# CESIAN BAZZITE AND THORTVEITITE FROM CUASSO AL MONTE, VARESE, ITALY: A COMPARISON WITH THE MATERIAL FROM BAVENO, AND INFERRED ORIGIN

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#### Abstract

The occurrence of thortveitite,  $Sc_2Si_2O_7$ , and bazzite,  $Be_3Sc_2Si_6O_{18}$ , in the miarolitic cavities of the granophyre of Cuasso al Monte, in Varese, Italy, is reported for the first time, together with additional data for the corresponding species from the granite of Baveno. Bazzite from both these localities is Mg-poor and contains notable amounts of cesium (up to 2.3 wt%  $Cs_2O$ ), which is not encountered in the corresponding samples from Alpine fissures, and which has been overlooked in the type material (from Baveno). These discoveries confirm the similarity between the Baveno and Cuasso al Monte occurrences, and suggest the possibility that scandium minerals are more widespread in granitic rocks than is inferred at present. The composition and paragenesis of these Sc-rich species indicate the importance of complexes in enhancing the different geochemical behavior of scandium with respect to the *REE*, and that of equilibria with species such as feldspars, where aluminum cannot be replaced by transition elements.

Keywords: scandium, thortveitite, bazzite, Baveno, Cuasso al Monte, Italy.

### Sommaire

Nous signalons pour la première fois la présence de thortvéitite,  $Sc_2Si_2O_7$ , et de bazzite,  $Be_3Sc_2Si_6O_{18}$ , dans les miaroles d'un granophyre à Cuasso al Monte, dans la province de Varese, en Italie, et nous fournissons des observations nouvelles sur les mêmes espèces dans le granite de Baveno. A chaque endroit, la bazzite a une faible teneur en Mg et est enrichie en césium (jusqu'à 2.3% de Cs<sub>2</sub>O, en poids), ce qui n'avait pas été signalé dans la bazzite de la localité-type (Baveno). Ce ne sont pas les caractéristiques d'échantillons de ces espèces récupérés des fentes alpines. Ces nouvelles observations confirment la ressemblance de Baveno et de Cuasso al Monte, et fait penser que les minéraux de scandium pourraient bien être plus répandus dans les roches granitiques que l'on ne le soupçonne présentement. La composition et la paragenèse des espèces à Sc montre l'importance de complexes aqueux à distinguer le comportement géochimique du scandium par rapport aux terres rares, et d'équilibres ioniques avec des espèces telles que les feldspaths, dans lesquels l'aluminium ne peut pas être remplacé par des éléments de transition.

Mots-clés: scandium, thortvéitite, bazzite, Baveno, Cuasso al Monte, Italie.

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### INTRODUCTION

The discovery of bazzite, Be<sub>3</sub>Sc<sub>2</sub>Si<sub>6</sub>O<sub>18</sub>, in miarolitic cavities of the Baveno granite, in the Lago Maggiore area of Italy, by Artini (1915) followed closely Eberhard's (1908, 1910) discovery of thortveitite in the Iveland region in Norway as the first known mineral in which scandium is present as an essential constituent. The original find at Baveno remained the only one there until about 1980, although several occurrences of bazzite have been discovered in Alpine fissures since 1939 (see Hänni 1980 for references). At the same time, additional scandium-rich species have been observed at Baveno: for instance, thortveitite Sc<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> occurs in very unusual specimens as tiny grevish or deep blue crystals, in miarolitic cavities (Orlandi 1990). Other important discoveries are the new minerals cascandite CaScSi<sub>3</sub>O<sub>8</sub>(OH) (Mellini & Merlino 1982, Mellini et al. 1982), jervisite NaScSi<sub>2</sub>O<sub>6</sub> (Mellini et al. 1982), and scandiobabingtonite Ca<sub>2</sub>(Fe<sup>2+</sup>,Mn)ScSi<sub>5</sub>O<sub>14</sub>(OH) (Orlandi et al. 1998). For a detailed history of all such discoveries, see Gramaccioli et al. (1998).

In recent years, the scandium-rich species and their paragenesis have received attention. Such an increase of interest is witnessed by a number of recent discoveries of scandium minerals (besides the literature concerning Baveno, see also Bergstøl & Juve 1988, Juve & Bergstøl 1990, Armbruster *et al.* 1995, Liferovich *et al.* 1997, 1998, Bernhard *et al.* 1998, Raade & Erambert 1999); furthermore, the geochemical behavior of Sc, which is distinct with respect to the rare-earth elements (*REE*), has been shown not to be due only to the differences in ionic radii. Recent observations have emphasized the importance of complexes of Sc in the depositing solutions (Gramaccioli *et al.* 1999a, b, 2000).

On considering the granophyre from Cuasso al Monte, Lombardy, Italy, and from the nearby locality of Carona in Canton Ticino, Switzerland, and its relationships with the Baveno granite (Bakos *et al.* 1990, Boriani *et al.* 1992), scandium minerals were expected to occur here for some time. However, in 1992 an interesting specimen was noticed by Mr. R. Appiani in a quarry (Cava Laghetto) at Cuasso al Monte: it consists of a group of very tiny (maximum length 0.1 mm) greyish blue hexagonal prismatic crystals with flat terminations and similar to bazzite from Baveno, perched upon "orthoclase" (microcline) in a miarolitic cavity, associated with quartz, albite, and a black biotite-like mineral.

Furthermore, in 1994, another mineral collector, Mr. F. Anderbegani, submitted to our attention a certain number of specimens of another mineral he had found in the same quarry, showing very tiny groups of whitish aggregates of crystals. These aggregates are perched upon "orthoclase", are associated with tourmaline, fluorite, quartz and albite, and are similar to greyish thortveitite from Baveno.

A preliminary energy-dispersion analysis showed the presence of notable amounts of scandium in both cases.

We thus decided to carry out a more detailed investigation of these minerals from Cuasso al Monte. At the same time, one cotype specimen of bazzite in good crystals and samples of thortveitite from Baveno had become available to us, thereby providing the possibility of obtaining improved crystallographic and compositional data on these minerals from both localities.

