Cascandite and jervisite, two new scandium silicates from Baveno, Italy

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Abstract

Two new silicate minerals, cascandite and jervisite, were found as small crystals in a geode from Cava Diverio, Baveno, Italy.

Cascandite Ca(Sc_{0.74}Mg_{0.02}Al_{0.01}Fe²⁺_{0.22})(Na_{0.01}Ca_{0.04}Mn_{0.10} $\square_{0.85}$)Si₃O_{8.02}(OH) or ideally CaScSi₃O₈OH, has triclinic symmetry, space group *P*I with lattice dimensions *a* = 7.529(11)Å, *b* = 7.051(12)Å, *c* = 6.755(9)Å, *a* = 92°7′(5), *β* = 93°40′(5), *γ* = 104°39′(5). The X-ray powder diffraction pattern has the strongest reflections at *d* = 3.62(m)(200), 3.10(m) (201,121,012), 2.968(m)(021,102,012), 2.821(s)(120), 1.429(m). Cascandite is structurally related to the wollastonite-pectolite-serandite group of minerals.

Jervisite $(Na_{0.43}Ca_{0.31}Fe_{0.14}^{2+}\Box_{0.12})(Sc_{0.66}Fe_{0.15}^{2+}Mg_{0.19})Si_2O_6$ has monoclinic symmetry, space group C2/c with lattice dimensions a = 9.853(11)Å, b = 9.042(10)Å, c = 5.312(7)Å, $\beta = 106^{\circ}37'(7)$. The X-ray powder diffraction pattern has the strongest reflections at d = 6.51(w)(110), $4.51(w)(021,\overline{1}11)$, $3.038(s)(\overline{2}21)$, 2.979(m)(310), 2.543 (m)(221,002), $1.647(m)(\overline{5}31,440)$. Jervisite is a scandium pyroxene and a natural analogue of the synthetic phase NaScSi₂O₆.

Introduction

We have recently studied some small crystals that occur in the granite from Baveno, Italy. The sample was obtained through the kindness of Dr. Enzo De Michele of the Museo Civico di Storia Naturale, Milan. The crystals are platy in habit (Fig. 1), light pink in color, and are associated with quartz, orthoclase and albite. The results of a qualitative energy dispersive analysis, which showed scandium as a major component, led to further study. A subsequent electron microprobe analysis, made on various crystal fragments, clearly indicated the presence of two different phases, both rich in scandium, but differing in sodium and calcium content.

We then reexamined the sample and found additional platelets that were light green in color. The results of the X-ray crystallographic study, together with the microprobe analytical data and the results of the subsequent crystal structure analyses, clearly indicated that the pale pink and the light green platelets corresponded to two distinct mineral 0003-004X/82/0506-0599\$02.00 phases, a scandium pyroxenoid and a scandium pyroxene, respectively. For these minerals we proposed the names cascandite from the chemical composition and jervisite in honor of William P. Jervis, who was curator of the Museo Industriale Italiano di Torino and author of the book "I Tesori sotterranei dell' Italia" on italian minerals. The new minerals and their names were approved by the I.M.A. Commission on New Minerals and Mineral Names.

X-ray crystallography

Rotation and Weissenberg photographs indicate that cascandite is triclinic, with unit cell parameters $a \approx 7.5$ Å, $b \approx 7.1$ Å, $c \approx 6.8$ Å, $\alpha \approx 92^{\circ}$, $\beta \approx 93^{\circ}$, $\gamma \approx$ 104°, space group P1 or P1̄; whereas jervisite is monoclinic with unit cell parameters $a \approx 9.8$ Å, $b \approx$ 9.0Å, $c \approx 5.3$ Å, $\beta \approx 107^{\circ}$, with space group C2/c or Cc, on the basis of the systematic absences (*hkl* absent for h + k = 2n + 1, *h0l* absent for l = 2n +1). Space groups P1̄ and C2/c, for cascandite and

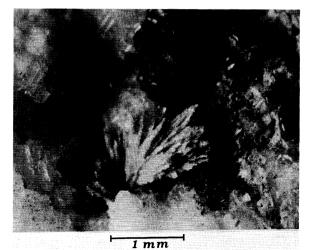


Fig. 1. Tuft in the center of the photograph is composed of platy crystals of iervisite and cascandite.

jervisite, respectively, were subsequently confirmed by the structure analysis.

