

## Jervisite, NaScSi<sub>2</sub>O<sub>6</sub>: a new occurrence, chemical data and crystal structure

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**ABSTRACT.** — Jervisite, scandium sodium pyroxene, has been found in cavities of the Baveno granite at Prini quarry, Piedmont (Italy). Electron microprobe analysis and single crystal X-ray diffraction study [space group *C2/c*, with cell parameters  $a = 9.844$  (2),  $b = 9.059$  (2),  $c = 5.328$  (2) Å,  $\beta = 106.55$  (2)°] pointed to an idealized crystal chemical formula (Na<sub>0.85</sub>Ca<sub>0.15</sub>)(Sc<sub>0.85</sub>Fe<sub>0.15</sub>)Si<sub>2</sub>O<sub>6</sub>. The structure was refined to a  $R_1 = 0.038$ . The average bond distances in the octahedral M1 (Sc,Fe) and eightfold coordinated M2 (Na,Ca) sites are M1-O 2.110 Å and M2-O 2.550 Å.

**RIASSUNTO.** — La jervisite, pirosseno di scandio e sodio, è stata ritrovata in cavità del granito di Baveno nella cava Prini (Piemonte, Italia). Analisi in microsonda elettronica e studi in diffrazione di raggi X a cristallo singolo [gruppo spaziale *C2/c*, con costanti di cella  $a = 9.844$  (2),  $b = 9.059$  (2),  $c = 5.328$  (2) Å,  $\beta = 106.55$  (2)°] hanno condotto alla formula cristallografica idealizzata (Na<sub>0.85</sub>Ca<sub>0.15</sub>)(Sc<sub>0.85</sub>Fe<sub>0.15</sub>)Si<sub>2</sub>O<sub>6</sub>. La struttura è stata raffinata sino ad un fattore  $R_1 = 0.038$ . Le distanze di legame medie nel sito ottaedrico M1 (Sc,Fe) e nel sito a coordinazione otto M2 (Na,Ca) sono M1-O 2.110 Å e M2-O 2.550 Å.

**KEY WORDS:** *Jervisite, scandium mineral, Baveno, microprobe analysis, crystal structure, crystal chemistry.*

### INTRODUCTION

Jervisite NaScSi<sub>2</sub>O<sub>6</sub> was first found, together with cascandite CaScSi<sub>3</sub>O<sub>8</sub>(OH), as small crystals in a miarolitic cavity of granite at Cava Diverio, Baveno, Italy (Mellini *et al.* 1982). At that time only three other scandium minerals were known, namely the phosphate kolbeckite and the silicates bazzite and thortveitite. In the meantime the list of approved scandium minerals has been enriched by four new entries (Table 1).

The study carried out on jervisite by Mellini *et al.* (1982) showed that jervisite is monoclinic, space group *C2/c* with lattice dimensions  $a = 9.853$  (11),  $b = 9.042$  (10),  $c = 5.312$  (7) Å,  $\beta = 106.62$  (12)°. The chemical composition, determined through electron probe analysis, pointed to the crystal chemical formula (Na<sub>0.43</sub>Ca<sub>0.31</sub>Mn<sub>0.01</sub>Fe<sub>0.29</sub>Mg<sub>0.17</sub>Sc<sub>0.66</sub>Al<sub>0.02</sub>Ti<sub>0.01</sub>)<sub>tot=1.89</sub>Si<sub>2</sub>O<sub>6.02</sub>. 'Thus jervisite is a scandium pyroxene that is intermediate in the Ca(Mg,Fe)Si<sub>2</sub>O<sub>6</sub> – NaScSi<sub>2</sub>O<sub>6</sub> series, analogous to the aegirine – augite series' (Mellini *et al.* 1982). No structural data have been so far published but jervisite is obviously isostructural with the synthetic phase NaScSi<sub>2</sub>O<sub>6</sub>, which was synthesized by Ito and Frondel (1968), and whose structure was refined by Hawthorne and Grundy (1973).

