Rengeite, $Sr_4ZrTi_4Si_4O_{22}$, a new mineral, the Sr-Zr analogue of perrierite from the Itoigawa-Ohmi district, Niigata Prefecture, central Japan

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ABSTRACT

Rengeite, Sr₄ZrTi₄Si₄O₂₂, is a new member of the perrierite-chevkinite group found in the jades from the Itoigawa-Ohmi district, central Japan. It is monoclinic, $P2_1/a$, a = 13.97(1), b = 5.675(7), c =11.98(1) Å, $\beta = 114.26(8)^{\circ}$, V = 866 Å³ and Z = 2. The six strongest lines in the X-ray powder diffraction pattern are 3.12 (s) (40-3), 3.05 (vvs) (31-3), 2.99 (vs) (311), 2.84 (s) (020), 2.74 (s) (004), 2.20 (s) (31-5). Electron microprobe analysis gave SiO₂ 22.58, TiO₂ 29.88, ZrO₂ 9.49, Nb₂O₅ 0.24, Ta2O5 0.07, Al2O3 0.20, FeO 0.10, CaO 0.43, SrO 34.32, BaO 0.13, La2O3 0.00, Ce2O3 0.38, Pr2O3 0.10, Nd₂O₃ 0.29, Sm₂O₃ 0.04, total 98.25 wt.%, corresponding to (Sr_{3.62}Ca_{0.08}Ce_{0.03}Nd_{0.02} $Ba_{0.01}Pr_{0.01})_{\Sigma 3.76} (Zr_{0.84}Ti_{0.09}Al_{0.04}Fe_{0.02}Nb_{0.02})_{\Sigma 1.01}Ti_{4.00}Si_{4.11}O_{22} \text{ on the basis of } O = 22. \text{ The unit$ cell parameters and chemical composition imply that rengeite is the Sr and Zr-analogue of perrierite or high- β analogue of strontiochevkinite. It is transparent, dark brown with adamantine lustre. Its streak is pale greenish brown, and no cleavage was observed. The hardness is $VHN_{100} 606-698 \text{ kg mm}^{-2}$ (Mohs 5–5.5). The calculated density is 4.12 g cm⁻³. It is strongly pleochroic from pale green to pale greenish brown where the *REE* contents are <1 wt.% and pale violet to greenish brown where the *REE* contents are between 3 and 10 wt.%. It occurs as anhedral grains in close association with titanite, zircon and tausonite in a pebble of blue titanian omphacite-jadeite rock from the seashore of Oyashirazu, Ohmi Town, in a boulder of lavender-coloured Ti-bearing jadeitite from the bed of the Kotaki-gawa river, Itoigawa City, and in a boulder of green jade from the bed of the Hime-kawa river, Itoigawa City, Niigata Prefecture, central Japan. Rengeite is considered to have crystallized by interaction between pre-existing minerals (rutile, anatase, titanite and zircon) and Sr-rich metamorphic fluid during later stage activity of high-P/T metamorphism. The name is for Mt. Renge near the locality and the Renge metamorphic belt where jadeitite deposits are found.

KEYWORDS: rengeite, new mineral, jadeite, perrierite, Renge metamorphic belt, Japan.

Introduction

THE Itoigawa-Ohmi district is the famous locality for jade in Japan (Kawano, 1939). The district is located in the easternmost part of the Renge belt (Nishimura, 1998) which is the oldest of the high-P/T metamorphic belts in the Japanese Islands and extends from northern Kyushu to the Itoigawa-Ohmi district, a distance of 850 km. The Renge belt is typically associated with meta-ophiolite sequences (470 to 340 Ma) including serpentinite. It is also characterized by ages of 330 to 280 Ma and the association of glaucophane-schist and epidote-amphibolite facies schists. During mineralogical and petrological research on jade from the Itoigawa-Ohmi district, we noticed anhedral grains of an interstitial mineral with high refractive indices and distinctive pleochroism