The crystals of cascandite are pale pink platelets with vitreous luster, elongated along [100] and flattened parallel to {001}, with good {100} and {001} cleavages. The dimensions of the platelets are up to $0.20 \times 0.08 \times 0.02$ mm, with observed forms {001} {100}, {120}, and {530} as shown in Figure 2. The only optical properties measured were n_1 (= 1.663) and n_2 (= 1.684) on (001).

The crystals of jervisite are light green in color, vitreous in luster, and have perfect (110) cleavage. Their habit and dimensions are similar to those of cascandite.

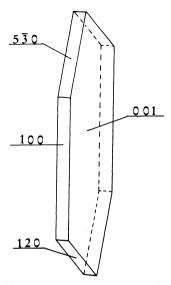


Fig. 2. Typical habit of cascandite.

Table 1 gives the X-ray powder diffraction pattern for cascandite. Because of the small quantity of available material, we obtained the powder pattern by the Gandolfi technique with Ni-filtered Cu*Ka* radiation ($\lambda = 1.5418$ Å), using a small crystal previously examined by single crystal methods. The same crystal was used to collect the intensity data for structure refinement (Mellini and Merlino, 1982). In addition, single crystal intensity data offered a check on the indexing of the powder pattern lines.

Table 2 compares the X-ray powder diffraction pattern of jervisite and the synthetic scandium analogue of aegirine, which was synthesized by Ito and Frondel (1968). The powder patterns, obtained by means of a Gandolfi camera with crystals previously examined with rotation and Weissenberg pho-

Table 1. X-ray powder diffraction pattern of cascandite

Cascandite			Cascandite		
d(A)	hk1	I	d(A)	hk1	I
7.22	100	Ψ.	2.249	122	w
				003	w
6.75	001	w			
4.46	110	w	2.220	220	w
3.84	111	w	2.190	103	w
				131	
3.62	200	m			
	020			321	
3.39	002	w	2.158	013	w
3.25	211	w		221	
3.14	102	w	2.128	321	
				310	w
	201				
3.10	121	m	2.060	221	w
	012		2.040	302	w
	021		1.779		w
2.968	102	m	1.717		w
	012		1.688		w
2.924	112	vw	1.642		w
2.821	120	s	1.623		w
2.753	211	vw	1.595		w
2.675	121	w	1.564		w
2.595	211	w	1.524		w
	112		1.447		w
2.421	300	w	1.429		m
2.337	301	w	1.398		w
	022		1.331		w
2.300	212	w	1.296		w
	311		1.257		w

600

j	ervisite		NaScSi ₂	⁰ 6 ^{syn}	je	ervisite		NaScSi	2 ⁰ 6 syn
d(A)	hk1	I	d(A)	I	d (A)	hk l	I	d(A)	I
6.51	110	w	6.52	m		312		1.714	vw
4.51	021	w	4.52	m	1.689	042	vw	1.697	m
4.51	111		4.52	ш	1.647	531	m	1.645	w
3.68	111		3.68	w		440		1.631	w
3.389	021	w	3.39	w	1.573	600	w	1.579	w
3.255	220	w	3.25	w		351		1.564	vw
3.038	221	S	3.045	vs		602		1.549	vw
2.979	310	m	2.952	m		621			••
2.607	ī31	w	2.607	m	1.528	402	w	1.525	w
2.543	221	m	2.523	s		332		1.511	vw
	002			-		060			••
2.304	400	vw	2.329	2.329 w		622		1.471	vw
	311		2.327 *			620		/1	••
2.233	112	vw	2.234	W	1.435	260	w	1.435	w
	022					351			
2.161	330	vw	2.169	mw		152		1.425	w
	331					531			
2.132	421	vw	2.135	w		243		1.397	vw
2.067	041	vw	2.068	mw		223			
	202		2.009	vw		261			
	132					712		1.352	w
	241		1.984	vw		533			
1.922	511	vw	1.916	vw	1.336	710	w	1.328	w
	422		1.876	vw	2.000	621	-	1.520	-
	222				1.304	314	w	1.301	w
	510		1.839	vw	1.259	352	w	1.257	w
	132								
1.778	150	w	1.778	mv					
	421		-						

Table 2. X-ray powder diffraction pattern of jervisite and its synthetic analogue

tographs, were indexed using single crystal diffractometer data as a check.

