Journal of Mineralogical and Petrological Sciences, Volume 98, page 137–141, 2003

Kozoite-(La), $La(CO_3)(OH)$, a new mineral from Mitsukoshi, Hizen-cho, Saga Prefecture, Japan

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Kozoite-(La), $(La,Nd,Ca)(CO_3)[(OH),(H_2O)]$, occurs in cavities of alkali olivine basalt at Mitsukoshi, Hizen-cho, Higashi Matsuura-gun, Saga Prefecture, Japan. Minute crystals of kozoite-(La) form a spherical aggregate with kozoite-(Nd). Concentric zoning textures of kozoite-(La) and kozoite-(Nd) can be observed on the fracture of the spherical aggregate. Kozoite-(La) is the La-analogue of kozoite-(Nd) and is a new member of ancylite group minerals. It is orthorhombic, *Pmcn*, a = 4.986(4) Å, b = 8.513(6) Å, c = 7.227(10) Å, V = 306.7(6) Å^3, Z = 4. The three strongest lines in the powder XRD patterns [d(Å), I/I_0, hkl] are (4.31, 100, 110 and 020); (3.69, 72, 111 and 021) and (2.93, 57, 121 and 102).

Introduction

During the fieldworks in Higashi Matsuura-gun, Saga Prefecture, three of the present authors (S. I., K. H. and I. Y.) recognized tiny pale violet spherules in the cavities of alkali basalt at Mitsukoshi, Hizen-cho in the area. One of them (S.I.) sent them to the National Science Museum, Tokyo for the mineralogical investigation. They gave a powder X-ray diffraction pattern almost identical to that of kozoite-(Nd), which was discovered in the alkali basalt of this area and was named after the late Professor Kozo Nagashima (1925-1985) (Miyawaki et al., 2000). The electron microprobe analysis revealed that the spherical particle was heterogeneous and consisted of not only Nd-dominant parts but also La-dominant parts. This La-analogue of kozoite-(Nd) was named as kozoite-(La) according to the Levinson rule. It is a member of ancylite-group minerals and a polymorph of hydroxylbasntäsite-(La). The mineral data and the name have been approved by the Commission on New Minerals and Mineral Names of IMA (no. 2002-054). The type specimen is deposited in the National Science Museum, Tokyo, under the registered number NSM-M28310.

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Occurrence

Kozoite-(La) occurs in small cavity in the alkali olivine basalt at Mitsukoshi, Hizen-cho, Saga Prefecture, Japan. The rock is the last-stage lava flow of Higashi Matsuura District. The detailed geology was reported by Aoki (1959). The mineral is found as spherical aggregates with diameter less than 1 mm (Fig. 1). Radial fine crystals are observed on the fracture of the spherical aggregate.

During the observation of back-scattered electron image, the spherule shows concentric chemical zoning between kozoite-(La) and kozoite-(Nd) (Fig. 2). The maximum radius of kozoite-(La) domain in spherule is 0.15 mm. Associated minerals in the cavity are kozoite-(Nd), lanthanite-(Nd), kimuraite-(Y), lokkaite-(Y), calcite, aragonite and opal (hyalite).

Physical and optical properties

Kozoite-(La) is extremely pale purple to white in color with a vitreous luster. The streak is white. No fluorescence was observed under short and long wave of UV light. The surface of spherule, with purplish color indicating to be kozoite-(Nd), is smooth and glassy. Due to the very small dimensions of the crystals and to the close association with kozoite-(Nd), the optical properties, hardness, cleavage and density could not be measured. The calculated density is 4.16 g/cm^3.

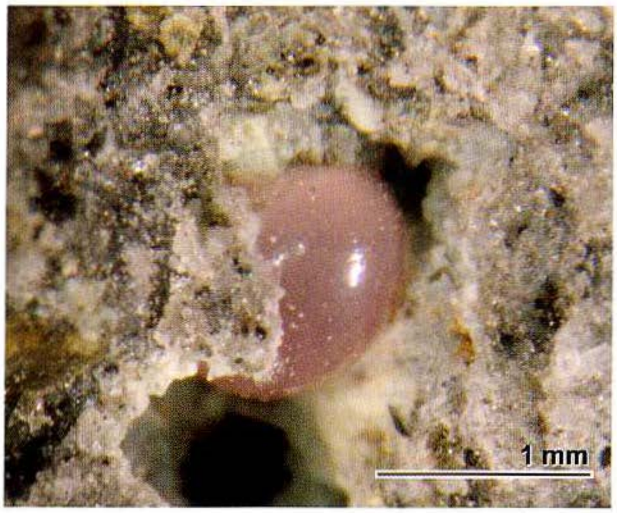

Figure 1 Photomicrographs of the spherical aggregate composed of kozoite-(La) and kozoite-(Nd).