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were revealed in a pebble of blue jade. A preliminary microprobe analysis showed that the mineral is a REE-bearing Sr-Ti-Zr silicate, compositionally similar to strontiochevkinite found in fenites from the Paraná Basin carbonatite, Paraguay, by Haggerty and Mariano (1983). Subsequently, X-ray diffraction (XRD) study proved the β angle to be closer to that of perrierite than that of strontiochevkinite. Perrierite is dimorphous with chevkinite. The mineral data and the name have been approved by the IMA Commission on New Minerals and Mineral Names (no. 98-055). The type specimens of rengeite are deposited at the National Science Museum, Tokyo, under the registered number NSM M-27921 and at Fossa Magna Museum, Itoigawa, Niigata, under the catalogue No. FMM00715

Occurrence

The Itoigawa-Ohmi district of the Renge belt is characterized by a serpentinite melange with high-P/T type schists, jade, albitite, rodingite, metagabbro and hornblende zoisite rock, etc., and various fragments of Palaeozoic accretionary complexes composed of greenstone, limestone, chert and mudstone, etc. (Nakajima *et al.*, 1992). Rengeite was first found in the blue jade from the Oyashirazu shore, Sea of Japan, Ohmi Town. Subsequently, other occurrences of rengeite were found in lavender jade from the bed of the Kotakigawa river, Itoigawa City and the Oyashirazu shore, and in green jade from the bed of the Himekawa river, Itoigawa City (Fig. 1).

Rengeite in the blue jade

The rengeite-bearing blue jade (FMM00715) which was found at the seashore of Oyashirazu, is a small pebble, ~5 cm diameter. The specimen is a dense blue greyish rock. It includes prismatic crystals <5 mm long, composed of acicular dark bluish titanian omphacite and dark brownish sodic amphibole corresponding to eckermannite and nyböite. Under the microscope, the major components are jadeite, titanian omphacite and sodic amphibole associated with minor titanite, zircon, rutile and/or anatase, strontium-apatite, tausonite and rengeite. Rengeite as anhedral grains ~0.5 mm across occurs interstitially within jadeite grains (Fig. 2a,b). The physical and chemical data for rengeite were obtained from this specimen.

Rengeite in the lavender jade

The rengeite-bearing lavender jade (FMM00716), which was found at the Oyashirazu shore, is a boulder ~30 cm in diameter, and is white to greyish purple. Under the microscope, the specimen is composed of essentially pure jadeite and Ti-bearing jadeite with minor amounts of rutile, titanite, zircon, an undetermined Sr-Ti silicate, native copper and rengeite. The specimen is characterized by the existence of rounded brownish rutile grains <3 mm in diameter rimmed by titanite coronae. The rengeite in this specimen is closely associated with rutile, titanite and zircon (Fig. 2*c*,*d*).

The other rengeite-bearing lavender jade (FMM01309) was found in the bed of the Kotaki-gawa river. It is a boulder ~50 cm in diameter, submitted by Mrs K. Ito of Kotaki Bussan Co. Under the microscope, it is composed of essentially pure jadeite, Tibearing jadeite and natrolite with minor constituents of lamprophyllite, titanite, zircon, rutile, tausonite, undetermined Sr-Ti silicate and rengeite. The specimen is characterized by the existence of nearly euhedral jadeite crystals in the natrolite matrix. The rengeite in the lavender jade comprises a fan-shaped aggregate of prismatic crystals <0.3 mm long with euhedral jadeite crystals (Fig. 2*e*).

Rengeite in the green jade

The rengeite-bearing green jade (FMM01310) was found in the bed of the Hime-kawa river. It was given to the first author by Mrs K. Ito for study of the jade. The specimen is a translucent greyish green boulder ~50 cm in diameter. Under the microscope, it is composed of essentially pure jadeite and omphacite with minor titanite, zircon and rengeite. The rengeite in the green jade occurs as elongate aggregates (~9 mm) of anhedral crystals in close association with titanite (Fig. 2f). The microhardness data for rengeite were obtained from this specimen.