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TABLE 1. – Scandium minerals, with indication of the chemical formula, occurrence and reference.

Mineral	Chemical formula	Occurrence	Reference
Bazzite	(Sc,Al,Fe) <sub>2</sub> Be <sub>3</sub> Si <sub>6</sub> O <sub>18</sub>	Baveno (Italy)	Artini (1915)
Kolbeckite	ScPO <sub>4</sub> ·2H <sub>2</sub> O	Schmiedeberg, Saxony (Germany)	Edelmann (1926)
Thortveitite	(Sc,Y) <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	Iveland (Norway)	Schetelig (1911)
Cascandite	CaScSi <sub>3</sub> O <sub>8</sub> (OH)	Baveno (Italy)	Mellini <i>et al.</i> (1982)
Jervisite	(Na,Ca)(Sc,Fe)Si <sub>2</sub> O <sub>6</sub>	Baveno (Italy)	Mellini <i>et al.</i> (1982)
Juonniite	CaMgSc(PO <sub>4</sub> ) <sub>2</sub> (OH)·4H <sub>2</sub> O	Kovdor massif, Kola (Russia)	Liferovich <i>et al.</i> (1997)
Pretulite	ScPO <sub>4</sub>	Pretulalpe, Styria (Austria)	Bernhard <i>et al.</i> (1998)
Kristiansenite	Ca <sub>3</sub> ScSn(Si <sub>2</sub> O <sub>7</sub> )[Si <sub>2</sub> O <sub>6</sub> (OH)]	Tørdal, Telemark (Norway)	Raade <i>et al.</i> (2002)
Scandiobabingtonite	Ca <sub>2</sub> (Fe,Mn)ScSi <sub>3</sub> O <sub>14</sub> (OH)	Baveno (Italy)	Orlandi <i>et al.</i> (1998)

#### NEW OCCURRENCE AND CHEMICAL DATA

After the first finding at Diverio quarry, jervisite, associated with cascandite, microcline, fluorite and quartz, has been subsequently found within a miarolitic cavity in the pink Baveno granite (Piedmont, Italy) at Prini quarry, far from the original occurrence. At Prini quarry jervisite occurs as acicular vitreous transparent colourless crystals elongated along [001] up to 0.5 mm. In the sample represented in Fig. 1, a sample which was provided us by the mineral collector Sergio Varvello and which is presently preserved at 'Museo di Storia Naturale e del Territorio' of the University of Pisa, the crystals of jervisite are terminated by a tuft of very minute tabular crystals of cascandite.

Preliminary chemical analyses (Philips 515 Scanning Electron Microscope equipped with EDS spectrometer) pointed to the presence of Si, Sc, Na, Ca, with minor contents of Fe and Mn. The actual composition of the mineral was definitely assessed through microprobe analyses carried on a wavelength-dispersive ARL-SEM-Q instrument, with operating conditions 15kV as accelerating voltage and 20nA as sample current, beam diameter 5µm. The standards were the pure metal for scandium and Amelia albite for Na, AB microcline for Si, Al and K, clinopyroxene for Ca, ilmenite for Fe and Ti.

The analytical data, collected on two crystals are reported in Table 2 as an average of seven analytical points in each crystal. The atomic contents have been recalculated on the basis of six oxygen atoms,

pointing to the following crystal chemical formulae for the two analysed crystals:

crystal 1 – (Na<sub>0.78</sub>Ca<sub>0.17</sub>Mn<sub>0.01</sub>□<sub>0.04</sub>)(Sc<sub>0.85</sub>Fe<sub>0.08</sub>Mn<sub>0.03</sub>Mg<sub>0.03</sub>Ti<sub>0.01</sub>)(Si<sub>1.98</sub>Al<sub>0.02</sub>)O<sub>6</sub>

crystal 2 – (Na<sub>0.75</sub>Ca<sub>0.21</sub>Mn<sub>0.02</sub>□<sub>0.02</sub>)(Sc<sub>0.80</sub>Fe<sub>0.11</sub>Mn<sub>0.03</sub>Mg<sub>0.05</sub>Ti<sub>0.01</sub>)(Si<sub>1.99</sub>Al<sub>0.01</sub>)O<sub>6</sub>

