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Nagashimalite, $Ba_4(V^{3+}, Ti)_4[(O, OH)_2|Cl|Si_8B_2O_{27}]$, a new mineral from the Mogurazawa mine, Gumma Prefecture, Japan

Satoshi MATSUBARA and Akira KATO

Department of Geology, National Science Museum, Tokyo 160, Japan

Abstract

Nagashimalite, $Ba_4(V^{3+}, Ti)_4[(O, OH)_2|Cl|Si_8B_2O_{27}]$, is orthorhombic, space group *Pmmn*, unit cell parameters: $a=13.937(3)$, $b=12.122(3)$, $c=7.116(2)$ Å, $Z=2$. The strongest lines in the X-ray powder pattern are: 3.854(25)(221), 3.319(15)(112), 3.173(15)(202), 3.030(60)(040, 411), 3.020(100)(420), 2.791(20)(041), 2.592(28)(501, 241), 1.785(15)(641), 1.287(15)(771). It is greenish black in colour, lustre submetallic to vitreous. Streak green. No cleavage. VHN (load 100 g) 606-681 kg/mm^2 ($\fallingdotseq 6$ (Mohs)). Specific gravity 4.08 (meas.), density 4.14 g/cm^3 (calc.). It is optically biaxial, positive, $2V=30°$ (obs.), $r>v$ strong; refractive indices $\alpha=1.750(2)$, $\beta=1.753(2)$, $\gamma=1.780(5)$; optical orientation $a=X$, $b=Z$, $c=Y$; pleochroism strong, X=greenish yellow, Y=green, Z=greenish brown, absorption $X<Y<Z$. The mineral occurs as prismatic crystals and their aggregates in massive rhodonite ore from a bedded manganese ore deposit of the Mogurazawa mine, Gumma Prefecture, Japan.

Introduction

During the mineralogical studies on the bedded manganese ore deposit of the Mogurazawa mine, Kiryu City, Gumma Prefecture, Japan, aggregates of greenish black prisms were found in massive rhodonite ore in association with barium- and vanadium-bearing silicates. A detailed investigation of this mineral indicated that it is a new barium vanadium borosilicate closely related to taramellite.

The name nagashimalite is given in honour of the late Mr. Otokichi Nagashima (1890-1969), the pioneer of Japanese amateur mineralogist. The mineral and the name have been approved by the Commission on New Minerals and Mineral Names, I. M. A. Type material (NSM M-21727) is preserved at Department of Geology, National Science Museum, Shinjuku, Tokyo, Japan.

Occurrence

There are more than two hundred bedded manganese ore deposits in Ashio Mountainland, where thick sedimentary rocks comprising chert, slate, limestone and basic rock are exposed together with three granitic intrusives. All of the manganese ore deposits are developed in chert or closely associated with chert or its contact metamorphosed equivalents. Among them, the ore deposit of the Mogurazawa mine is located in bedded chert accompanied by shale and conglomerate including chert and sandstone blocks. Recently the occurrence of Triassic conodonts is known in nearby chert (S. Hayashi, priv. comm.). The