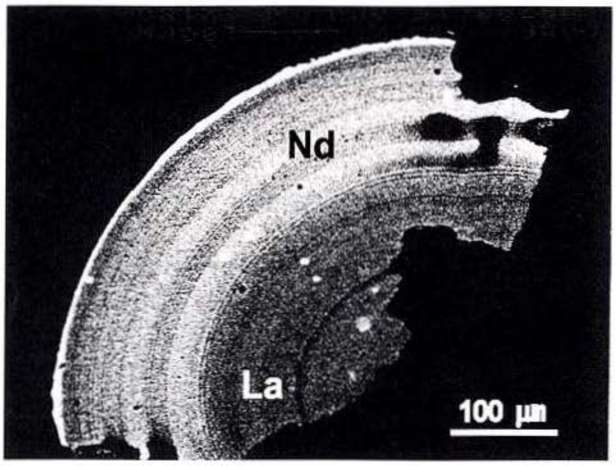

Figure 2. The BEI of polished section of the spherical aggregate. La dominates in the dark gray parts, and Nd in the light gray parts. The scattering powers of La and Nd are very close to each other. The difference in the contrast may come from the difference in the Ca concentrations.

The infrared absorption spectrum was obtained by an FT-IR spectrometer (JASCO FT/IR-420) using the KBr method in transmission mode. The spectrum exhibited absorption bands due to the OH group (3050-3500 cm^{-1}) and those due to the carbonate group (1300-1500 cm^{-1}).

Chemical composition

This mineral is readily soluble with effervescence in dilute hydrochloric acid. Preliminary chemical analysis by SEM-EDS (JEOL JSM-5400) indicated that the mineral consisted of RE (rare earth elements), Ca, and small amount of Sr. No other element with atomic number greater than ten was detected. A quantitative analysis was carried out with JEOL JXA-8800M WDS

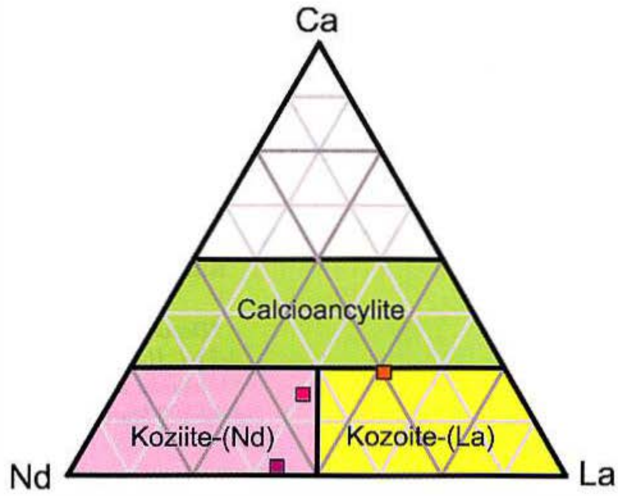

Figure 3. Ternary diagram showing the defined boundaries among kozoite-(La), kozoite-(Nd) and calcioancylite-(Nd). The orange square indicates kozoite-(La), the pink square is kozoite-(Nd) associated within the same spherical aggregate. The purple square shows the composition of type material of kozoite-(Nd) (Miyawaki, et al., 2000). The right part of calcioancylite is La-analogue of calcioancylite-(Nd), which has not been known as a mineral species.

electron microprobe analyzer (15 kV and 10 nA). Carbon and hydrogen could not be determined due to the occurrence mode. The values for carbonate ion, hydroxyl ion, and water molecule were calculated based on the general formula of ancylite group minerals; $RE^{3+}{}_xM^{2+}{}_{2-x}(CO_3)_2(OH)_x\cdot(2-x)H_2O$: The number of carbon atoms was set to be equal to the total number of the cations (RE + Sr + Ca). The number of hydroxyl ion and water molecule are calculated to be equal to the number of RE^{3+} and $(Ca,Sr)^{2+}$, respectively.