The distribution of the metal cations in the sites M1, dominated by Sc<sup>3+</sup>, and M2, dominated by Na<sup>+</sup>, in accordance with the values of their radii, was straightforward apart from the case of Mn<sup>2+</sup>, which may be located on both sites. In the proposed distributions, after completion of the occupancy in the smaller octahedrally coordinated M1 site, the residual Mn<sup>2+</sup> cations are placed in the larger M2 site (see next section).



Fig. 1 – Elongated crystals of jervisite terminated by tufts of minute crystals of cascandite. The white bar corresponds to 0.1 mm.

TABLE 2 – Analytical data obtained through electron microprobe analyses of jervisite. The oxide wt% of crystals 1 and 2 (average of 7 analysed points in each crystal) are presented in the columns 1 and 2 (the very low amounts of K<sub>2</sub>O, 0.004 and 0.001 wt% in the two crystals, are not reported). The corresponding atomic contents, recalculated on the basis of 6 oxygen atoms, are given in columns 1' and 2'.

Oxide	1	2	Atom	1'	2'
SiO <sub>2</sub>	52.17	51.35	Si	1.98	1.99
Al <sub>2</sub> O <sub>3</sub>	0.40	0.31	Al	0.02	0.01
Sc <sub>2</sub> O <sub>3</sub>	25.62	23.60	Sc	0.85	0.80
TiO <sub>2</sub>	0.31	0.27	Ti	0.01	0.01
FeO	2.58	3.41	Fe	0.08	0.11
MnO	1.24	1.38	Mn	0.04	0.05
MgO	0.54	0.80	Mg	0.03	0.05
Na <sub>2</sub> O	10.62	10.02	Na	0.78	0.75
CaO	4.27	5.03	Ca	0.17	0.21
total	97.76	96.17		3.96	3.98

The crystal chemical formulae we have just presented clearly indicate that the crystals of the new finding have composition nearer to that of the end member NaScSi<sub>2</sub>O<sub>6</sub> in the solid solution series Ca(Mg,Fe)Si<sub>2</sub>O<sub>6</sub> – NaScSi<sub>2</sub>O<sub>6</sub> than the crystals of the original finding.

#### CRYSTAL STRUCTURE REFINEMENT

A structural study has been carried out by collection of X-ray diffraction data on a Siemens P4 four-circle diffractometer operating under the following working conditions: voltage of 50 kV, current of 40 mA and graphite-monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71703 \text{ \AA}$ ). Cell parameters were determined from a least-squares analysis of the setting angles of 20 reflections in the range  $10^\circ < 2\theta < 30^\circ$ , which led to parameters  $a = 9.844 (2)$ ,  $b = 9.059 (2)$ ,  $c = 5.328 (2) \text{ \AA}$ ,  $\beta = 106.55 (2)^\circ$ ,  $V = 455.45 \text{ \AA}^3$ .

The reflection intensities were recorded in the  $4^\circ$  to  $50^\circ$   $2\theta$  range and in the  $hkl$  range:  $-11 < h < 1$ ,  $-10 < k < 1$  and  $-6 < l < 5$ . After the Lorentz-polarization correction of the 515 reflections, equivalent reflections were averaged in the space group  $C2/c$ , which led to a set of 363 unique reflections ( $R_{\text{int}} = 0.045$ ), of which 272 satisfied the criterion  $F_0 > 6\sigma(F_0)$ . No absorption correction

was made due to the very small dimensions of the crystal (a very thin platelet elongated [001], with volume of  $0.004 \times 0.02 \times 0.26 \text{ mm}^3$ ). Neutral atom scattering factors from International Tables for Crystallography, Volume C (1992), were used throughout.