# X-RAY DATA

#### Bazzite

A fragment of a tiny blue, bazzite-like crystal from Cuasso al Monte was examined using a Nonius CAD–4 single-crystal X-ray diffractometer. Although the poor quality of the crystal prevented the possibility of refining the structure, the data were sufficient for deducing the Laue symmetry 6/*mmm* and the unit-cell parameters; these results are reported in Table 1. On this basis, the identity of the mineral from Cuasso al Monte with bazzite is confirmed; final proof was provided by quantitative electron-microprobe analysis (see below). The large unit-cell dimensions constitute a peculiarity of bazzite from this new locality; the high value of *c* may relate to the presence of notable amounts of divalent ions, such as Fe<sup>2+</sup>, substituting for Sc<sup>3+</sup>, but the high value of *a* cannot easily be explained.

TABLE 1. UNIT-CELL PARAMETERS OF BAZZITE, AND COMPARISON WITH A FEW SELECTED VALUES FOR BERYL-GROUP MINERALS AT ROOM TEMPERATURE

	a (Å)	c (Å)
Bazzite, Cuasso al Monte, present work (1.3% Cs <sub>3</sub> O)	9.628(3)	9.234(3)
Bazzite, Baveno, present work (2.3% Cs <sub>2</sub> O)	9.549(2)	9.163(2)
Bazzite, Baveno (1)	9.51(1)	9.11(1)
Bazzite (cesian), Kazakhstan (0.3% Cs <sub>2</sub> O) (2)	9.521(5)	9.165(5)
Bazzite, Val Strem, Switzerland (3)	9.50	9.18
Bazzite, Furkabasistunnel, Switzerland (4)	9.501(1)	9.178(1)
Bazzite, Furkabasistunnel, Switzerland (5)	9.515(3)	9.191(5)
Bazzite, Gotthard Pass, Switzerland (5)	9.530(6)	9.193(3)
Bazzite, Alpe Iol, Fibbia, Gotthard, Switzerland (5)	9,508(5)	9.195(3)
Bazzite (cesian), Tørdal, Norway (3% Cs,O) (6)	9.549	9.152
Bazzite, (cesian), Heftetjern, Tørdal, Norway (3.1% Cs,O) (7)	9.555(3)	9.160(2)
Be <sub>3</sub> Sc <sub>2</sub> Si <sub>6</sub> O <sub>18</sub> (pure, synthetic) (8)	9.56	9.16
$Be_3Sc_{1.75}Fe_{0.25}Si_6O_{18}$ (9) (Fe = Fe <sup>3+</sup> )	9.552(2)	9.165(3)
Beryl, Tørdal, Norway, yellow and colorless (6)	9.205 -	9.191 -
	9.215	9.201
Beryl (9)	9.2088(5)	9.1896(7)
Beryl, var. "aquamarine", Brazil (10)	9.218(2)	9.197(2)
Beryl, var. "morganite" (cesian), Brazil (2.04% Cs2O) (10)	9.208(2)	9.197(2)
Cesian beryl (4.13% Cs <sub>2</sub> O) (8)	9.200	9.227
Highly cesian beryl (11.3% Cs <sub>2</sub> O) (8)	9.208	9.266
Beryl, Fe- and Mg-rich, Monte Leone,		
Swiss-Italian border (Al <sub>1.31</sub> Fe <sub>0.37</sub> Mg <sub>0.33</sub> ) (11)	9.274(1)	9.191(1)
$Be_3Al_2Si_6O_{18}$ (pure, synthetic) (12)	9.210	9.199
Stoppaniite (Fe,Al,Mg) <sub>4</sub> [Be <sub>6</sub> Si <sub>12</sub> O <sub>36</sub> ](H <sub>2</sub> O) <sub>2</sub> (Na, $\Box$ ) <sub>2</sub> (13)	9.397(1)	9.202(2)

Where no figures within parentheses are given, the experimental uncertainty is not stated. Sources: (1) Peyronel (1956), (2) Chistyakova *et al.* (1966), (3) Bergerhoff & Nowacki (1955), (4) Armbruster *et al.* (1995), (5) Hänni (1980), (6) Juve & Bergstøl (1990), (7) our data, (8) Frondel & Ito (1968), (9) Morosin (1972), (10) Artioli *et al.* (1993), (11) Hänni (1980), (12) Evans & Mrose (1968), (13) Ferraris *et al.* (1998). The proportion of Cs<sub>2</sub>O is given in wt%.

The cotype specimen of bazzite from Baveno examined is a part of the old Bazzi collection, which is now preserved in the mineralogical collection of Dipartimento di Scienze della Terra, University of Milan. From this sample, a very tiny fragment of a crystal was selected, and very good data were obtained using a CAD– 4 single-crystal diffractometer, permitting accurate refinement of the structure (Demartin *et al.* 2000). The unit-cell values (Table 1) are in line with recent values obtained for bazzite from other localities, but are notably different with respect to the previous set determined by Peyronel (1956) on type (or cotype) material as well. Such a difference is almost certainly due to the poor accuracy of the older measurements, especially reflected in the anomalously small value of *c*.

#### Thortveitite

For the other scandium-bearing mineral from Cuasso al Monte and all thortveitite specimens from Baveno, no single crystals providing reliable X-ray data could be found. The X-ray powder-diffraction patterns of two different samples of this mineral from Cuasso al Monte, obtained using a Gandolfi camera, are reported in Table 2, together with those of a sample from Norway and of pure synthetic thortveitite for comparison. The corresponding patterns obtained from four different samples of thortveitite from Baveno are reported in Table 3, and the unit-cell parameters, obtained from a least-squares fit of these powder data, are reported in Table 4. They do not differ significantly, and agree satisfactorily with the corresponding data on "classic" occurrences in Norway and Madagascar (Bianchi et al. 1988), as well with those for a pure synthetic sample of Sc<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>.