Physical and optical properties

The rengeite is transparent dark greenish brown with adamantine lustre. It shows a strong pleochroism; from pale green to pale greenish brown in *REE*-poor areas ($\Sigma REE < 1 \text{ wt.\%}$) and pale violet to greenish brown in *REE*-rich areas ($\Sigma REE 3 \text{ to } 10 \text{ wt.\%}$). These different areas may coexist in a single grain and the boundary



FIG. 1. Index map of the Itoigawa-Ohmi district (modified from Komatsu, 1990).

between them may be irregular (Fig. 2*b*). No cleavage was observed. The Vickers microhardness is $606-698 \text{ kg mm}^{-2}$ (100 g load), corresponding to 5-5.5 on the Mohs scale. The density could not be measured due to the lack of material, but the calculated density is 4.12 g cm^{-3} . There is no fluorescence in the either long- or short-wave ultraviolet radiation. Rengeite is optically biaxial positive. The refractive indices are higher than titanite, though they could not be measured because they are too high for normal liquid.

Chemistry

An electron microprobe using wavelength dispersion methods (JEOL JXA-8800, beam diameter 2 to 3 μ m, 15 kV accelerating voltage, 20 nA probe current, and standard ZAF correction) was used for chemical analysis of rengeite. The standards used were sillimanite (Al), wollastonite (Si and Ca), TiO₂ (Ti), Zr (Zr), Fe₂SiO₄ (Fe), Nb (Nb), Ta (Ta), SrF₂ (Sr), BaF₂ (Ba) and *REE*P₅O₁₄ (*REE*). Backscattered electron images (Fig. 2*b*) and chemical analysis demonstrate that the



FIG. 2. (*a*) Photomicrograph (PPL) of rengeite shows interstitial crystals between subhedral jadeite in the blue jade (FMM00715) from the Oyashirazu seashore. (*b*) Back-scattered electron (BSE) image of rengeite shows compositional heterogenity of *REE* within the grains in the blue jade (FMM00715) from the Oyashirazu seashore. (*c*) BSE image of rengeite shows its close association with titanite and rutile in the lavender jade (FMM00716) from the Oyashirazu seashore. (*d*) BSE image of rengeite shows its close association with titanite and rutile in the lavender jade (FMM00716) from the Oyashirazu seashore. (*e*) Photomicrograph (PPL) of rengeite shows fan-shaped aggregates with jadeite and natrolite in the lavender jade (FMM01309) from the riverbed of the Kotaki-gawa river. (*f*) BSE image of rengeite shows its close association with titanite in the green jade (FMM01310) from the bed of the Hime-kawa river. Abbreviations: Jad = jadeite, Nat = natrolite, Ren = rengeite, Rtl = rutile, Ttn = titanite and Ust = undetermined Sr-Ti silicate.

composition of rengeite varies from grain to grain and within individual grains, mainly in the total *REE* contents. The average of six measurements of *REE*-poor rengeite (Table 1) leads to the empirical formula,

$(Sr_{3.62}Ca_{0.08}Ce_{0.03}Nd_{0.02}\ Ba_{0.01}Pr_{0.01})_{\Sigma 3.76}$

 $(Zr_{0.84}Ti_{0.09}Al_{0.04} Fe_{0.02} Nb_{0.02})_{\Sigma 1.01}Ti_{4.00}Si_{4.11}O_{22}$

on the basis of O = 22. The average of 3 measurements of *REE*-rich rengeite leads to the empirical formula,

 $\begin{array}{l} (Sr_{3.06}Ce_{0.33}La_{0.19}Ca_{0.10}Nd_{0.09}Pr_{0.04}Ba_{0.01})_{\Sigma 3.83} \\ Zr_{0.92}(Ti_{3.31}Al_{0.26}Fe_{0.19}Nb_{0.14}Ta_{0.09})_{\Sigma 3.99}Si_{4.11}O_{22} \end{array}$

on the basis of O=22. Consequently, the ideal formula is $Sr_4ZrTi_4Si_4O_{22}$.

The polymorphs perrierite and chevkinite have the ideal stoichiometry $A_4^{3+}B^{2+}C_2^{3+}\text{Ti}_2\text{Si}_4\text{O}_{22}$ (Ito, 1967) where A = REE, B = (Fe, Mg), C = (Fe, Al). They are distinguished by their different monoclinic β angle (113° and 100° respectively), associated with different cation–oxygen bond length patterns in their structures (Calvo and Faggiani, 1974): a rare example of bond length isomerism.