The positional parameters obtained by Hawthorne and Grundy (1973) in their structural study of the synthetic compounds NaScSi<sub>2</sub>O<sub>6</sub> were used as the initial structural model. On the basis of the results of the electron probe analyses, mixed occupancies by scandium and iron in M1 site and by sodium and calcium in M2 site were assumed and the corresponding site populations were included among the refined parameters. After several cycles of least-squares refinement carried on  $|F|^2$ , with anisotropic thermal parameters for all the atoms, final reliability indices  $R_1 = 0.038$  for 272 reflections with  $F_0 > 6\sigma(F_0)$  and  $R_1 = 0.053$  for all 363 reflections were obtained ( $wR_2 = 0.109$ ,  $\text{GoF} = 0.959$ ). All the structural calculations were executed through the SHELXL-97 software (Sheldrick, 1997). Final atomic coordinates and refined cationic occupancies in M1 and M2 sites are reported in Table 3. Anisotropic displacement parameters are given in Table 4. The list of the  $F_0/F_c$  data for jervisite is available from the authors upon request.

TABLE 3 – Atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for jervisite.  $B_{eq}$  is defined as  $8\pi^2 U_{eq}$ , where  $U_{eq}$  is one third of the trace of the orthogonalized  $U^{ij}$  tensor.

Site	Occupancy	$x$	$y$	$z$	$B_{eq}$
M1	$\text{Sc}_{0.91}\text{Fe}_{0.09}$	0	0.8985(2)	1/4	0.58(5)
M2	$\text{Na}_{0.81}\text{Ca}_{0.19}$	0	0.3037(3)	1/4	1.31(12)
Si	Si	0.2902(2)	0.0885(2)	0.2420(4)	0.68(6)
O1	O	0.1184(5)	0.0807(5)	0.1466(9)	0.89(9)
O2	O	0.3604(5)	0.2468(5)	0.3129(9)	1.00(10)
O3	O	0.3509(5)	0.0110(5)	0.0122(8)	0.84(9)

TABLE 4 – Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for jervisite. The anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^*U^{11} + \dots + 2hka^*b^*U^{12}]$ .

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
M1	7(1)	8(1)	4(1)	0	-3(1)	0
M2	23(2)	13(2)	6(2)	0	-9(1)	0
Si	8(1)	10(1)	5(1)	0(1)	-3(1)	-1(1)
O1	7(2)	13(2)	10(3)	0(2)	-5(2)	0(2)
O2	15(2)	12(2)	7(3)	1(2)	-3(2)	-2(2)
O3	10(2)	12(2)	7(3)	-3(2)	-3(2)	-1(2)

## DISCUSSION

Jervisite is isostructural with the other sodic pyroxenes, as jadeite, aegirine, kosmochlor, characterized by a M2 site, occupied by sodium cation, with distorted cubic antiprismatic coordination and by a M1 site, occupied by the trivalent cation, with distorted octahedral coordination. As regards the site occupation in jervisite, the result of the structural refinement, carried out assuming Na and Ca in M2, Sc and Fe in M1, confirm the microprobe data. In fact the agreement is fairly good for the occupancies of the M2 site; as regards the M1 site, the slight excess of Sc (the lighter atom in the pair) indicated by the refinement is obviously compensating for the actual presence of the light Mg in that site. A simplified crystal chemical formula which at best reconciles the chemical and structural data for jervisite from Prini quarry is:  $(\text{Na}_{0.85}\text{Ca}_{0.15})(\text{Sc}_{0.85}\text{Fe}_{0.15})\text{Si}_2\text{O}_6$ .