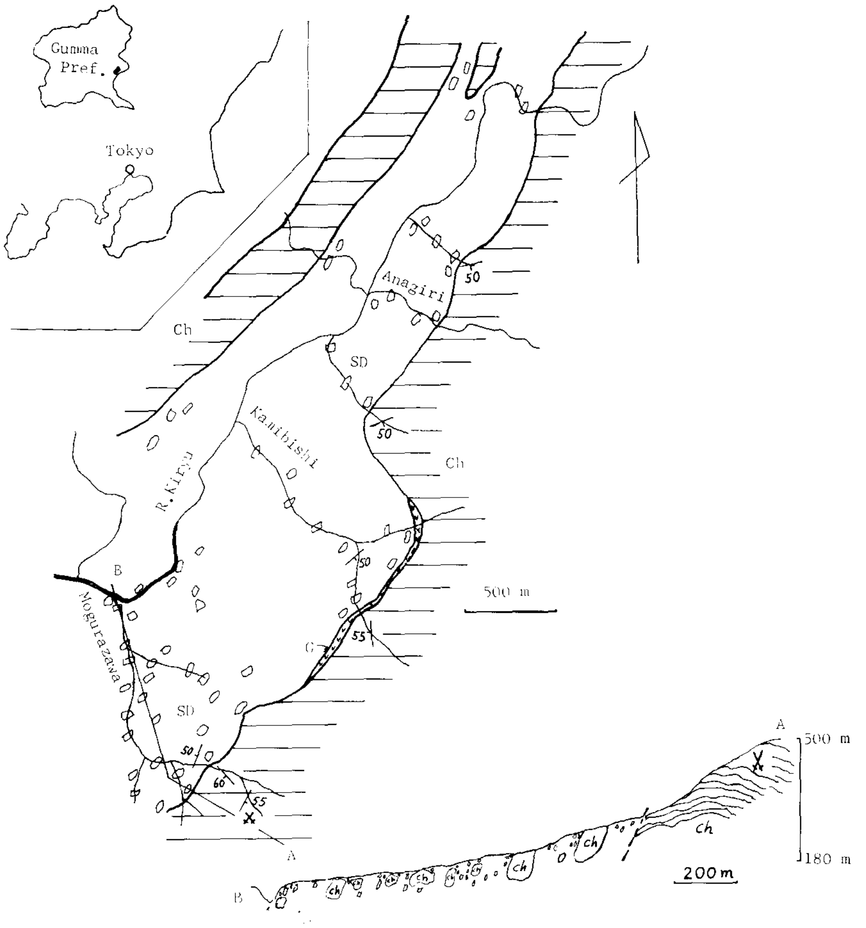

FIG. 1. Geological sketch map of the adjacent area of the Mogurazawa mine. Ch: bedded chert. G: greenstone. SD: deposits due to submarine sliding, shale and conglomerate including chert and sandstone blocks.

geologic outline of the area around the deposit is shown in Fig. 1.

It is said that the mining activity ceased more than 25 years ago and all the studied materials were collected from the dumps. The principal ore minerals are rhodochrosite, rhodonite, tephroite, hausmannite and manganosite in the order of decreasing amount, accompanied by minor amounts of pyrochroite, jacobsite, alleghanyite, spessartine, and helvine. Nagashimalite is found exclusively in massive aggregates of fine-grained rhodonite ore including minor rhodochrosite, barite, quartz, barian roscoelite, unnamed barium analogue of haradaite, alabandite, digenite, bornite and tetrahedrite as accessory constituents.

The crystals of nagashimalite are tabular on {001} and elongated along the *b*-axis up to 15 mm long and form subparallel aggregates (Fig. 2). On {001} striations are developed parallel to the *b*-axis forming some vicinal faces expressed as (*h*0*l*) where *h* is very large as compared with *l* (Fig. 3).

Above mentioned barium-bearing silicates are generally formed along fissures cutting the rhodonite ore, and they are considered as hydrothermal minerals of

FIG. 2. Photomicrographs of nagashimalite (N) in association with rhodonite (R) and quartz (Q). Left: one polar. Right: crossed polars. Bar indicates 0.2 mm.

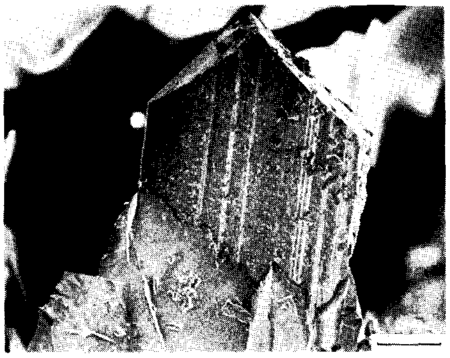

FIG. 3. Electron microphotograph of nagashimalite crystal. Bar indicates 0.05 mm.

later formation than rhodonite. As discussed later, all the barium-bearing silicates found as fissure minerals cutting manganese ores are intimately accompanied by rhodonite. This suggests that the hydrothermal solution could transport silica and favoured the formation of silica-saturated minerals in the fissure.

Optical and physical properties

Nagashimalite is greenish black in colour with a submetallic to vitreous lustre and the streak is green. No cleavage is discerned. Specific gravity measured by Berman microbalance is 4.08, which is reasonably close to the calculated density 4.14 g/cm^3 using the normalized empirical formula. Vickers microhardness is 606-681 kg/mm^2 (100 g load) ($\doteqdot$6(Mohs)).

It is optically biaxial positive, 2V about 30° (meas.), dispersion $r > v$, strong. Refractive indices $\alpha=1.750(2)$, $\beta=1.753(2)$, $\gamma=1.780(5)$ by the immersion method. Optical orientation: $a=X$, $b=Z$, $c=Y$. Pleochroism is strong with axial colours: X=greenish yellow, Y=green, Z=greenish brown with absorption $X<Y<Z$.

X-ray studies

The X-ray powder diffraction pattern of nagashimalite obtained by the powder diffractometer method using Cu/Ni radiation is given in Table 1 in which that of taramellite (JCPDS Card No. 17-479) is shown for comparison. The indexing was based on the single crystal data, orthorhombic, space group *Pmmn*, $a=13.937$, $b=12.122$, $c=7.116$Å measured by automated four-circle diffractometer (Syntex $P2_1$) using monochromatized MoKα radiation (Matsubara, 1980).