The results of the analyses are given in Table 1. The empirical formula on the basis of the 2 cations per formula unit is: $(La_{0.83}Nd_{0.40}Y_{0.13}Pr_{0.11}Sm_{0.03}Gd_{0.03})_{\Sigma 1.53}(Ca_{0.43}Sr_{0.05})_{\Sigma 0.48}(CO_3)_2(OH)_{1.52}\cdot 0.48H_2O$. The simplified formula is $(La,Nd,Ca)(CO_3)[(OH),(H_2O)]$, and the ideal formula is $La(CO_3)(OH)$, which requires La_2O_3 75.45: CO_2 20.38, H_2O 4.17(wt.%).

Crystallography

Powder X-ray diffraction data were obtained using a 114.6 mm Gandolfi camera employing Ni-filtered Cu *Kα* radiation. The data were recorded on an Imaging Plate, and processed with a Fuji BAS-2500 bio-imaging analyzer and a computer program by Nakamuta (1999). The unit cell parameters were refined from the powder X-ray diffraction data with internal Si standard (NBS, #640b) using a computer program by Toraya (1993). The diffraction data and refined lattice parameters are listed in Table 2 with those of kozoite-(Nd) within the

Table 1. Chemical compositions of kozoite-(La) and kozoite-(Nd) in the spherical aggregate from Mitsukoshi, Saga, Japan

	Kozoite-(La)					Kozoite-(Nd)				Standard
	1	2	3	4	Average	1	2	3	Average	
wt.%										
La_2O_3	36.03	36.07	35.21	34.90	35.55	22.40	20.90	22.39	21.90	LaP_5O_{14}
Ce_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	CeP_5O_{14}
Pr_2O_3	4.88	4.53	4.94	4.35	4.68	6.06	5.58	6.18	5.94	PrP_5O_{14}
Nd_2O_3	17.55	16.49	18.05	18.32	17.60	25.54	26.47	25.90	25.97	NdP_5O_{14}
Sm_2O_3	1.15	1.09	1.05	1.31	1.15	3.24	3.40	3.21	3.28	SmP_5O_{14}
Eu_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Gd_2O_3	1.33	1.29	1.58	1.77	1.49	3.41	3.20	2.88	3.16	GdP_5O_{14}
Tb_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Dy_2O_3	0.00	0.08	0.07	0.21	0.09	0.86	0.84	1.05	0.91	DyP_5O_{14}
Er_2O_3	0.02	0.03	0.01	0.09	0.04	0.42	0.34	0.34	0.37	ErP_5O_{14}
Y_2O_3	3.49	3.26	4.46	4.32	3.88	5.12	3.98	5.56	4.88	YP_5O_{14}
CaO	6.14	6.20	6.42	6.45	6.30	4.58	4.99	5.04	4.87	Wollastonite
SrO	1.21	1.24	1.58	1.41	1.36	0.74	1.01	0.90	0.88	Slawsonite
CO_2*	22.94	22.54	23.67	23.56	23.17	22.19	21.87	22.81	22.29	
H_2O*	5.79	5.72	6.01	5.98	5.87	5.34	5.37	5.56	5.42	
total	100.53	98.52	103.05	102.68	101.19	99.89	97.93	101.80	99.87	
No. atoms [$\Sigma(RE^{3+} + M^{2+}) = 2$]										
La	0.85	0.86	0.80	0.80	0.83	0.55	0.52	0.53	0.53	
Ce	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Pr	0.11	0.11	0.11	0.10	0.11	0.15	0.14	0.14	0.14	
Nd	0.40	0.38	0.40	0.41	0.40	0.60	0.63	0.59	0.61	
Sm	0.03	0.02	0.02	0.03	0.03	0.07	0.08	0.07	0.07	
Eu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Gd	0.03	0.03	0.03	0.04	0.03	0.07	0.07	0.06	0.07	
Tb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Dy	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.02	0.02	
Er	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	
Y	0.12	0.11	0.15	0.14	0.13	0.18	0.14	0.19	0.17	
ΣRE^{3+}	1.54	1.52	1.52	1.52	1.52	1.65	1.60	1.62	1.62	
Ca	0.42	0.43	0.43	0.43	0.43	0.32	0.36	0.35	0.34	
Sr	0.04	0.05	0.06	0.05	0.05	0.03	0.04	0.03	0.03	
ΣM^{2+}	0.46	0.48	0.48	0.48	0.48	0.35	0.40	0.38	0.38	
C*	2	2	2	2	2	2	2	2	2	
H*	2.46	2.48	2.48	2.48	2.48	2.35	2.40	2.38	2.38	

* Calculated based on the formula of $(RE_xM_{2-x})(CO_3)_2(OH)_x{\cdot}(2-x)H_2O$.

same spherical aggregate. No single-crystal work could be carried out because of the occurrence mode, especially the small dimension of the crystals.