Titanium is an essential element in the perrierite-chevkinite group and the reported range of TiO₂ is 15 to 23 wt.%, corresponding to 2.35 to 3.47 titanium cations per formula unit (p.f.u.: O = 22). However, for rengeite these reach 30 wt.% or 4.09 p.f.u. *REE*₂O₃ is also assumed to be essential at 40 wt.%, corresponding to 2.77 to 3.82 p.f.u. But these reach only 10 wt.% or 0.65 p.f.u. for rengeite. Iron is also rich in the group (5 to 18 wt.% FeO, corresponding 0.86 to 3.13 p.f.u.). However, FeO is <2 wt.% (0.02 to 0.19 p.f.u.) for rengeite. The highest SrO content in the perrierite–chevkinite group is for strontio-chevkinite (20.48 wt.% or 2.30 p.f.u.) from fenite in the Paraná Basin carbonatite, Paraguay

TABLE 1. Representative chemical compositions for rengeite.

	RE	E-poor reng	geite		RE	E-rich renge	ite
	Wt.%	cation nu	mber $O = 2$.2	Wt.%	cation num	ber $O = 22$
SiO_2	22.58	Si	4.11	SiO_2	22.04	Si	4.14
TiO ₂	29.88	Ti	4.09	TiO_2	23.60	Ti	3.33
ZrO_2	9.49	Zr	0.84	ZrO_2	10.11	Zr	0.93
Nb_2O_5	0.24	Nb	0.02	Nb_2O_5	1.33	Nb	0.11
Ta ₂ O ₅	0.07	Та	0.00	Ta ₂ O ₅	0.01	Та	0.00
Al_2O_3	0.20	Al	0.04	Al_2O_3	1.70	Al	0.38
FeO	0.10	Fe	0.02	FeO	1.19	Fe	0.19
MgO	0.00	Mg	0.00	MgO	0.00	Mg	0.00
CaO	0.43	Ca	0.08	CaO	0.52	Ca	0.11
SrO	34.32	Sr	3.62	SrO	28.24	Sr	3.07
BaO	0.13	Ba	0.01	BaO	0.16	Ва	0.01
La_2O_3	0.00	La	0.00	La_2O_3	2.73	La	0.19
Ce_2O_3	0.38	Ce	0.03	Ce_2O_3	4.81	Ce	0.33
Pr_2O_3	0.10	Pr	0.01	Pr_2O_3	0.63	Pr	0.04
Nd_2O_3	0.29	Nd	0.02	Nd_2O_3	1.40	Nd	0.09
Sm_2O_3	0.04	Sm	0.00	Sm_2O_3	0.06	Sm	0.00
Total	98.25	Total	12.89	Total	98.53	Total	12.92
REE-poo	or rengeite						
A	l site:	(Sr _{3.62} 0	Ca _{0.08} Ce _{0.03} 1	Nd _{0.02} Ba _{0.01} Pr _{0.0}	$(1)_{\Sigma 3.76}$		
E	site:	(Zr _{0.84})	Гі _{0.09} Аl _{0.04} F	$e_{0.02}Nb_{0.02})_{\Sigma 1.01}$			
C	C site:	Ti _{2.00}					
REE-ricl	n rengeite						
A	l site:	(Sr _{3.07} 0	$Ce_{0.33}La_{0.19}C$	$Ca_{0.11}Nd_{0.09}Pr_{0.0}$	$_{04}Ba_{0.01})_{\Sigma}$	3.84	
E	3 site:	(Zr _{0.93})	Γi _{0.01}) _{Σ0.94}				
C	C site:	(Ti _{1.32} /	Al _{0.38} Fe _{0.19} N	$b_{0.11})_{\Sigma 2.00}$			