Chemical composition

Electron microprobe analysis using barite (for Ba), analysed vanadium-bearing aegirine (for V), TiO_2 (for Ti), analysed rhodonite (for Mn and Si) and analysed pyrosmalite (for Cl), and wet chemical analysis for B_2O_3 on about 10 mg handpicked material gave the results shown in Table 2. The wet chemical analysis proved the presence of H_2O but the paucity of material impeded the qualitative measurement. Vanadium was found to be trivalent after the X-ray photoelectron spectrometric method. Spectroscopic analysis showed the traces of Mg, Al, Pb, Fe, Sb and Cu.

The empirical formula is calculated as: $Ba_{4.00}(V^{3+}{}_{3.30}Ti_{0.51}Mn_{0.10})_{\Sigma 3.91}B_{1.71}Si_8O_{27.64}Cl_{0.72}(OH)_{1.28}$ on the basis of Si=8 after addition of H_2O 0.77 wt.% to give Cl+(OH)=2. The ideal formula is $Ba_4(V^{3+}, Ti)_4B_2Si_8O_{28}(Cl, OH, O)_2$, which is

TABLE 1. X-ray powder data for nagashimalite and taramellite.

1				2		
hkl	$d_{obs.}$	$d_{calc.}$	I/I_0	*hkl*	*d*	I/I_0
110	9.22	9.17	3			
200	6.98	6.97	10	200	6.89	16
101	6.32	6.34	2			
020	6.09	6.06	12	011, 002	6.04	16
111	5.63	5.62	2			
021	4.61	4.61	3			
121	4.384	4.381	4			
310	4.345	4.340	5			
221	3.854	3.846	25	212	3.83	50
311	3.708	3.704	8	311	3.68	25
002	3.559	3.558	2			
400	3.487	3.484	10			
				013	3.47	8
112	3.319	3.317	15	121	3.30	40
321	3.273	3.274	6			
202	3.173	3.172	15	220	3.16	40
231	3.136	3.136	6			
022	3.066	3.069	8			
				402	3.06	25
040 411	3.030	3.030 3.029	60			
420	3.020	3.021	100	004	3.01	100
041	2.791	2.787	20			
				222, 313+	2.783	30
510	2.717	2.717	8	114, 501	2.713	16
132	2.621	2.623	6		2.617	8
501 241	2.592	2.595 2.588	28		2.584	55
511	2.538	2.538	3		2.530	8
402	2.490	2.489	10		2.480	45
341	2.393	2.390	12		2.383	25
332	2.318	2.315	5			
530	2.294	2.294	6			
440	2.288	2.286	8			
601	2.209	2.208	6		2.204	8
441	2.178	2.176	12		2.169	16
512	2.159	2.159	8		2.153	20
223	2.107	2.105	2		2.105	8
313	2.080	2.081	2			
621	2.074	2.075	6		2.068	12b

(cont.)

1				2		
hkl	$d_{obs.}$	$d_{calc.}$	I/I_0	*hkl*	d	I/I_0
351	2.059	2.058	8			
060	2.022	2.020	3			
152	1.984	1.983	5			
710	1.963	1.965	2			
061	1.943	1.943	5			
161	1.925	1.924	10		1.924	25
711	1.893	1.894	5		1.889	16
333	1.873	1.872	8		1.870	16
640	1.845	1.844	5			
550	1.830	1.829	2			
503 243	1.805	1.806 1.804	8		1.802	25
641	1.785	1.785	15		1.781	25
460	1.748	1.748	12			
800	1.743	1.742	10			
731	1.732	1.732	8			
214 262	1.705	1.706 1.704	5			
461	1.698	1.697	2			
071	1.682	1.682	2			
603	1.659	1.660	2			
253	1.647	1.647	5		1.644	20
271	1.636	1.636	3			
651	1.633	1.633	3			
034	1.628	1.628	2		1.627	8
623	1.601	1.601	2		1.599	12
					1.584	8
063	1.538	1.538	2			
424	1.533	1.533	8		1.533	16
144	1.525	1.525	3			
080	1.516	1.515	10		1.515	16
751	1.504	1.504	3		1.500	8
841 372	1.477	1.477 1.476	8		1.475	8
344	1.457	1.457	2			
912	1.410	1.410	5		1.408	20
842	1.390	1.390	8		1.391	8
823	1.368	1.368	8		1.369	8
305 10.1.1	1.360	1.361 1.359	8		1.360	8
941	1.355	1.354	5			

(cont.)

