Itoigawaite, a new mineral, the Sr analogue of lawsonite, in jadeitite from the Itoigawa-Ohmi district, central Japan

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ABSTRACT

Itoigawaite, SrAl₂Si₂O₇(OH)₂·H₂O, is a new member of the lawsonite group found in the Itoigawa-Ohmi district, central Japan. It is orthorhombic, *Cmcm*, a = 6.031(2), b = 8.945(2), c = 13.219(4) Å, Z = 4. The strongest lines in the X-ray powder diffraction pattern are 4.68 (s) (111), 4.26 (vs) (021), 3.31 (vs) (113), 2.75 (vs) (114, 202), 2.68 (vvs) (130), 2.63 (s) (131), 2.50 (s) (220, 203, 132), 2.45 (s) (221). Electron microprobe analysis gave SiO₂ 32.98, TiO₂ 0.87, Al₂O₃ 27.67, Fe₂O₃ 0.39, MgO 0.27, CaO 0.45, SrO 27.71, H₂O (diff.) 9.66, total 100.00 wt.%, corresponding to (Sr_{0.97}Ca_{0.03}Mg_{0.02})_{Σ1.02} (Al_{1.97}Ti_{0.04}Fe_{0.02})_{Σ2.03}Si_{1.99}H_{3.89}O₁₀ on the basis of O = 10. It is transparent, blue in colour with vitreous lustre. The streak is white and the cleavage good in one direction. The hardness is 5–5.5. The calculated density is 3.3 g cm⁻³. It is colourless in thin section and optically biaxial positive with $\alpha =$ 1.664 (2), $\beta = 1.674$ (2), $\gamma = 1.688$ (2) and 2V(calc.) = 81°. It occurs in a thin veinlet cutting a lavender-coloured Ti-bearing jadeitite. The veinlet includes irregularly-shaped aggregates composed of minute tabular crystals of itoigawaite up to 50 µm across and minute jadeite crystals with interstitial natrolite aggregates. Itoigawaite is considered to be crystallized from fluid during later stage activity of high-*P/T* metamorphism. The name is for the locality.

Keywords: itoigawaite, new mineral, strontium, jadeite, jadeitite, lawsonite, Renge metamorphic belt, Itoigawa-Ohmi district, Japan.

Introduction

THE Itoigawa-Ohmi district in the most eastern part of the Renge belt (Nishimura, 1998) is where the first jadeitite in Japan was found (Kawano, 1939; Ohmori, 1939).

In 1996 a bluish mineral on a lavendercoloured jadeitite (Fig. 1) was collected from the seashore of the Itoigawa-Ohmi district, Niigata Prefecture, Japan. It was submitted to the first author for identification by the fourth author. A preliminary microprobe analysis showed it to be a Sr-Al silicate possibly including elements with atomic numbers <9. Subsequent X-ray powder study proved the diffraction pattern of the mineral to be very close to that of the lawsonite group of minerals. The mineral data and the name have been approved by the Commission on New Mineral and Mineral Names of the

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International Mineralogical Association. The type specimens of itoigawaite are deposited at the National Science Museum, Tokyo, under the registered number NSM M-27872 and at Fossa Magna Museum, Itoigawa, Niigata, under the calalogue no. FMM00662.

Occurrence

The Itoigawa-Ohmi district of the Renge belt is characterized by the serpentinite melange with high-P/T type schists and various fragments of Palaeozoic accretionary complexes composed of greenstone, limestone, chert and mudstone, etc. (Nakajima *et al.*, 1992). Although no outcrops of jadeitite had been found to date, jadeitite is considered to be closely associated with serpentinite melange. Boulders and pebbles of jadeitite have been recognized in several riverbeds,

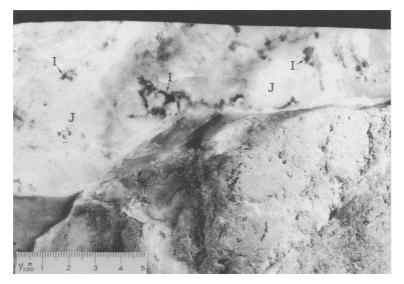


FIG. 1. Itoigawaite on jadeitite from the Itoigawa-Ohmi district. I = itoigawaite, J = jadeite.

including the River Himekawa running through the serpentine melange zone, and on the seashore of the Itoigawa-Ohmi district where they spread towards the west from the mouth of the River Himekawa, Itoigawa City. The itoigawaitebearing jadeitite was collected on the seashore of Oyashirazu, situated ~15 km WSW of Itoigawa Station (Fig. 2).