(Haggerty and Mariano, 1983). Strontium contents are generally low in perrierite, and 7.73 wt.% as maximum SrO content, corresponding to 0.87 p.f.u., has been reported for the material from syenite pegmatites in the Burpala alkali massif, North Baikal, Russia (Portnov, 1964). In rengeite, the SrO content reaches 34 wt.% which corresponds 3.62 p.f.u. Thus strontium contents and the occupancy in the Asite of rengeite far exceed those in the perrieritechevkinite group. Zirconium was detected in strontian perrierite (4.85 wt.% ZrO2 or 0.46 p.f.u.) from Baikal (Portnov, 1964), in chevkinite (1.17 wt.% ZrO₂ or 0.11 p.f.u.) from California (McDowell, 1979) and in strontiochevkinite (10.60 wt.% ZrO₂ or 1.00 p.f.u.) from the Paraná Basin (Haggerty and Mariano, 1983). In rengeite, the ZrO contents reach 9.49 wt.% or 0.84 p.f.u. In summary, the chemical composition of rengeite is characterized by very high Sr, Ti and Zr, and very low *REE* and Fe compared to other members in the perrierite–chevkinite group.

X-ray study

The X-ray powder diffraction pattern for rengeite was obtained using a Gandolfi camera of 114.6 mm diameter employing Ni-filtered Cu-K α radiation (Table 2). Single crystal studies were made by precession and a 4-circle diffractometer. Because rengeite is very poor in uranium and thorium, it is non-metamict and gives excellent powder data from unheated material. The refined unit-cell parameters are; a= 13.97(1), b = 5.675(7), c = 11.98(1) Å, β = 114.26(8)° and V = 866 Å³. It is monoclinic, space group $P2_1/a$ and Z = 2. Long-exposure precession photographs show the very weak superstructure

TABLE 2. X-ray powder diffraction data for rengeite.

