorer in calcium than calcioancylite-(Nd) from Baveno, Italy. The unit cell of kozoite-(Nd) is slightly larger than that of calcioancylite-(Nd): $a = 4.976(2)$, $b = 8.468(2)$, $c = 7.212(2)$ Å, $\alpha = 90.04(3)^\circ$ (Orlandi et al. 1990). Pekov et al. (1997) described calcioancylite-(Ce) from several localities and reviewed the chemical compositions of ancylite group minerals. Bulakh et al. (1988) analyzed ancylite-(Ce) from the Kola Peninsula and compared the solid solution chemistry with literature data. These two reports, reviewing the plots of chemical compositions of "ancylites" and "calcioancylites," showed that the value "x" in the general formula, $RE^{3+}M_{2-x}^{2+}(CO_3)_2(OH)_x \cdot (2-x)H_2O$ ($M = Ca, Sr, Pb$), always exceeded 1 for all samples except one from the Kola Peninsula, Russia (Fig. 6b). This indicates that ancylite group minerals are not intermediate solid solutions between $RE(CO_3)(OH)$ and $M^{2+}(CO_3) \cdot H_2O$. The end members of this group are $RE^{3+}(CO_3)(OH)$ and $RE^{3+}M^{2+}(CO_3)_2(OH) \cdot H_2O$ as suggested by Sarp and Bertrand (1985), and minerals in the ancylite group can be described as solid solutions among ancylite, calcioancylite, gysinite and kozoite from the viewpoint of chemical composition (Fig. 6a).

Figure 6b is the ternary composition diagram for "kozyote," "ancylite" and "calcioancylite." Kozoite-(Nd) from Saga is free from Sr and is extremely poor in Ca. The value of "x" of the present specimen is 1.96. These value is much larger than those previously reported: 1.4 for calcioancylite-(Nd) from the type locality (Italy) (Orlandi et al. 1990); 1.46 for calcioancylite-(Ce) from Ilímaussaq, Greenland (Pekov et al. 1997); 1.46 for ancylite-(Ce); 1.47 for calcioancylite-(Ce) from the Polar Urals, Russia (Pekov et al. 1997) and 1.34 for gysinite-(Nd) from Shaba, Congo (Zaire) (Chabot and Sarp 1985).