Three specimens of itoigawaite are recognized. Type itoigawaite occurs as a thin veinlet, <0.8 mm wide, cutting the jadeitite composed essentially of lavender-coloured and colourless jadeites with minor constituents of Sr-bearing pectolite, rutile, titanite and an undetermined Sr-Ti silicate. The veinlet includes outer fillings of long prismatic jadeite crystals which are elongated perpendicular to the wall of the veinlet, and inner fillings of irregularly-shaped aggregates composed of minute tabular crystals of itoigawaite, up to ~50 µm across, with interstial natrolite (Fig. 3). Jadeite is absent from the inner part of the veinlet. The specimen is characterized by the existence of Sr-rich minerals and euhedral jadeite crystals in the natrolite matrix (Fig. 4).

Physical and optical properties

Itoigawaite is blue with vitreous lustre, and is colourless in thin section. The cleavage is good in one direction. Fluorescence is not observed under short wavelength ultraviolet light. The Vickers microhardness is 550–680 kg mm⁻² (100 g load). It corresponds to 5–5.5 on Mohs' hardness scale. The density could not be measured because of the close association with natrolite. The calculated density is 3.37 g cm⁻³. It is optically biaxial positive with refractive indices $\alpha = 1.664(2)$, $\beta = 1.593(2)$, $\gamma = 1.688(2)$, and $2V(\text{calc.}) = 81^{\circ}$.

Chemistry

Chemical analyses were carried out using an energy dispersive X-ray spectrometer, Link QX 2000 (Table 1). The operating conditions included a beam diameter of $2-3 \mu m$, 15 kV and 10 nA probe current, and standard ZAF correction. The standards used were albite (for Na), Mg₂SiO₄ (for Mg), sillimanite (for Al), wollastonite (for Si and Ca), orthoclase (adularia) (for K), TiO₂ (for Ti), Cr₂O₃ (for Cr), tephroite (for Mn), Fe₂SiO₄ (for Fe) and celestine (for Sr). Chemical analyses and BEI observations show no compositional variation within single grains or between adjacent grains. X-ray diffraction patterns of the other lawsonite group minerals indicate that the difference between them and itoigawaite is water content. The water content of itoigawaite could not be measured because of the small quantity of sample available for analysis. The close association with natrolite adds to this

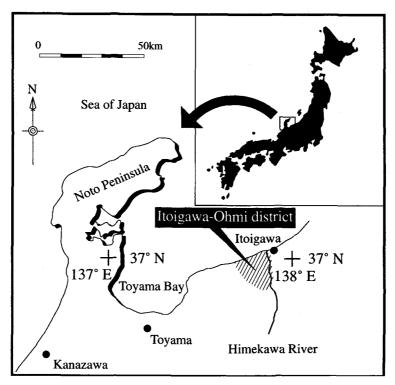


FIG. 2. Index map of the Itoigawa-Ohmi district, Niigata Prefecture, central Japan.

	1	2	3	4	5	6	7	Average
SiO ₂	33.13	33.08	33.15	33.00	33.19	32.55	32.74	32.98
TiO ₂	n.d.*	n.d.	n.d.	n.d.	0.89	0.86	n.d.	0.25
Al ₂ O ₂	28.17	27.83	27.88	27.73	27.23	26.84	28.00	27.67
FeO	n.d.	n.d.	n.d.	n.d.	0.37	0.33	n.d.	0.10
MgO	n.d.	n.d.	n.d.	0.27	0.27	0.26	n.d.	0.11
CaO	0.26	0.46	0.60	0.26	0.43	0.55	0.65	0.46
SrO	28.32	27.77	27.29	28.04	27.54	27.61	27.41	27.71
H ₂ O**	10.12	10.86	11.08	10.70	10.08	11.00	11.20	10.72
Total	100	100	100	100	100	100	100	100
Formula	e on the bas	is of O = 8						
Si	1.997	2.006	2.008	2.001	1.996	1.986	1.991	1.998
Ti					0.040	0.039		0.011
Al	2.000	1.989	1.990	1.981	1.931	1.930	2.006	1.975
Fe					0.019	0.017		0.005
Mg				0.024	0.025	0.024		0.010
Ca	0.016	0.030	0.039	0.017	0.028	0.036	0.042	0.300
Sr	0.990	0.976	0.959	0.986	0.961	0.977	0.966	0.973
Total	5.003	5.000	4.996	5,009	4.998	5.009	5.006	5.003