k	l	$d_{\rm obs}$	d_{calc}	Ι	h	k	l	$d_{\rm obs}$	$d_{\rm cal}$	I _{obs}
0	1	11.30	10.95	VW	4	2	5	1.78	1.78	w
0	1	6.97	6.87	VVW	<u></u> 6	2	3		1.78	
0	0	6.45	6.38	VW	<u></u> 6	2	1	1.76	1.77	VW
0	2	5.49	5.47	W	6	0	2	1.74	1.75	VW
0	2	5.24	5.38	VW	4	0	4		1.75	
1	1	5.04	5.02	W	$\overline{8}$	0	3		1.75	
0	1	4.77	4.73	VVW	$\overline{8}$	0	2	1.71	1.73	VVW
1	2	4.16	4.12	m	0	2	5		1.73	
0	3	3.98	3.94	W	3	3	2		1.73	
0	3	3.69	3.65	W	$\overline{8}$	0	1	1.68	1.68	W
1	1	3.62	3.60	W	3	3	3	1.67	1.67	VW
1	2	3.52	3.48	W	3	3	1	1.64	1.66	W
1	2	3.45	3.44	W	$\overline{8}$	0	5		1.65	
0	0	3.21	3.19	m	7	1	1	1.62	1.62	W
0	3	3.13	3.12	S	3	1	5		1.62	
1	3	3.06	3.03	VVS	7	1	6	1.61	1.61	VW
0	4	3.00	3.00	VS	5	1	7		1.60	
1	1		2.98		6	2	1		1.60	
2	0	2.86	2.84	S	5	3	2	1.57	1.56	VVW
1	3		2.77		0	0	7		1.56	
0	1	2.79	2.77	m	$\overline{8}$	0	6		1.56	
2	1		2.74		4	0	8	1.50	1.50	vvwb
0	4	2.75	2.74	W	8	0	1	1.49	1.49	vvwb
0	4	2.71	2.69	W	7	1	7		1.48	
2	1	2.63	2.62	VW	3	3	5		1.48	
1	4	2.60	2.61	VVW	$\overline{8}$	0	7	1.45	1.45	W
2	0		2.59		2	2	7		1.45	
2	2	2.55	2.52	VW	$\overline{8}$	2	1		1.44	
2	2		2.51		1	1	7	1.43	1.43	VW
1	2	2.51	2.50	m	$\overline{8}$	2	5		1.43	
2	1	2.44	2.43	W	0	4	0	1.42	1.42	W
	$\begin{array}{c} k \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 1 \\ 0 \\ 1 \\ 0 \\ 1 \\ 0 \\ 1 \\ 0 \\ 1 \\ 2 \\ 1 \\ 0 \\ 2 \\ 2 \\ 2 \\ 1 \\ 2 \\ 2 \\ 1 \\ 2 \\ 2 \\ 1 \\ 2 \\ 2$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	k l d_{obs} d_{calc} I h k l 0 1 11.30 10.95 vw $\overline{4}$ 2 5 0 1 6.97 6.87 vvw $\overline{6}$ 2 3 0 0 6.45 6.38 vw $\overline{6}$ 2 1 0 2 5.49 5.47 w 6 0 2 0 2 5.24 5.38 vw $\overline{8}$ 0 3 0 1 4.77 4.73 vvw $\overline{8}$ 0 2 1 2 4.16 4.12 m 0 2 5 0 3 3.98 3.94 w $\overline{3}$ 3 3 1 1 1 3.62 3.60 w $\overline{3}$ 3 3 1 1 1 3.62 3.60 w $\overline{3}$ 3 3 1 1 1 3.62 3.60 w $\overline{3}$ 3 3<	k l d_{obs} d_{calc} I h k l d_{obs} 0 1 11.30 10.95 vw $\overline{4}$ 2 5 1.78 0 1 6.97 6.87 vvw $\overline{6}$ 2 3 0 0 6.45 6.38 vw $\overline{6}$ 2 1 1.76 0 2 5.24 5.38 vw 4 0 4 1 1 5.04 5.02 w $\overline{8}$ 0 3 0 0 1 4.77 4.73 vvw $\overline{8}$ 0 2 1.71 1 2 4.16 4.12 m 0 2 5 0 3 3.98 3.94 w $\overline{3}$ 3 1 1.68 1 1 3.62 3.60 w $\overline{3}$ 3 1 1.64 1 2 3.45 3.44 w $\overline{8}$ 0 5 1 1 1	k l d_{obs} d_{calc} I h k l d_{obs} d_{cal} 0 1 11.30 10.95 vw $\overline{4}$ 2 5 1.78 1.78 0 1 6.97 6.87 vvw $\overline{6}$ 2 1 1.76 1.77 0 2 5.49 5.47 w 6 0 2 1.74 1.75 0 2 5.24 5.38 vw 4 0 4 1.75 1 1 5.04 5.02 w $\overline{8}$ 0 2 1.71 1.73 0 1 4.77 4.73 vvw $\overline{8}$ 0 2 1.71 1.73 0 3 3.98 3.94 w $\overline{3}$ 3 1.67 1.67 1 2 4.16 4.12 m 0 2 5 1.73 0 3 3.69 3.65 w $\overline{8}$ 0 1 1.68 1.66 1

h k	: 1	$d_{\rm obs}$	$d_{\rm calc}$	Ι	h	k	l	$d_{\rm obs}$	$d_{\rm cal}$	$I_{\rm obs}$
4 0	2	2.38	2.37	vvw	5	3	2	1.38	1.38	W
ō 0	2	2.34	2.33	VW	6	2	3		1.38	
4 0	5	2.30	2.30	m	9	1	0	1.37	1.37	vwb
ō 0	1	2.27	2.27	W	$\bar{10}$	0	2		1.37	
0 2	3		2.24		7	3	2		1.37	
3 1	5	2.20	2.20	VS	7	3	3		1.37	
4 2	1		2.19		0	0	8		1.37	
4 2	2	2.17	2.19	VW	$\overline{8}$	2	6		1.37	
ō 0	4		2.16		5	3	6	1.34	1.34	VW
6 0	0		2.13		10	0	6		1.33	
4 2	0	2.13	2.12	VW	4	4	0	1.30	1.30	W
4 2	3	2.11	2.10	VW	ē	2	8		1.29	
ō 0	5		1.98		4	4	3		1.29	
2 0	6	1.99	1.98	VW	6	2	4	1.27	1.27	VW
4 0	6		1.97		3	3	7		1.27	
0 2	4	1.97	1.97	W	7	3	1	1.26	1.26	vwb
2 2	3		1.96		0	4	4		1.26	
6 0	1	1.95	1.94	VVW	3	3	5		1.26	
5 1	2	1.91	1.90	VW	5	3	7	1.25	1.25	VW
71	2	1.89	1.88	W	$\overline{8}$	0	9	1.23	1.24	VW
71	3		1.88		11	1	4		1.24	
<u>2</u> 2	5	1.83	1.83	VW	0	2	8	1.22	1.23	VVW
71	1		1.83		11	1	5		1.23	
71	4	1.83	1.82	VW	11	1	2	1.21	1.21	VVW
Ī 1	6		1.82		6	4	2		1.21	
51	6	1.80	1.80	W	4	4	5		1.21	
ō 0	6	1.79	1.79	VW	4	2	9		1.21	
					11	1	6		1.21	