The unit cell parameters for cascandite and jervisite were refined by a least squares method using the powder pattern lines and are reported in Table 3, together with the unit cell parameters of synthetic NaScSi₂O₆, as given by Hawthorne and Grundy (1973).

Chemical composition

Two crystal fragments, identified as cascandite and jervisite by X-ray single crystal methods, were analyzed by electron microprobe. The standards used in the analysis were metallic scandium for Sc, analyzed actinolite for Fe, Na, Mn, Ti. Raw data were corrected by the MAGIC IV program of J. Colby. Three electron probe analyses were made on each crystal fragment, and the average values are reported in Table 4 as oxide weight percent. It was assumed that the iron present was Fe^{2+} , and that the water content in cascandite corresponded to one molecule in the unit cell, as indicated by the structural data discussed in the following paragraph. In Table 4 the cell contents for jervisite and cascandite are given, on the basis of three and two silicon atoms in the unit cell, respectively.

Structural and crystal chemical considerations

The crystal structure of cascandite was determined by Mellini and Merlino (1982) and that of jervisite by Mellini and Merlino and Rossi (to be published). The structures refined to R values of 0.04 and 0.05, respectively.

Jervisite is isostructural with the synthetic phase $NaScSi_2O_6$, which was synthesized by Ito and Frondel (1968), and whose structure was refined by

	cascandite	jervisite	syn NaScSi 0
Space group	PĪ	C2/c	C2/c
a	7.529(11)Å	9.853(11)Å	9.8438(4)Å
b	7.051(11)	9.042(10)	9.0439(4)
c	6,755(9)	5.312(7)	5.3540(2)
a	92°7'(5')		
β	93°40'(5')	106°37'(7')	107.215°(2)
γ	104°39'(5')		

Table 3. Unit cell parameters of cascandite, jervisite and its synthetic analogue

Hawthorne and Grundy (1973). From the chemistry (unit cell contents) given in Table 4, $(Na_{0.43} Ca_{0.31} MN_{0.01} Fe_{0.29}^{2+} Mg_{0.17} Sc_{0.66} Al_{0.02} Ti_{0.01})_{tot.=1.89}$ Si₂O_{6.02}, the following crystal chemical formula may be derived on the basis of structural data: $(Na, Ca, Fe^{2+})(Sc, Mg, Fe^{2+})Si_2O_6$ with Na > Ca, Fe²⁺; Sc > Mg, Fe²⁺. Thus jervisite is a scandium pyroxene, that is intermediate in the Ca(Mg, Fe) Si₂O₆-NaScSi₂O₆ series, analogous to the aegirineaugite series.

Cascandite is structurally related to the wollastonite-pectolite-serandite group. The crystal structure analysis clearly indicates that in cascandite, as in pectolite and serandite, there is an intrachain hydrogen bond. The hydrogen atom was located by a difference Fourier synthesis. The two octahedral sites, which are both occupied by calcium cations in pectolite and by manganese cations in

Table 4. Chemical composition of cascandite and jervisite

Oxide	Weight cascandite	per cent jervisite	Element	Atoms per for cascandite	iervisite
sio ₂	51.83	50.42	Si	3.00	2.00
Sc203	14.74	18.48	Sc	0.74	0.64
Fe0	4.50	8.59	Fe	0.22	0.29
MgO	0.20	2.80	Mg	0.02	0.17
TiO ₂	0.08	0.55	Ti	0.01	0.02
A1203	0.11	0.42	A1	0.01	0.02
MnO	2.32	0.44	Mn	0.11	0.01
Ca0	16.83	7.25	Ca	1.04	0.31
Na ₂ 0	0.06	5.55	Na	0.01	0.43
н,0	(2.59)		0	8.54	6.02
-			н ₂ 0	0.5	

serandite, host different cations in casandite: one is occupied by calcium and the other by scandium
with minor Fe²⁺ cations. The site where sodium cations are located in pectolite and serandite, has an extremely low occupancy in cascandite (Mellini and Merlino, 1982).