TABLE 1. Chemical analyses of itoigawaite

* not detected

** calculated by difference

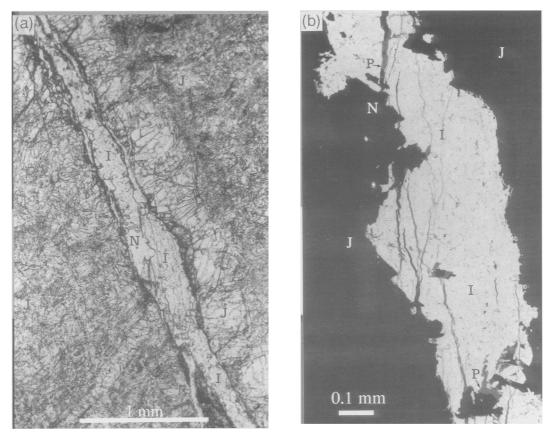


FIG. 3. (a) Photomicrograph (PPL) and (b) back-scattered electron image of the veinlet including itoigawaite. I = itoigawaite, N = natrolite, J = jadeite, P = Sr-bearing pectolite.

difficulty. Thus, the H₂O content of itoigawaite was estimated by difference. The average of seven analyses lead to the empirical formula, $(Sr_{0.97}Ca_{0.03}Mg_{0.02})_{\Sigma 1.02}(Al_{1.97}Ti_{0.04}Fe_{0.02})_{\Sigma 2.03}$ Si_{1.99}H_{3.89}O₁₀ which gives the ideal formula SrAl₂Si₂O₇(OH)₂·H₂O.

X-ray study

Because of the minute grainsize of the material studied, the X-ray powder diffraction pattern for itoigawaite was obtained using a Gandolfi camera, 114.6 mm in diameter, employing Ni-filtered Cu- $K\alpha_1$ radiation. Single crystal studies could not be carried out due to the small crystal size. As shown in Table 2, the notable coincidence of the patterns suggests that itoigawaite is isostructural with lawsonite and hennomartinite. The refined unit cell parameters are; a = 6.031(2), b = 8.945(2),

c = 13.219(4) Å. Therefore, the proposed space group is *Cmcm*, given the comparison with the lawsonite group.

Discussion

Itoigawaite is the Sr-Al member of the lawsonite group of sorosilicates of general formula $A^{2+}B_2^{3+}Si_2O_7(OH)_2 \cdot H_2O$. Features of the four known members of the group are summarized in Table 3. The cell parameters and density of itoigawaite are larger than those of lawsonite and are smaller than those of hennomartinite. These are attributed to the difference in the ionic radius and atomic weight between Sr and Ca, and Al and Mn, respectively.

The chemical composition for slawsonite, $SrAl_2Si_2O_8$, is close to that for itoigawaite. It is monoclinic, space group $P2_1/a$, in the specimen



FIG. 4. Euhedral crystals of jadeite in natrolite (PPL). J = jadeite, N = natrolite.

from Oregon, USA, corresponding to the Sr analogue of paracelsian (Griffen *et al.*, 1977), and is triclinic, space group *P*1, in that from Sarusaka, Japan (Tagai *et al.*, 1995). Although the ideal formula of itoigawaite is equivalent to that of slawsonite with two additional water molecules, the density of itoigawaite, 3.37 g cm^{-3} , is greater than that of slawsonite, 3.10 g cm^{-3} . The same relationship can be observed between lawsonite, 3.09 g cm^{-3} , and anorthite, 2.76 g cm^{-3} . The coexistence with jadeite, as well as the difference in density between itoigawaite and slawsonite, indicates that itoigawaite has a higher pressure paragenesis than slawsonite.

Itoigawaite occurs in a veinlet, cutting jadeitite (Fig. 2). The vein-filling constituents are prismatic jadeite crystals along the vein wall, with aggregates of itoigawaite and natrolite in the inner part. Thus, it is concluded that these minerals were crystallized from fluid intruding into a fracture in the jadeitite. The concentration of Sr in the fluid increased gradually, because the ionic radius of Sr is too large to be accepted in the M2 site of jadeite. In the latter stage, Sr was saturated, then itoigawaite and natrolite crystallized from the residual liquid. The absence of jadeite in the inner part of veinlet indicates that jadeite could not have crystallized at the latter stage. This may be attributed to the lowering of pressure at the latter stage and/or increasing activities of silica and water. Natrolite in association with itoigawaite is considered to have crystallized from the fluid instead of jadeite.

Kobayashi *et al.* (1987) described the occurrence of stronalsite in jadeitite from Mt Ohsa, Okayama, the western range of the Renge belt (Nishimura, 1998). This is the only description of Sr-rich minerals in jadeitite. During mineralogical and petrological research of jadeitites and omphacitites from the Itoigawa-Ohmi district, however, many species of Sr-rich minerals such as tausonite, Sr-apatite, itoigawaite, stronalsite, lamprophyllite, slawsonite, and the Sr-Zr analogue of perrierite etc. have been found (Miyajima *et al.*, 1998*a*,*b*,*c*,*d*). The discovery of these Sr-rich minerals is important in understanding the formation mechanism of jadeitite.