TABLE 2 (contd).

reflections corresponding to $5 \times c$ axis. The reported unit-cell parameters for members in the perrierite–chevkinite group are given in Table 3. The average unit-cell volume for chevkinite, perrierite and strontiochevkinite are 829, 842 and 844 Å³, respectively. That for rengeite ($V = 866 \text{ Å}^3$) is the largest in the group. It may be attributed to abundant Sr²⁺ with larger ionic radius in comparison to lanthanides. The crystal structure analysis is currently being performed by the authors.

Discussion

Site occupancy of cations

The crystal structures were analysed for synthetic compounds using the perrierite and chevkinite structures devised by Calvo and Faggiani (1974). According to them, the *A* site can be divided into

two crystallographic sites; the A(1) site has eightto nine-fold coordination and the A(2) site has nine-fold coordination. In synthetic $La_4Mg_2Ti_3Si_4O_{22}$ with perrierite structure, the B and C sites are octahedral sites. The B site is the largest octahedral site which is completely occupied by Mg^{2+} . The C site is divided into C(1) and C(2) sites; the C(1) site is the second smallest octahedral site and is occupied by Ti⁴⁺ and Mg^{2+} , and the C(2) site is the smallest octahedral site, almost completely occupied by Ti^{4+} . The ionic radius of Zr^{4+} in six-fold coordination is the same as that of Mg²⁺ (0.72 Å as determined by Shannon and Prewitt, 1969). Thus, it is very likely that Zr^{4+} occupies the B site rather than the C(1) site in rengeite. In the case of strontiochevkinite, (Sr₂ Ca_{0.5} $REE_{1.5})_{\Sigma4}$ (Fe²⁺_{0.5} Fe³⁺_{0.5})_{$\Sigma1$}(Ti₃Zr₁)_{$\Sigma4$}Si₄O₂₂, however, Fe and Zr occupy the B and C sites,

Locality	a (Å)	b (Å)	<i>c</i> (Å)	β (°)	V (Å ³)	Reference	Remarks
Rengeite Itoigawa-Ohmi, Japan	13.97	5.68	11.98	114.26	866	This study	unheated
Perrierite Nettuno, Italy Oslo region, Norway Nebraska, USA Viroinia IISA	13.59 13.70 13.59	5.61 5.66 5.62 5.62	11.61 11.83 11.73	113.28 113.79 113.95 113.5	813 839 819 837	Bonatti (1959) Segalstad and Larsen (1978) Izett and Wilcox (1968) Mitchell (1966)	unheated heated unheated
North Markel, Russia Urals, Russia La ₄ Mg ₂ Ti ₃ Si ₄ O ₂₂ average of perrierite	13.95 13.52 13.78 13.68	5.62 5.65 5.67 5.67	11.70 11.71 11.78 11.73	114.53 113.3 113.7 113.7	834 822 823 829	Portnov (1964) Ito (1967) Ito (1967)	unheated recrystalized synthetic
Chevkinite Cape Ashizuri, Japan Oslo region, Norway Oslo region, Norway Oslo region, Norway Kansas, USA Utah, USA New Mexico, USA Virginia, USA New Hampshire, USA Madagascar La ₄ Fe ₂ Ti ₃ Si ₄ O ₂₂ average of chevkinite	13.46 13.43 13.43 13.44 13.44 13.37 13.37 13.32 13.32 13.44 13.26 13.44 13.26 13.42	5.775 5.7755 5.7755 5.7755 5.7755 5.7755 5.7755 5.7755 5.77555 5.77555 5.7755555555	11.35 11.07 11.07 11.09 11.28 11.28 11.24 11.21 11.10 11.10	$\begin{array}{c} 100.86\\ 100.58\\ 100.53\\ 100.53\\ 100.72\\ 100.72\\ 100.72\\ 100.7\\ 100.7\\ 100.69\end{array}$	852 837 837 837 838 837 837 837 840 840 846 840 840 840 840 840	Imaoka and Nakashima (1994) Segalstad and Larsen (1978) Segalstad and Larsen (1978) Segalstad and Larsen (1978) Izett and Wilcox (1968) Izett and Wilcox (1968) Mitchell (1966) Jaffe <i>et al.</i> (1956) Ito (1967) Ito (1967)	unheated heated heated heated unheated unheated unheated heated recrystalized synthetic
Strontiochevkinite Sarambi, Paraguay	13.56	5.70	11.10	100.32	844	Haggerty and Mariano (1983)	unheated