The chemical contents reported in Table 4 can be conveniently expressed by the formula:

$$\begin{array}{c} Ca(Sc_{0.74}Mg_{0.02}Al_{0.01}Fe_{0.22}^{2+}Mn_{0.01})\\ (Na_{0.01}Ca_{0.04}Mn_{0.10}\Box_{0.85})Si_{3}O_{8.02}(OH). \end{array}$$

The crystal chemical formula that better summarizes the chemical as well as the structural data is $Ca(Sc_{0.8}^{3+}M_{0.2}^{2+})(M_{0.2}^{2+}\Box_{0.8})Si_3O_{8.2}(OH)_{0.8}$ with $M^{2+} = (Fe^{2+},Mn^{2+})$, approximating the ideal composition $CaScSi_3O_8(OH)$.

Conclusions

The two new mineral phases, cascandite and jervisite, join kolbeckite $ScPO_4 \cdot H_2O$, bazzite $Be_3(Sc,Fe)_2Si_6O_{18}$ and thortveitite $(Sc,Y)_2Si_2O_7$, as rare minerals in which scandium occurs as an essential, major constituent. It seems remarkable that three of the four scandium silicates were found in the granite of Baveno. The three other phases with relatively high scandium content $(Sc_2O_3 \ 2-6 wt.\%)$ are: Sc-ixiolite $(Ta,Nb,Sn,Mn,Fe,Sc,\ldots)_2O_4$ (Borisenko *et al.*, 1969), Sc-perrierite (Ce,La,Ca)₄ (Fe²⁺,Sc)(Ti,Fe³⁺)_2Ti_2(O_4/Si_2O_7)_2 (Semenov *et al.*, 1966), magbasite KBa(A1,Sc)Fe²⁺Mg_5F_2Si_6O_{20} (Semenov *et al.*, 1965).

The rarity of scandium minerals is a result of its crystal chemical behavior. In fact, in the first study of scandium geochemistry, Goldschmidt and Peter (1931) emphasized that the bulk of the element is dispersed in very small amounts among minerals formed in the early stages of magmatic differentiation, mainly pyroxenes, amphiboles and biotite. Only a very small amount passes through the magmatic stage and enters pegmatitic, pneumatolitic and hydrothermal deposits.

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References

Borisenko, L. F., Maksimova, N. V. and Kazakova, M. Y. (1969) Scandium ixiolite, a new tantalum-niobate species with

formula $(A,B)_n O_{2n}$. Doklady Akademie Nauk SSSR, 193, 167–170.

- Goldschmidt, V. M. and Peter, C. (1931) Zur Geochemie des Scandium. Nachrichten von der königlichen Gesellschaft der Wissenschaften zü Gottingen—Geologie und Mineralogie IV, 257-259.
- Hawthorne, F. C. and Grundy, H. D. (1973) Refinement of the crystal structure of $NaScSi_2O_6$. Acta Crystallographica, B29, 2615–2616.
- Ito, J. and Frondel, C. (1968) Syntheses of the scandium analogues of aegirine, spodumene, andradite and melanote-kite. American Mineralogist 53, 1276–1280.
- Mellini, M. and Merlino, S. (1982) Crystal structure of cascandite. American Mineralogist 67, 604–609.
- Semenov, Y. I., Khomakov, A. P. and Bykova, A. V. (1965) Magbasite, a new mineral. Doklady Akademie Nauk SSSR, 163, 718–719.
- Semenov, Yl I., Kulakov, M. P., Kostynina, M. Y., Kazakova, M. Y. and Dudykina, A. S. (1966) Scandium content in the quartz-fluorite pegmatites of Kazakhstan. Geokhimiya 2, 244– 246.

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