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	Itoigawaite*			Lawson	nite**	Hennomartinite***	
h k l	$d_{ m obs.}$	$d_{\rm calc.}$	Ι	d	Ι	d	Ι
0 0 2	6.60	6.61	vw	6.58	35		
110				4.84	60	5.149	30
111	4.68	4.68	S	4.57	30	4.804	86
021	4.26	4.24	vs	4.18	40	4.287	56
112	4.00	3.99	w	3.91	5		20
22^{-1}	3.70	3.70	m	3.66	60	3.725	26
113	3.31	3.31	vs	3.26	35	3.373	66
) 0 4	3.30	3.31		5.20	33	3.347	22
) 2 3			m			5.547	22
200	3.15	3.14	w	0.005	45		
				2.925	45	2 007	
114	2.75	{ 2.76	vs	2.726	70	2.807	82
202		<u></u> रे 2.74	•3	2.680	50	2.833	100
130	2.68	2.67	vvs	2.624	100	2.715	58
024						2.695	98
131	2.63	2.62	s	2.573	5	2.666	24
220		(2.50					
203	2.50	{ 2.49	s				
132		2.48		2.433	40	2.518	48
221	2.45	2.46	s	2.395	30		
222		(2.34		2.284	20	2.401	68
115	2.33	2.34	m	2.311	15	2.379	26
025		(2.28		2.254	35	2.575	20
040	2.27	2.24	m	2.190	15		
006		(2.24		2.190	15		
041	2.21	{ 2.20	m				
223	2.17	2.17	~	2.129	60	2.231	54
042	2.17	2.17	8			2.231	54
134	2.00	3 00		2.089	5	2 1 1 2	20
	2.09	2.08	vw	2.053	5	2.113	20
116				1.990	5	0.010	•
) 4 3	1.993	<i>{</i> 1.994	s	1.965	30	2.018	20
224	1.775	1.994	5				
311				1.884	15	2.009	20
135				1.852	5		
225				1.786	5		
206	1 7 (7	<i></i> {1.779		1.752	35	1.819	40
117	1.767	1.767	s			1.795	14
) 2 7	1.743	1.740	m	1.726	20		
242				1.697	15		
) 4 5				1.685	5		
314	1.687	1.687	w	1.657	5		
243	-1007	(1.663		2.007	-		
152	1.662	1.660	S	1.631	30		
226	1.002	1.653	3	1.626	30 40	1.687	38
332		1.055		1.626	40 10	1.007	20
) 4 6	1 540	1 560					
154	1.568	1.569	8	1.550	80		
154)60	1 400	1 401		1.501	10		
	1.490	1.491	W	1.464	40		

TABLE 2. X-ray powder diffraction data for itoig	gawaite, lawsonite and hennomartinte
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* Itoigawaite: a = 6.031(2), b = 8.945(2), c = 13.219 (4) Å (present study) ** Lawsonite: $a = 5.846 \pm 0.006$, $b = 8.788 \pm 0.008$, $c = 13.129 \pm 0.010$ Å (Davis and Pabst, 1960) *** Hennomartinite: a = 6.255(1), b = 9.034(1), c = 12.397(2) Å (Armbruster *et al.*, 1993)

A,B in formula Crystal system Space group Cell parameters	Itoigawaite* Sr, Al orthorhombic (Cmcm)	Lawsonite** Ca, Al orthorhombic (<i>Cmcm</i>)	Hennomartinite [†] Sr, Mn orthorhombic (<i>Cmcm</i>)	Noélbensonite ^{††} Ba, Mn orthorhombic (<i>Cmcm</i>)
a, Å	6.031(2)	5.846	6.255(1)	6.325(1)
b, Å	8.945(2)	8.788	9.034(1)	9.120(1)
<i>c</i> , A	13.219(4)	13.129	13.397(2)	13.618(1)
V, Å ³	713.1	674.5	757.03	785.5
Z	4	4	4	4
Colour	blue	colourless-pale blue	yellow-brown	dark brown
Hardness (Mohs)	5-5.5	6	~4	~4
$D_{\rm calc.}, {\rm g \ cm^{-3}}$	3.37	3.08 - 3.09	3.68	3.87
Colour in thin section	colourless	colourless	yellow-brown	orange yellow– brownish orange
Refractive indices				6
α	1.664(2)	1.663 - 1.655	n.d.	1.82
β	1.674(2)	1.672 - 1.675	n.d. $(n^3, 1.82)$	1.835
γ	1.668(2)	1.682 - 1.686	n.d.	1.85
2V, °	81 (calc.)	76-87	63	46

TABLE 3. The comparison of crystallographic, physical and optical data for the lawsonite group minerals, $A^{2+}B_2^{3+}Si_2O_7(OH)_2 \cdot H_2O$. Standard deviations given in parentheses

* Present study

**Davis and Pabst (1960)

[†] Armbruster et al. (1993)

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