TABLE 3. Unit-cell parameters for rengeite, perrierite, chevkinite and strontiochevkinite.

respectively (Haggerty and Mariano, 1983). Haggerty and Mariano (1983) did not refine the structure of strontiochevkinite. They have grouped the B/C cations in order of charge rather than intending to specify site occupancies. Their idealized formula can be rearranged to put Zr on B:

 $\begin{array}{l} (Sr_2Ca_{0.5}\textit{REE}_{1.5})_{\Sigma 4}(Zr)_{\Sigma 1} \\ (Fe_{0.5}^{2+}\ Fe_{0.5}^{3+}Ti)_{\Sigma 2}Ti_2Si_4O_{22} \\ This is related to ideal Fe^{2+}-chevkinite by: \\ (Sr,Ca)_2Zr - \textit{REE}_2Fe^{2+} \\ (Sr,Ca)_{0.5}Ti_{0.5} - \textit{REE}_{0.5}Fe_{0.5}^{3+} \\ Fe_{0.5}^{2+}Ti_{0.5} - Fe^{3+} \end{array}$

The first two of these substitutions are basically the same as those relating perrierite and rengeite, implying that rengeite is indeed the high- β analogue of strontiochevkinite. In the case of synthetic La₄Fe(Fe,Ti)Ti₂Si₄O₂₂ with the chevkinite structure (Ito, 1967), Fe occupies both the Band C sites. It therefore appears that whether the B site is occupied by Fe or Zr depends on the overall chemical composition. The ideal formula of the perrierite-chevkinite group has been proposed as $A_4^{3+}B^{2+}C_2^{3+}\text{Ti}_2\text{Si}_4\text{O}_{22}$ (Ito, 1967). Using to the same format, the ideal formula for rengeite can be written as Sr₄ZrTi₂Ti₂Si₄O₂₂. The *A*, *B* and *C* sites in rengeite are occupied by Sr²⁺, Zr⁴⁺ and Ti⁴⁺ ions instead of trivalent, divalent and trivalent cations, respectively. However, the charge is balanced within these three sites.

Paragenesis

In the blue and the lavender jades from Ovashirazu, rengeite occurs as anhedral and interstitial crystals between jadeite (Fig. 2a,b,c), suggesting that rengeite was formed after the crystallization of jadeite. However, in the lavender jade from the Kotaki-gawa river, rengeite shows fan-shaped aggregates with euhedral to subhedral jadeite in the natrolite matrix (Fig. 2d). This suggests that rengeite was able to form at the same stage of the crystallization of jadeite. In both cases rengeite is closely associated with rutile, titanite and zircon (Figs 2c, d, f), which may have been the sources for the Ti and Zr of rengeite, since these elements may be relatively immobile during metamorphism (Cann, 1970; Coish, 1977; Wood et al., 1976; Tatsumi and Kogiso, 1995). Rengeite is considered to have crystallized by interaction between pre-existing minerals (rutile, anatase, titanite and zircon) and Sr-rich metamorphic fluid during later stage activity of high-P/T metamorphism.

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