Discussion

Kozoite-(La) and kozoite-(Nd) from the present locality, Mitsukoshi, Saga, Japan, contain considerable amount of Ca (Table 1). However, the values "x" in the general formula, $RE^{3+}_xM^{2+}_{2-x}(CO_3)_2(OH)_x{\cdot}(2-x)H_2O$ (M = Ca, Sr, Pb), exceed 1.5 that is boundary between kozoite and calcioancylite (Miyawaki et al., 2000) (Fig. 2). Thus, these minerals are not calcioancylite but are kozoite.

Kozoite-(La) and kozoite-(Nd) from Mitsukoshi show different lanthanides distribution patterns compared with those of the kimuraite-(Y) and lokkaite-(Y) (Fig. 4). They are much richer in light REE, e.g., lanthanum, and are poorer in heavy REE, e.g., dysprosium and erbium. The cerium anomaly, which appears as a spike on the REE distribution pattern, is remarkable for kozoite-(La) and kozoite-(Nd) in the spherical aggregate. The cerium contents in these specimens were so low to be determined in the present electron microprobe analysis. Kozoite-(La) as well as kozoite-(Nd) can be characterized to be crystallized

Table 2. Powder X-ray diffraction data obtained with a Gandolfi camera and an Imaging Plate

			Kozoite-(La)			Kozoite-(Nd)		
h	*k*	*l*	I/I_0	$d_{obs.}$	$d_{calc.}$	I/I_0	$d_{obs.}$	$d_{calc.}$
0	1	1	32	5.54	5.51	31	5.49	5.50
1	1	0	100	4.31	4.30	100	4.29	4.29
0	2	0			4.26			4.24
1	1	1	72	3.69	3.70	66	3.68	3.69
0	2	1			3.67			3.66
0	1	2	23	3.32	3.33	22	3.32	3.33
1	2	1	57	2.93	2.95	48	2.92	2.95
1	0	2			2.93			2.92
1	1	2	7	2.75	2.77	5	2.75	2.76
0	2	2			2.75			2.75
0	3	1	30	2.64	2.64	25	2.64	2.63
2	0	0	29	2.49	2.49	25	2.48	2.48
1	2	2	13	2.41	2.41	12	2.41	2.41
1	3	1	50	2.33	2.33	42	2.33	2.33
2	2	0	12	2.15	2.15	12	2.14	2.14
0	4	0	19	2.13	2.13	15	2.12	2.12
2	2	1	48	2.06	2.06	44	2.05	2.06
0	4	1	19 sh	2.04	2.04	16 sh	2.04	2.04
2	1	2	35	1.994	1.995	32	1.990	1.990
1	2	3	18 *	1.934	1.933	15 *	1.930	1.931
1	4	1	10	1.889	1.889	9	1.885	1.884
0	3	3	17	1.839	1.836	18	1.834	1.835
2	3	1	14	1.813	1.813	12	1.805	1.807
1	4	2	11	1.724	1.721	10	1.717	1.717
2	1	3	7	1.702	1.698	6	1.696	1.695
1	1	4	9	1.666	1.666	9	1.661	1.666
3	1	0	8 *	1.634	1.631	8 *	1.623	1.625
1	5	0	11	1.612	1.611	9	1.608	1.606
2	2	3	9	1.607	1.605			1.602
3	1	1	6	1.592	1.591	6	1.586	1.586
2	4	1	8	1.580	1.579	8	1.575	1.575
0	5	2	5	1.542	1.540	6	1.537	1.537
3	2	1	10	1.515	1.514	8	1.508	1.509
3	0	2	8	1.509	1.510			1.506
2	3	3	9	1.480	1.479	8	1.473	1.476
2	1	4	4	1.446	1.442			1.440
3	2	2	4	1.422	1.423			1.419
0	6	0	4	1.419	1.419			1.415
3	3	1	7	1.406	1.407			1.402
0	5	3	4	1.393	1.390			1.388
1	1	5	5	1.376	1.370			1.370
1	4	4	5	1.329	1.328			1.326
2	5	2	10	1.310	1.310	7	1.306	1.307
3	4	1	4	1.289	1.289			1.285
1	6	2	8	1.274	1.277	5	1.274	1.273
1	3	5	7 *	1.247	1.247	8 *	1.242	1.247
4	0	0			1.246			1.242
2	6	0	8	1.233	1.233	5	1.229	1.229
3	1	4	8	1.213	1.211	7	1.207	1.209
1	5	4			1.203			1.201
2	2	5	9	1.203	1.200	6	1.196	1.199
0	7	1			1.199			1.196
0	4	5			1.196			1.195
4	2	1	4	1.179	1.180			1.176
3	5	1	4	1.174	1.173			1.170
1	7	1	6	1.168	1.166	6	1.162	1.163
0	7	2	5	1.155	1.153			1.150
3	4	3	3	1.150	1.151			1.148
			a = 4.986(4) Å			a = 4.968(4) Å		
			b = 8.513(6) Å			b = 8.488(5) Å		
			c = 7.227(10) Å			c = 7.231(7) Å		
			V = 306.7(6) Å^3			V = 304.9(4) Å^3		