The composition of thortveitite is variable; in some cases, the mineral is almost pure, and in others it contains notable quantities of yttrium, zirconium, and the heaviest REE. As was shown by several authors (Smolin & Shepelev 1970, Voloshin et al. 1983, 1985, Bianchi et al. 1988, Gramaccioli et al. 1999b, Foord et al. 1993), the unit-cell parameters a and b increase appreciably on replacing Sc by Y and the *REE*, whereas c and  $\beta$  remain almost constant. By following only this criterion, and considering the data reported in Table 4, the first specimen from Cuasso al Monte and the blue specimens from Baveno represent a Y- (and REE-)poor variety of thortveitite (see below). For the second specimen from Cuasso al Monte, the data were insufficient to deduce the unit-cell parameters, and the X-ray powder-diffraction pattern (Gandolfi) only supports the identification.

#### CHEMICAL COMPOSITION

In addition to a series of preliminary EDS analyses, quantitative chemical analyses were performed on polished samples using an Applied Research Laboratories electron microprobe fitted with six wavelength-dispersion spectrometers and a Tracor Northern energy-dispersion spectrometer; the results are reported in Tables 5 and 6. The system was operated at an accelerating voltage of 15 kV, a sample current on brass of 10 nA, and a counting time of 10 or 20 seconds on the peaks, and 5 or 10 seconds on the backgrounds. Kaersutite (for Mg, Na,Ti, K), spessartine (for Fe and Mn), omphacite (for Si and Ca), pollucite (for Cs), and zircon (for Zr)

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR THORTVEITITE FROM CUASSO AL MONTE\*

		Cuasso 1		Cuasso 2	JCP	DS	JCP	DS
hkl	<i>d</i> .	<i>d</i> .	T	d.	#19- d	I 125	#20-1 data	I
	obs	calc	•	Cobs			005	_
110	5.120	5.101	24		5.18	60	5.09	16
001	4,570	4,572	25		4.58	18	4.57	8
020					4.31	2	4.257	4
Ī11					3.76	2		
200					3.25	4		
111	3.145	3.140	98	3.12	3.18	45	12 121	100
021	3.113	3.116	100		3.14	100	55.151	100
201	2.931	2.936	94	2.95	2.965	65	2.926	45
130	2.592	2.592	49		2.627	30	2.588	16
220	2.554	2.550	47		2.596	50	2.543	14
<u>7</u> 21					2.439	2		
201	2.385	2.378	10		2.421	8	2.373	4
<u>1</u> 31	2.371		8		2.367	2		
002	2.281		8		2.287	2	2.279	2
112					2.236	2	2.236	2
131	2.172	2.173	60	2.18	2.200	25	2.169	18
040	2.129	2.128	18		2.155	4	2.126	4
221					2.110	10		
310					2.105	1		
202		• • • • •			2.091	6	2 084	10
202	2.081	2.089	41				2.084	10
221	0.050	0.050	60		2 079	10	2.073	16
311	2.052	2.050	58		2.078	18	2.045	2
022	1.020	1.020	14		1.049	4	1 027	6
041 322	1.930	1.930	14		1.940	12	1.927	14
122	1.0/3	1.875	42		1.803	12	1 794	2
711	1.793	1.797	12		1 743	4	1 720	4
241	1.725	1.723	48		1 730	12	1.696	8
330	1.070	1.700	40		1 716	8	1 690	10
202					1 710	8	1.685	10
150					1 666	6		
132	1 645	1.643	70		1.658	14	1.640	20
400	1 594	1.593	27		1.625	8	1.587	6
T 5 1					1.594	2		
222	1.576		17		1.589	4		
<b>4</b> 21					1,537	18		
420					1.522	2		
151	1.516	1.520	40				1.519	6
203							1.507	10
332	1.497	1.497	27		1.509	6	1.493	6
242							1.489	6
<b>4</b> 02	1.469	1.468	8		1.482	4	1.462	2
023					1.437	4		
060	1.420	1.419	28				1.418	8
113	1.392	1.394	14				1.391	4
T 3 3	1.371	1.369	23				1.366	8
421	1.340		8				1.335	4
351	1.328		20				1.323	6

<sup>\*</sup> Room temperature; radiation used: CuKα; interplanar distances in Å

Cuasso 1: Sc-rich sample, the corresponding data are reported in Table 4 (first line) and in Table 6 (second column).

Cuasso 2: sample rich in other elements, extremely small aggregate of crystals. JCPDS File#19-1125: thortveitite sample from Tuftane, Norway.

JCPDS File#20-1037: synthetic sample of Sc<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>.

The values of  $d_{obs}$  for which no corresponding  $d_{oalc}$  is reported have not been used in deriving the unit-cell data.

		#1			#2			#3			#4	
hkl	$d_{ m obs}$	$d_{\rm calc}$	I	$d_{\rm obs}$	d <sub>calc</sub>	I	$d_{\rm obs}$	$d_{\rm calc}$	I	$d_{\rm obs}$	$d_{\rm calc}$	I
110				5.09	5,107	17	5.10	5.110	16	5.093	5.105	12
001	4 570	4 594	14	4.56	4.574	12	4.55	4.580	11	4.56	4.574	9
021	3 116		100	3.111	3.115	100	3.125	3.119	100	3,121	3.117	100
201	2,953	2,959	66	2,932	2.938	82	2,939	2.940	58	2.933	2.938	72
130	2 602	2 613	28	2.590	2.592	26	2,594	2.595	28	2.591	2.594	42
220	2.602	2.585		2.551	2.554	24	2,557	2.555	20	2.551	2.553	35
201	2.428	2.419	5	2.383	2.384	5	2.386	2.385	4	2.379	2.381	9
002				2.287			2.282		2	2.286		10
ī12										2.247		8
131	2,196	2.192	28	2.173	2.174	34	2.176	2.176	33	2.173	2.174	65
040				2.127	2.127	6	2.128	2.130	7	2.130	2.129	19
310							2.085	2.091	17			
202	2.103	2.094	11	2.084	2.089	22				2.082	2.090	43
311	2.084	2.073	25	2.053	2.053	32	2.056	2.054	23	2.052	2.052	53
022				2.011			2.015		2	2.014		
041				1.928	1.929	8	1.931	1.931	7	1.931	1.930	21
$\bar{2}22$	1.879	1.881	27	1.875	1.875	34	1.876	1.877	21	1.875	1.876	53
T 3 2	1.801	1.803	5	1.794	1.796	6	1.798	1.798	3	1.797	1.797	14
				1.759			1.750			1.748		
$\bar{2}41$	1.731	1.735	14	1.724	1.723	8	1.725	1.725	7	1.724	1.724	19
330	1.713	1.723	20	1.699	1.702	19	1.699	1.704	17	1.698	1.702	42
132	1.656	1.656	25	1.645	1.644	36	1.646	1.646	36	1.645	1.644	65
	1.629		5									
400	1.594		8	1.598	1.596	15	1.599	1.597	10	1.597	1.594	32
222				1.576		7	1.577		7	1.576		15
				1.559		1	1.560		1			
151	1.537	1.532	18	1.518	1.520	20	1.521	1.522	19	1.518	1.521	46
$\overline{2}03$	1.505		13									
332	1.480		6	1.497	1.497	14	1.498	1.499	10	1.497	1.498	30
<b>4</b> 02				1.470	1.469	7	1.470	1.470	4	1.470	1.469	13
060				1.420	1.418	12	1.421	1.420	13	1.421	1.419	31
113				1.395	1.395	4	1.396	1.397	5	1.394	1.395	13
133	1.372	1.373	11	1.370	1.369	15	1.372	1.370	9	1.371	1.369	30
421			-	1.343		3	1.344			1.342		
351				1.329		10	1.329			1.329		