1				2		
hkl	$d_{obs.}$	$d_{calc.}$	I/I_0	*hkl*	*d*	I/I_0
190	1.340	1.341	8			
390	1.294	1.293	8			
425	1.287	1.287	15			
771	1.285	1.285	12			
10.4.0	1.266	1.266	12			
491	1.237	1.237	5			

1. Nagashimalite. CuKα radiation. Diffractometer method. Indexed on an orthorhombic cell, $a=13.937$, $b=12.122$, $c=7.116$Å.
2. Taramellite. Candoglia, Italy. CoKα radiation. Camera (dia. 114.6 mm) method. Indexed on an orthorhombic cell, $a=13.95$, $b=7.05$, $c=12.01$Å. (JCPDS Card No. 17-479)

TABLE 2. Chemical analysis of nagashimalite.

	1	2	3
BaO	41.36	4.01	40.95
V_2O_3	16.65	3.30	17.21
TiO_2	2.75	0.51	2.99
MnO	0.48	0.10	
SiO_2	32.37	8	32.10
B_2O_3	4.0	1.71	4.65
Cl	1.73	0.73	2.37
H_2O	(0.77)	1.27	0.26
$-O=Cl_2$	−0.39		−0.53
total	99.72%		100.00%

1. Nagashimalite. Weight percent. H_2O content is calculated.
2. Molecular numbers on the basis of Si=8.
3. Theoretical weight percentages for $Ba_4(V^{3+}{}_{3.44}Ti_{0.56})_{\Sigma 4}Si_8B_2O_{28}Cl[(OH)_{0.44}O_{0.56}]$.

written as $Ba_4(V^{3+}, Ti)_4$ $[(O, OH)_2|Cl|Si_8B_2O_{27}]$ after the structural analysis (Matsubara, 1980).

Discussion

As seen in the similarity of X-ray powder pattern, nagashimalite is the V^{3+} analogue of taramellite (Tacconi, 1908), if minor titanium partially replacing it is not considered. The result of structural analysis of nagashimalite (Matsubara, 1980) indicates that this mineral is a borosilicate comprising $[Si_8B_2O_{27}]$ and the isostructural relation to taramellite strongly suggests the presence of the same silicate framework in the taramellite structure, though no boron is given in the original chemical analysis.

The association of barium, trivalent vanadium, boron and chlorine in a single silicate mineral is new to our geochemical knowledge but the collection of more detailed geochemical informations on the above elements is necessary before the discussion of the geochemical implication on the occurrence of this mineral.

There is no doubt that some of bedded manganese ore deposits in older sedimentary rocks or their metamorphic equivalents in Japan are also the sites of concentration of tri- or tetravalent vanadium, which forms such independent vanadium minerals as haradaite (Watanabe *et al.*, 1974) and goldmanite (Momoi, 1964) or is contained as a minor constituent in manganberzeliite (Matsubara, 1975) and in aegirine (Kato *et al.*, 1974). In these cases, the appearance of vanadium-bearing minerals requires effects of metamorphic or hydrothermal processes, which favoured the formation of silica-saturated mineral assemblage as represented by the presence of rhodonite.

There are at least three different mode of occurrence of barium-bearing minerals in Japanese bedded manganese ore deposits in older sedimentary rocks inclusive of their metamorphic equivalents. The first is in ores with a bedded texture, in which these minerals are distributed conformably with the texture as seen kinoshitalite from Hokkejino, Kyoto Prefecture (Matsubara *et al.*, 1976) and in orthoericssonite from the Hijikuzu mine, Iwate Prefecture (Matsubara and Nagashima, 1976). These are considered to reserve the original texture of ores and the concentration of barium was responsible for the formation of specific minerals, revealing bedded texture more clearly.

The second one is represented by the occurrence in fissures or veins cutting manganese silicate ores as seen in yoshimuraite from the Noda-Tamagawa mine, Iwate Prefecture (Watanabe *et al.*, 1961). In this case the precipitation of fissure-filling or vein-forming minerals is considered to have been precipitated from a hydrothermal solution which could also be carrier of barium and other contained in the barium minerals. The close association of barium-bearing minerals of this mode of occurrence with rhodonite suggests the prevalence of silica-rich environment. As far as inferable from the known examples, the distinction of this type from the previous one is responsible for the preference of barium-bearing minerals to be formed.

The third one is found in the form of manganese dioxide minerals developed in the oxidation zones of ore deposits. Barium is generally found as accessory constituents in cryptomelane, todorokite and some other manganese dioxide minerals or as a principal constituents in psilomelane.

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Postscript

The crystal structure of taramellite from the original locality has been described by Mazzi and Rossi (*Amer. Miner.*, 65, 123-128 (1980)) just after the refereeing of manuscript. Although no revised chemical analysis is given in their paper, their structural model includes $[B_2Si_8O_{27}]$ as the fundamental unit of framework.