* Estimated from data with the external Si-standard.
sh, Shoulder.

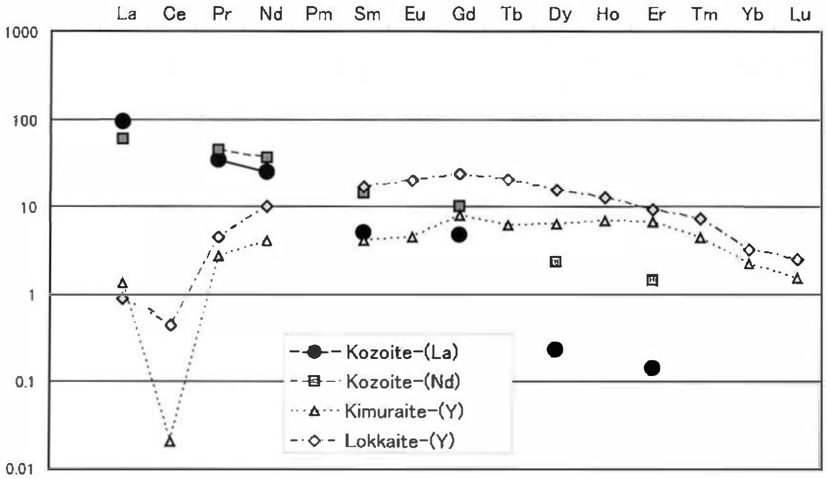

Figure 4. Chondrite-normalized lanthanide distribution patterns of kozoite-(La), kozoite-(Nd), kimuraite-(Y) and lokkaite-(Y) from Saga Prefecture, Japan. Data for kimuraite-(Y) and lokkaite-(Y) are from Nagashima et al. (1986).

under condition of the biased lanthanides distribution pattern with Ce-anomaly.

Kozoite-(La) is significantly Sr-poor. The associated kozoite-(Nd) is even poorer in Sr than kozoite-(La). This is consistent with chemical feature observed as a correlation between Nd/La and Ca/Sr for calcioancylite-(Ce) from Ilímasussaq (Pekov et al., 1997).

The unit cell volume of kozoite-(La), 306.7 Å^3, is slightly smaller than that of type specimen of kozoite-(Nd), 308.05 Å^3 (Miyawaki et al., 2000). It is, at the first glance, in contradiction because the larger La^{3+} ions are dominant in kozoite-(La) instead of the smaller Nd^{3+} ions in kozoite-(Nd). The Ca content affects the cell volume in kozoite – calcioancylite solid-solution series. The cell volume of calcioancylite, 303.9 Å^3 (Orlandi et al., 1990), is smaller than these species. As described above, kozoite-(La), as well as the associated kozoite-(Nd), contains considerable amounts of Ca and has a chemical composition very close to the boundary between kozoite and calcioancylite (Fig. 3). These kozoite specimens with high Ca contents have smaller unit cell volumes in comparison with the almost Ca-free kozoite-(Nd) (Miyawaki et al., 2000). A slight enlargement of the unit cell volume can be observed for kozoite-(La) in comparison to kozoite-(Nd) in the present spherical aggregates with comparable Ca. The enlargement can be attributed to the replacements of Nd^{3+} and Ca^{2+} with larger La^{3+} and Sr^{2+}, respectively.

Acknowledgements

We thank to Mrs. M. Shigeoka for her preparing the polished thin sections. Special thanks are extended to Prof. Y. Nakamuta of Kyushu University and for Dr. K. Sugiyama of the University of Tokyo for their suggestions on the XRD investigations.

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Manuscript received: 6 May, 2003
Manuscript accepted: 28 July, 2003