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR THORTVEITITE FROM BAVENO\*

\* All these data (unpublished until now) were obtained by P. Orlandi in occasion of his discovery of thortveitite from Baveno (1990).

The values of  $d_{obs}$  for which no corresponding  $d_{calc}$  is reported have not been used in deriving the unit-cell data.

#1 Needle-like crystal, colorless (Orlandi's file No. 3184). #2 Blue globules (file 3187). #3 Blue globules (file 3047). #4 Blue globules (file 3081).

were employed as standards; with respect to Sc,Y, Zr, Hf, and the *REE*, the lines, the standards used and the procedures followed to account for interferences are described in detail in Bianchi *et al.* (1988), Demartin *et al.* (1991) and Mannucci *et al.* (1986). The results were processed for matrix effects using a modified version of the MAGIC IV program.

### Bazzite

Our results are reported in Table 5, together with significant data from other localities taken from the literature. There is a noticeable compositional difference between the samples from Alpine fissures and those from the other locations; the former contain important amounts of magnesium, and the latter contain instead non-negligible amounts of heavy alkalis, especially cesium. This element was overlooked in previous investigations of the type material (Bertolani 1948); its presence was first noticed on examining EDS spectra of type and cotype specimens (Gramaccioli *et al.* 1998).

Bertolani (1948) used spectrographic analysis to detect the presence of Y and *REE* in type (or cotype) specimens. These elements have not been detected with our electron microprobe, as with material from other localities (see, for instance, Hänni 1980); such a discrepancy is certainly due to the higher sensitivity of a spectrographic analysis, which, on the other hand, should have revealed the presence of cesium; the early volatilization of Cs in the emitting source with respect to the other elements considered is a probable reason for this error.

As in beryl (Hänni 1980, Aurisicchio *et al.* 1988, Artioli *et al.* 1993), the charge balance in bazzite to account for the presence of divalent ions like Mg or Fe<sup>2+</sup> in the 4(*c*) Sc (or Al) site can be achieved mainly owing to the presence of alkali metal ions (Na<sup>+</sup> and Cs<sup>+</sup>) in the channels; a similar observation could also be drawn for

 TABLE 4. UNIT-CELL PARAMETERS OF THORTVEITITE

 AT ROOM TEMPERATURE

Mineral	a (Å)	b (Å)	c (Å)	β (°)
Cuasso al Monte, sample #1, present work	6.532(7)	8.514(6)	4.688(4)	102.77(9)
Baveno, greyish white, sample #1 (file 3184)	6.633(19)	8.564(19)	4.699(12)	102.2(3)
Baveno, blue variety, sample #2 (file 3187)	6.545(5)	8.509(4)	4.689(3)	102.69(6)
Baveno, blue variety, sample #3 (file 3047)	6.547(5)	8.520(4)	4.694(3)	102.68(6)
Baveno, blue variety, sample #4 (file 3081)	6.539(6)	8.516(5)	4.690(3)	102.76(8)
Iveland, Norway, Y-rich (17.7% Y.O.) <sup>(1)</sup>	6.650(1)	8.616(1)	4.686(1)	102.20(1)
Montana, Y-poor $(2.3\% Y_2 \Omega_2)^{(2)}$	6.5304(4)	8.5208(4)	4.6806(5)	102.630(7)
Madagascar, Y-poor (2.3% Y.O.) <sup>(1)</sup>	6.527(1)	8.507(1)	4.691(1)	102.78(1)
$Sc_2Si_2O_7$ (synthetic) <sup>(3)</sup>	6.503(2)	8.498(3)	4.682(2)	102.77(7)

Sources: (1) Bianchi et al. (1988), (2) Foord et al. (1993), (3) Smolin & Shepelev (1970).

the newly discovered species stoppaniite, the Fe-rich member of the beryl group (Ferraris *et al.* 1998, Della Ventura *et al.* 2000). If all the iron in the specimen from Baveno is assumed to occupy the 4(c) sites in the form of Fe<sup>2+</sup>, the charge of the alkali metals in the channels would be balanced almost exactly on replacing the Sc<sup>3+</sup> ions by the 2+ (and 4+) ions present in the structure. The same, however, does not happen for the specimen from Cuasso al Monte, and on these grounds, the presence of some Fe<sup>3+</sup> instead of Fe<sup>2+</sup> might be assumed as well (Aurisicchio *et al.* 1988, Artioli *et al.* 1993).