The bond distances in the three cationic sites M1, M2 and Si are reported in Table 5, where they

are compared with the corresponding distances in synthetic  $\text{NaScSi}_2\text{O}_6$ . Table 5 shows that the corresponding average bond lengths in the two compounds are quite similar: M1-O is 2.110 and 2.102  $\text{\AA}$ , M2-O is 2.550 and 2.564  $\text{\AA}$ , Si-O is 1.634 and 1.632  $\text{\AA}$  in jervisite and in the synthetic  $\text{NaScSi}_2\text{O}_6$ , respectively. In keeping with the relationships between the average M2-O distance and the radius of the M1 cation presented by Ribbe and Prunier (1977), the size of the M2 polyhedron in jervisite and in the corresponding synthetic compound is significantly larger than those of the sodium polyhedra in  $\text{NaAlSi}_2\text{O}_6$  [ $\langle\text{Na-O}\rangle$  2.469  $\text{\AA}$  (Cameron *et al.* 1973)], in  $\text{NaCrSi}_2\text{O}_6$  [ $\langle\text{Na-O}\rangle$  2.489  $\text{\AA}$  (Clark *et al.* 1969)], in  $\text{NaFeSi}_2\text{O}_6$  [ $\langle\text{Na-O}\rangle$  2.518  $\text{\AA}$  (Clark *et al.* 1969)] and similar to that found in K-rich clinopyroxenes [ $\langle\text{M2-O}\rangle$  2.566  $\text{\AA}$  (Bindi *et al.* 2002)]. However, at difference from the 8-fold coordination of the M2 site in K-rich clinopyroxenes, the M2 site in jervisite and in synthetic  $\text{NaScSi}_2\text{O}_6$  displays a (6+2)-coordination.

TABLE 5 – Bond lengths [Å] for jervisite (at left), compared with the corresponding values in the synthetic NaScSi<sub>2</sub>O<sub>6</sub> (Hawthorne and Grundy 1973) (at right).

M1-O2	2.038(5) × 2	2.017(2) × 2
-O1	2.111(5) × 2	2.105(5) × 2
-O1'	2.180(5) × 2	2.183(2) × 2
M2-O2	2.387(5) × 2	2.411(6) × 2
-O1	2.472(5) × 2	2.490(2) × 2
-O3	2.495(5) × 2	2.461(6) × 2
-O3'	2.845(5) × 2	2.894(3) × 2
Si-O2	1.590(5)	1.592(2)
-O1	1.623(4)	1.630(3)
-O3	1.663(5)	1.653(2)
-O3'	1.659(5)	1.653(3)

The [ScO<sub>6</sub>] octahedron is the constant structural module in all the minerals listed in Table 1, apart one. As the effective ionic radius of <sup>VI</sup>Sc<sup>3+</sup> is 0.73 Å (Shannon and Prewitt 1969) the expected average Sc-O bond distance (with <sup>IV</sup>O<sup>2-</sup>, effective ionic radius 1.38 Å) in the scandium octahedra is 2.11 Å, in keeping with the values found in jervisite, in bazzite [2.101 Å in bazzite from Baveno with population in octahedral site Sc<sub>0.76</sub>Fe<sub>0.24</sub> (Demartin *et al.* 2000)], in thortveitite [2.132 Å in thortveitite from Madagascar with scandium occupancy 0.92 in octahedral site and very minor Y, Fe, Zr (Bianchi *et al.* 1988)], in cascandite [2.132 Å, with population Sc<sub>0.75</sub>Fe<sub>0.25</sub> in the octahedral site (Mellini and Merlino 1982)].

The interesting exception is presented by the eightfold coordination of scandium in the anhydrous phosphate pretulite ScPO<sub>4</sub>, with an average bond distance Sc-O of 2.210 Å, closely corresponding to the value 2.23 Å, calculated on the basis of the effective ionic radii, <sup>VIII</sup>Sc<sup>3+</sup> 0.87 Å and <sup>III</sup>O<sup>2-</sup> 1.36 Å. The increase of the scandium coordination from six to eight in a low pressure compound may be favoured by the relatively high electronegativity of the P atoms, which draw electrons out of the Sc-O bonds, thus lengthening them and decreasing their mutual repulsion, a situation quite similar to that occurring in Si-O bonds in some polymorphs of SiP<sub>2</sub>O<sub>7</sub> presenting silicon with octahedral coordination (Liebau 1971).

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