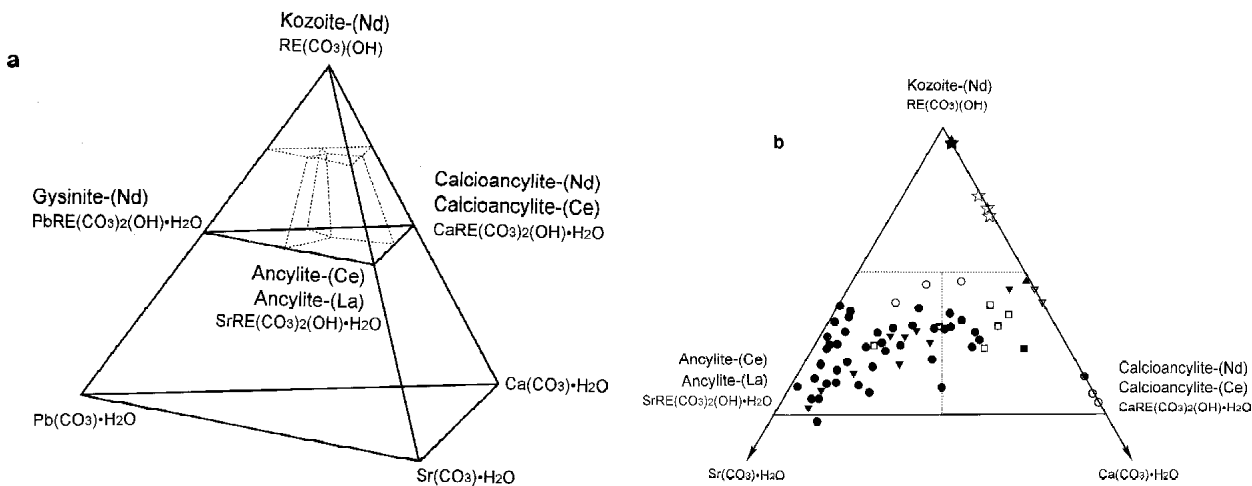


FIGURE 6. The compositional relationships among the ancylite-group minerals. (a) Quaternary diagram, showing the system $RE(CO_3)(OH)$, $Sr(CO_3) \cdot H_2O$, $Ca(CO_3) \cdot H_2O$, and $Pb(CO_3) \cdot H_2O$. (b) Ternary diagram showing the defined boundaries among kozoite-(Nd), [ancylite-(Ce) and ancylite-(La)], and [calcioancylite-(Nd) and calcioancylite-(Ce)] with plots of chemical compositions. \star = kozoite-(Nd) from Saga, Japan (present study), \star = kozoite-(Nd) from Saga, Japan (Miyawaki et al. 1998), \blacktriangle = Ilímaussaq, Greenland (Pekov et al. 1997), ∇ = Baveno, Italy (Pekov et al. 1997), \blacktriangledown = Narssárssuk, Greenland (Pekov et al. 1997), \square = Mont Saint-Hilaire, Canada (Pekov et al. 1997), \blacksquare = Cornog, U.S.A. (Pekov et al. 1997), \circ = Urals, Russia (Pekov et al. 1997), \bullet = Kola Peninsula, Russia (Pekov et al. 1997; Bulakh et al. 1988), and "triangle in circle" = Western land of Russia (Pekov et al. 1997).

A total of three crystal structures have been reported for synthetic compounds with composition of $RE^{3+}(CO_3)(OH)$: Nd(CO_3)(OH), orthorhombic, $Pmcn$, $a = 4.953$, $b = 8.477$, $c = 7.210$ Å (Dexpert and Caro 1974), Nd(CO_3)(OH), hexagonal, $P\bar{6}$, $a = 12.32$, $c = 9.88$ Å (Christensen 1973), and Y(CO_3)(OH), orthorhombic, $P2_12_12_1$, $a = 4.809(1)$, $b = 6.957(1)$, $c = 8.466(1)$ Å (Beall et al. 1976). The present Reitveld analysis for kozoite-(Nd) is in good agreement with the crystal structure analysis for the orthorhombic Nd(CO_3)(OH) with the ancylite structure (Dexpert and Caro 1974). The crystal structure of the hexagonal Nd(CO_3)(OH) (Christensen 1973) shows close structural similarity with bastnäsite-(Ce) as pointed out by Miyawaki and Nakai (1993), and can be described as the distorted bastnäsite structure. In the crystal structure of the orthorhombic Y(CO_3)(OH) (Beall et al. 1976), the Y cations are coordinated with 8 anions, whereas the coordination number for the Nd cations in the ancylite type orthorhombic Nd(CO_3)(OH) is 9. Miyawaki and Nakai (1993) introduced these phases as an example pair showing the difference between large Ce-group rare earths and smaller Y-group rare earths. Kozoite-(Nd) from Saga is therefore the first naturally occurring equivalent of the synthetic orthorhombic $RE^{3+}(CO_3)(OH)$.

The possibility of monoclinic symmetry for kozoite-(Nd) could not be ruled out from the present crystallographic investigation, because of the lack of any suitable single crystals for the examination of the Laue symmetry. The successful indexing of the diffraction data with the orthorhombic system indicates that the unique angle should be close to 90° even if the true lattice is monoclinic. Moreover, it would be difficult to detect the ordering in the (RE^{3+}, M^{2+}) site because there are only trace amounts of M^{2+} cations such as Ca^{2+} and Sr^{2+} in kozoite-(Nd).

The similarity between the shape of aggregate of kozoite-(Nd) and the habit of lanthanite-(Nd) crystal suggests that kozoite-(Nd) is a dehydration product of lanthanite-(Nd). The resemblance in the lanthanide distribution patterns between kozoite-(Nd) and lanthanite-(Nd) (Fig. 2) supports a strong genetic relationship between the two minerals.

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