Similarly, bazzite from Alpine fissures contains more magnesium than necessary to balance the charges in this way, even without considering a possible role of iron. Therefore, in agreement with Armbruster et al. (1995), the presence of some 2+ ions in the channels cannot be ruled out, at least in some cases. Furthermore, other ways of balancing the charges cannot be excluded: these possibilities are the presence of OH<sup>-</sup> groups in the structure, or the partial substitution of Si<sup>4+</sup> by Be<sup>2+</sup> (see below) or even of Be<sup>2+</sup> by Li<sup>+</sup>. Therefore, in view of these possibilities and in lack of additional information, no attempt has been made to derive the Fe<sup>2+</sup>:Fe<sup>3+</sup> ratio. The low analytical total in some cases (including bazzite from Cuasso al Monte) is almost certainly due to neglect of the presence of H<sub>2</sub>O, which might also be present in the channels.

An adequate crystal-chemical characterization of all the minerals in the beryl group would imply an accurate determination of the contents of the lightest elements, such as Be, Li, or H, on a significant number of specimens. In view of the lack of such information, most data concerning Be and H reported in Table 5 have been derived from simple assumptions (*e.g.*, by imposing a value of 0.5 to the atomic ratio Be/Si), or using the results of the crystal-structure refinement; however, such procedures may not be entirely correct. The actual contents of beryllium were determined by Chystyakova *et al.* (1966) for bazzite from Kazakhstan, by Juve & Bergstøl (1990) for bazzite from the Heftetjern pegmatite, Tørdal, Norway, and by Della Ventura *et al.* (2000) for type stoppaniite. In these instances, an excess of Be

TABLE 5. CHEMICAL COMPOSITION OF SAMPLES OF BAZZITE

	Baveno	Cuasso al Monte	Heftetjern Tørdal,	Kazakh- stan	Furka	Fleiss- tal
	(1)	(2)	Norway (3)	(4)	(5)	(6)
MgO wt%	0.13	0.43	0.10	0.82	2.11	4.00
MnO	0.10	0.48	1.43	1.58	0.33	
Al <sub>2</sub> O <sub>3</sub>	0.14	0.52	0.80	0.25	0.17	1.85
$Fe_2O_3$	6.62	6.97	5.70	6.25	5.68	4.77
$Sc_2O_3$	16.24	14.36	14.50	14.44	14.28	10.75
ZrO <sub>2</sub>	0.30					
Na <sub>2</sub> O	2.13	2.11	1.60	2.82	1.62	1.90
K₂Õ	0.00	0.03	0.13	0.22	0.00	0.10
RĎ,O	0.00	0.03	0.25	0.04		
Cs <sub>2</sub> O	2.30	1.28	2.93	0.31		
CaÕ	0.00	0.03			0.05	0.20
SiO <sub>2</sub>	58.18	57.59	58.00	58.80	59.79	58.05
ЗеÕ	<sup>§</sup> 12.11	<sup>\$</sup> 12.51	14.50	12.90	<sup>\$</sup> 12.50	<sup>\$</sup> 12.08
Li <sub>2</sub> O			0.24			
H <sub>2</sub> O	<sup>¶</sup> 2.72		1.10	2.60	<sup>¶</sup> 2.40	
otal	100.97	96.34	101.28	101.58	98.93	93.70
		Ato	mic contents*			
Ma anfu	0.019	0.067	0.014	0.012	0 314	0.614
Mn	0.009	0.043	0.112	0.133	0.028	0.011
41	0.016	0.064	0.090	0.030	0.020	0 223
Fe	0.496	0.546	0 399	0.470	0.428	0.372
Sc.	1 409	1 303	1 182	1 262	1 248	0.968
7.r	0.014	1.505	1.102	1.202	1.210	0.200
ΞA	1.963	2.023	1.797	1.907	2.038	2.177
т.	0.410	0.405	0.000	0.540	0.202	0.279
Na Z	0.412	0.423	0.292	0.349	0.302	0.576
N	0.000	0.004	0.017	0.031	0.000	0.015
XD 7-	0.000	0.002	0.013	0.002		
_s ~-	0.096	0.000	0.116	0.013	0.005	0.025
Ja To	0.000	0.003	0.440	0.504	0.003	0.023
L B	0.508	0.490	0.440	0.594	0.307	0.441
Si	6.000	6.000	5.431	5.905	6.000	6.000
Be	0.000	0.000	0.569	0.095	0.000	0.000
E C	6.000	6.000	6.000	6.000	6.000	6.000
Зе	3.000	3.000	2.909	3.000	3.000	3.000
i			0.091			
E D	3.000	3.000	3.000	3.000	3.000	3.000
H	¶1.80		0.699	1.742	<sup>1</sup> 1.607	

The last two columns refer to material from Alpine fissures.

\* Normalized to 9 (Si + Be) atoms per formula unit (apfu).

§ On assuming Be/Si = 0.5

<sup>1</sup> Calculated on the basis of crystal-structure refinement.

(1) Cotype specimen from the collection of Dipartimento di Scienze della Terra, Università di Milano, average of 9 points; Y,Dy,Er,Yb,Ti are below the detection limits. The unit-cell data are reported in the 2<sup>nd</sup> line of Table1.

(4) From Chistyakova et al. (1966). The unit-cell data are reported in the 4<sup>th</sup> line of Table1.

(5) From Armbruster *et al.* (1995). The unit-cell data are reported in the 6<sup>th</sup> line of Table1.

(6) From Hänni (1980). The unit-cell data are reported in the 7th line of Table1.

<sup>(2)</sup> Average of 8 points; Ti is below the detection limit. The unit-cell data are reported in the 1st line of Table1.

<sup>(3)</sup> From Juve & Bergstøl (1990). The unit-cell data are reported in the 10<sup>th</sup> line of Table1.

was interpreted as evidence for partial replacement of Si by Be, corresponding to the proportions  $Si_{5.93}Be_{0.07}$ ,  $Si_{5.7}Be_{0.3}$ , and  $Si_{5.53}Be_{0.44}$  at the Si site, respectively; for stoppaniite, such a replacement is in agreement with the crystallographic results obtained by Ferraris *et al.* (1998). This possibility was considered in our crystal-structure refinement of the sample from Baveno and of another sample from Tørdal, Norway; however, no definite conclusions in this respect could be achieved using X-ray data only (Demartin *et al.* 2000).

### Thortveitite

The electron-microprobe data for thortveitite from both Cuasso al Monte and Baveno (Table 6) confirm the results obtained from X-ray diffraction, the analyzed specimens being reasonably pure. Instead, the EDS spectrum of sample #2 from Cuasso al Monte shows the presence of non-negligible amounts of Y, the *REE*, and Zr; unfortunately, no suitable fragments were available for a quantitative chemical analysis.

In view of the extreme scarcity of the thortveitite from Baveno, as well as of the very small dimensions and powdery nature of the samples, an electron-microprobe analysis could not be performed on the same specimens from which X-ray data were obtained. However, the almost identical EDS spectra provided by a series of different samples of the blue variety suggest that our X-ray data should indeed correspond to the chemical composition indicated in Table 6. Further evidence in this respect is provided by the constancy of the unit-cell parameters of all the samples of the blue variety here examined, in view of the evident relationships between such parameters and the Y (and *REE*) content.

Since the main substituents of Sc in thortveitite are generally Y and the REE, on the whole the poorest samples in these elements should be the richest in Sc. In the analyzed specimen from Bayeno and in the sample from Kola studied by Voloshin et al. (1991), the Y content is the lowest on record; owing to replacement by notable amounts of Ca and especially of Mn, the Sc content for the former is appreciably lower than that for the latter. Since Mn<sup>3+</sup> is an intense absorber (Rossman 1988), as in a number of deep blue or violet Mn-bearing minerals such as purpurite, piemontite or "violane", the peculiar blue color of the unusual variety of thortveitite from Baveno could be ascribed to the presence of this ion, thereby providing a possible clue to its origin (Gramaccioli et al. 1999b; see also below). For the specimen from Cuasso al Monte, notable amounts of Fe substitute for Sc (up to nearly 3 wt% Fe<sub>2</sub>O<sub>3</sub>).

#### DISCUSSION

A general picture concerning the formation of scandium-rich minerals and their geological significance has not been established yet, owing to the scarcity of reliable physical–chemical data and of natural examples. The geochemical behavior of scandium is peculiar and apparently contradictory: in igneous rocks, Sc is usually concentrated in ferromagnesian minerals, and for this reason it usually prefers mafic assemblages, but notable exceptions are found in some carbonatites, where the accessory minerals are instead the major hosts of Sc (Eby 1973).

Other important concentrations of this element occur in hydrothermal or pneumatolitic veins in granitic rocks, in association with fluorine-rich minerals, such

TABLE 6. CHEMICAL COMPOSITION OF SAMPLES OF THORTVEITITE

	Baveno deep blue (1)	Cuasso al Monte #1 (2)	Kola (3)	Iveland (4)	Madagascar (5)	Montana (6)
MgO wt%				0.26		0.06
CaO	1.6	0.04		0.19		0.10
MnO	#2.8	0.92	0.0	0.67	0.30	0.03
Fe <sub>2</sub> O <sub>3</sub>	1.5	2.89	1.6	2.06	1.39	1.48
$Sc_2O_3$	43.4	44.01	48.9	25.01	47.81	44.60
$Y_2O_3$	1.9	2.59	1.9	17.73	2.31	2.28
Ce <sub>2</sub> O <sub>3</sub>			0.3			0.08
$Gd_2O_3$			0.1			0.14
$Dy_2O_3$	0.6	tr.	0.4	1.38	0.00	0.26
Er <sub>2</sub> O <sub>3</sub>	0.2	0.37	0.3	1.65	0.00	0.22
$Tm_2O_3$			0.1	0.54		0.04
$Yb_2O_3$	0.1	0.72	0.7	7.01	0.18	0.41
$Lu_2O_3$			0.2	1.68	0.00	0.08
ZrO <sub>2</sub>	2.0	0.36		2.28	1.65	0.20
$HfO_2$				0.55		0.02
SiO <sub>2</sub>	44.4	45.19	46.2	37.59	44.63	44.60
$Al_2O_3$	1.1	0.07		0.61	1.05	0.81
total	99.6	97.16	100.7	99.21	99.32	**99.72
		Ator	mic contents	*		
Mg apfu				0.020		0.004
Ca	0.075	0.002		0.011		0.005
Mn	0.093	0.034		0.030	0.011	0.001
Fe	0.049	0.096	0.052	0.081	0.046	0.049
Sc	1.655	1.694	1.844	1.138	1.816	1.705
Y	0.044	0.061	0.044	0.493	0.054	0.053
Ce			0.005			0.001
Gd			0.002			0.002
Dy	0.008	tr.	0.005	0.023	0.000	0.004
Er	0.003	0.005	0.004	0.027	0.000	0.003
Tm			0.001	0.009		0.001
Yb	0.001	0.010	0.009	0.112	0.002	0.006
Lu			0.003	0.026	0.000	0.001
Zr	0.043	0.008		0.058	0.035	0.004
Hf				0.008		0.000
$\Sigma A$	1.964	1.910	1.969	2.036	1.963	1.838
Si	1.943	1.997	2.000	1.962	1.946	1.958
Al	0.057	0.003		0.038	0.054	0.042
$\Sigma B$	2.000	2.000	2.000	2.000	2.000	2.000

" Ascribed to Mn<sub>2</sub>O<sub>3</sub> instead of MnO because of its color. tr.: traces

<sup>##</sup> The total includes other elements present in minor amounts; see Foord *et al.* (1993). \* Normalized to 2 (Si + Al) atoms per formula unit (*apfu*).

(1) Average of three points; sought, but not found: Hf, Nb.

<sup>(2)</sup> Average of 11 points; sought, but not found: Hf, Nb; same specimen as in line 1 in

Table 4.

(3) From Voloshin *et al.* (1991).

<sup>(4)</sup> Same *REE*- and Y-rich specimen as in line 6 of Table 4; Bianchi et al. (1988).

<sup>(5)</sup> Same Y- and *REE*-poor specimen as in line 8 in Table 4; Bianchi et al. (1988).

<sup>(6)</sup> Same Y- and REE-poor specimen as in line 7 in Table 4; Foord et al. (1993).

as zinnwaldite, fluorite, and topaz [see, for instance, Phan (1963), and references therein]; the miarolitic cavities at Baveno and Cuasso al Monte are related to this kind of occurrence. It should be remarked that Sc, together with other elements that commonly occur in these veins, especially Zr, Be, Al, Fe and the *REE*, forms very stable fluoride complexes.

In order to account for the origin of specific Sc minerals, since scandium is rare, and as its properties are similar to those of Y and the *REE*, a process of very selective enrichment of this element is needed, and the role of formation and disruption of such complexes may be essential (Gramaccioli *et al.* 1999 a, b, 2000).

Here, some thermodynamic data are available. For instance, the first stability constants,  $K = [MeF^{(n-1)+}]/[Me^{n+}][F^-]$ , of such complexes (as a decimal logarithm, at room temperature) range from 9.80 (Zr) to 7.65 (Th), 7.10 (Al), 7.08 (Sc), 6.04 (Fe<sup>3+</sup>), 5.89 (Be), 5.76 (Mn<sup>3+</sup>), 4.85 (Sn), 4.81 (Y), 4.48 (Yb), 3.56 (La), *etc.*; for the subsequent stability constants concerning complexes richer in fluorine,  $K = [MeF_2^{(n-2)+}]/[MeF^{(n-1)+}][F^-]$ , *etc.* the trend is similar, *i.e.*, those of Zr being the most stable, followed by those of Th, *etc.*; an exception to this trend is the couple Al–Sc, where the stability commonly is reversed (Lourié 1975), thereby enhancing the possibility of complexing scandium.

In view of the great differences in the stability of such complexes, in the presence of adequate concentrations of the fluoride ion in the depositing solutions, even if the concentrations of all these elements in the solutions were comparable, the values of the activity of the corresponding free ions could easily differ by several orders of magnitude. Accordingly, the chemical behavior of scandium in these conditions should notably differ from that of yttrium and the *REE* on one hand and from that of zirconium on the other (Gramaccioli *et al.* 1999a, b, 2000).

If the activity of the fluoride ion in a solution is reduced, a *dramatic* increase in the activity of the "free" cations necessarily follows, owing to the disruption of the fluoride complexes. For instance, such a case can occur as a consequence of the deposition of fluorinerich minerals (such as fluorite or micas such as zinnwaldite, *etc.*, which are abundant in the miarolitic cavities at Baveno and Cuasso al Monte); this deposition may result from variations of temperature (or pressure), or may also be due to mixing with an externally derived fluid phase.

On examining the present results obtained for Cuasso al Monte and Baveno, evidence in favor of such a process is available. First of all, in spite of the chemical similarity among Sc, Y and the *REE*, bazzite, cascandite, jervisite, and scandiobabingtonite are always pure (Mellini & Merlino 1982, Mellini *et al.* 1982, Orlandi *et al.* 1998), and thortveitite is commonly very pure.

Whereas the structures of the other Sc minerals appear to be selective, that of thortveitite in particular can host notable quantities of other elements such as Y, Zr, and the *REE* (Table 6) without extensive rearrangement. This low selectivity is further confirmed by the existence of well-known synthetic and natural *REE*- or Zrdominant equivalents of this mineral (Smolin & Shepelev 1970, Voloshin *et al.* 1983, 1985, Roelofsen-Ahl & Peterson 1989). For this reason, the relative purity of some samples of thortveitite cannot be entirely ascribed to crystal-chemical reasons, and must reflect the importance of the chemistry of the depositing solutions.

Since the same process leading to enrichment of Sc in minerals necessarily leads to its depletion in the depositing solutions, with consequent relative enrichment of Zr, Y or of the *REE*, this accounts for the existence in the same locality of pure and impure varieties of thortveitite formed at various stages. If other more selective Sc minerals are being formed, the same process leads to the eventual deposition of specific *REE* minerals, such as complex *REE* oxides, gadolinite, or even zircon, of which a Sc-rich variety occurs at Baveno (Gramaccioli *et al.* 1998).

On these grounds, in the presence of a sufficient concentration (activity) of fluorides or other ligands in the depositing solutions, we might expect that the chemical behavior of Sc and of the other elements should more or less follow the range of the stability constants of the corresponding complexes. It is interesting to note that in the range of stability constants shown above, the elements ranging from Al to Be are just those occurring (besides Si) in bazzite, and at least many of those ranging from Sc (Zr) to Yb are the most significant components of thortveitite or of the others Sc-rich species from Baveno.

However, in spite of the stability of its complexes, aluminum does not seem to follow the other elements; it always remains a minor component of these scandium-rich minerals, although it is difficult to believe that it is not available in the depositing solutions. Whereas the selectivity of the crystal structure can account for most instances, bazzite in particular should not be too selective, its Al-dominant counterpart being beryl.

The remarkably limited content of Al in bazzite was taken as an indicator of partial miscibility occurring between this mineral and beryl (Hänni 1980, Weibel *et al.* 1990, Della Ventura *et al.* 2000); such a conclusion is in agreement with early observations by Frondel & Ito (1968), who found that substitution of Fe, Cr, *etc.* for Sc, but not for Al, can be extensive but does not extend to the Sc-free end-member composition. Although the existence of a miscibility gap would not contradict our theory concerning the formation of Sc minerals, the presently available data are not, in our opinion, sufficient to draw a definitive conclusion, and other possibilities should be considered.

For instance, at thermodynamic equilibrium or near equilibrium, the activity of the components in bazzite and in the depositing solutions should be strictly connected with the activity of the corresponding chemical species in the accompanying minerals. Among these minerals, feldspars are always in close association, and locally are intergrown with bazzite, as in the Norwe-gian occurrence (Juve & Bergstøl 1990).

A possible equilibrium between beryl (here considered as a component of a certain mineral of its group) and an alkali feldspar can be expressed as follows:

$$\begin{array}{l} Be_{3}Al_{2}Si_{6}O_{18}+2K^{+}+4\ H^{+}\rightarrow 2KAlSi_{3}O_{8}\\ +\ 3Be^{2+}+2H_{2}O\end{array}$$

If the activity of  $KAlSi_3O_8$  is considered to be constant, and the solution is dilute, then:

$$K = \exp(-\Delta G^{\circ}/RT) = [aBe^{2+}]^{3}/([aK^{+}]^{2}[aH^{+}]^{4}$$
  
[\gamma.x Be\_{3}Al\_{2}Si\_{6}O\_{18}])

where *a* represents the activities of the corresponding species in the depositing solution. For the beryl compound Be<sub>3</sub>Al<sub>2</sub>Si<sub>6</sub>O<sub>18</sub>, the product  $\gamma$ .x between its activity coefficient and the molar fraction in the crystal has been used *in lieu* of the activity. On these grounds, such a molar fraction depends very strongly upon the pH, and it is instead (formally) independent of the Al activity in the depositing solution: in particular, a low value of pH in the depositing solution prevents the formation of an Al-rich member of the beryl group, and *vice versa*.

Therefore, for a low pH, even if a non-negligible concentration of the Be<sup>2+</sup> ion were present in these solutions, no deposition of "common" beryl would take place, and if this mineral were present already, it would be destroyed to deposit feldspar. However, as an alternative, the deposition of another beryl-group mineral containing Be<sub>3</sub>Al<sub>2</sub>Si<sub>6</sub>O<sub>18</sub> as a minor component could equally occur, provided the pH and the activity of the Be<sup>2+</sup> ion are not too low, the activity of alkali ions is not too high, and "free ions" of elements replacing Al are present in sufficient concentration. Such chemical parameters might not differ extensively in most of the observed localities yielding bazzite, thereby accounting for its almost constant composition.

Among these "free ions", the most important for our purposes are  $Sc^{3+}$  and  $Fe^{3+}$ , which can derive from dissociation of their fluoride complexes and cannot enter the feldspar structure in substantial amounts. In other words, the corresponding equilibrium reaction between Sc-substituted (or Fe-substituted) beryl:

$$\begin{array}{l} Be_{3}Sc_{2}Si_{6}O_{18}+2K^{+}+4\ H^{+}\rightarrow 2KScSi_{3}O_{8}\\ +\ 3Be^{2+}+2H_{2}O\end{array}$$

cannot proceed beyond a certain point, because the feldspar structure can hardly accommodate scandium (or iron); this crystal-chemical detail involving an accompanying mineral, together with the particular stability of the beryl structure, which captures scandium, may account for the very existence of bazzite even in absence of other scandium-rich minerals; moreover, this is another reason (apart from the values of the ionic radii) for explaining the presence of notable amounts of Fe (instead of Al) in all natural specimens of bazzite (Table 5).

The highest Fe content (up to nearly 7 wt%  $Fe_2O_3$ ) observed in bazzite might be interpreted as corresponding approximately to the limit of solubility of this element in the mineral. However, in view of the isomorphism between Sc3+ and Fe3+ in octahedral coordination, it is difficult to imagine that there are limits for such a substitution. In any case, Frondel & Ito (1968) synthesized a series of Sc-doped compositions, but they could not obtain the pure end-member Be<sub>3</sub>Fe<sup>3+</sup><sub>2</sub>Si<sub>6</sub>O<sub>18</sub>. The synthetic bazzite obtained by these authors contains a maximum of 1/3 Fe (atomic), although they argued that the series "may extend to about 50% Fe<sup>3+</sup> or somewhat over". On the contrary, this end-member was actually synthesized by Hänni (1980) from chemical reaction of the solutions with the steel container, and a mineral of a similar composition, stoppaniite, has been discovered recently (Ferraris et al. 1998, Della Ventura et al. 2000).

A possible explanation of the conflicting views concerns the oxidation state of iron, which was apparently not checked by Frondel & Ito in their products. If most Fe is present as  $Fe^{2+}$  instead of  $Fe^{3+}$  (as seems to be the case with many natural specimens) and only considering the requirements of charge balance, it is quite reasonable to imagine that a limit to the Mg or Fe<sup>2+</sup> content in beryl or bazzite should exist, thereby providing a reason for the limited Fe (and Mg) content of bazzite. This limit may vary with temperature, or with the presence of alkali ions in the structure, which favor charge balance. It should be remarked, however, that such a process cannot proceed beyond a certain limit, because a high concentration of the alkali ions in the solution (which should be in equilibrium with the corresponding concentration in the crystal) shifts the above-described chemical equilibrium in favor of feldspar.

Another possibility might be that the complexes of  $Fe^{2+}$  are less stable than those of  $Fe^{3+}$ , and therefore in reducing conditions the position of iron in the series of stability constants is not so close to that of scandium. In any case, the question is still open. The very likely presence of the easily hydrolyzable  $Mn^{3+}$  in the blue variety of thortveitite is another point in favor of the presence of notable amounts of fluorides in the depositing solutions (Gramaccioli *et al.* 1999b, 2000).

A paragenetic sequence of the minerals deposited in the miarolitic cavities at Baveno and Cuasso al Monte has been reported by Pezzotta *et al.* (1999) and is in substantial agreement with our present theory. Following this sequence, at Baveno the deposition of fluoriderich minerals such as especially zinnwaldite led to breakdown of the Be complexes, enhancing the activity of the free Be<sup>2+</sup> ion in the solution and allowing the deposition of beryllium minerals, such as bavenite, bertrandite, gadolinite, or gugiaite; a subsequent deposition of fluorite led to the breakdown of the most stable complexes, such as those of Sc, thereby allowing for the formation of bazzite first (when the concentration of the Be ion was still reasonably high in the solution), and finally of thortveitite or of the other scandium minerals, such as cascandite, jervisite, or scandiobabingtonite, of which Baveno is the type locality.

According to the same authors, at Cuasso al Monte many late-stage minerals, including Be silicates, were deposited by late hydrothermal fluids, thereby altering the sequence observed at Baveno. It should be remarked that these beryllium minerals at Cuasso al Monte are not exactly the same found at Baveno: for instance, bavenite, for which Baveno is the type locality, is altogether absent at Cuasso al Monte.

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