

Stoppaniite, $(\text{Fe,Al,Mg})_4(\text{Be}_6\text{Si}_{12}\text{O}_{36})^*(\text{H}_2\text{O})_2(\text{Na},\square)$ a new mineral of the beryl group from Latium (Italy)

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Abstract: This paper relates the finding of stoppaniite, a new mineral of the beryl group, at Capranica, Vico volcanic complex, Latium, Italy. Stoppaniite occurs inside the miarolitic cavities of a volcanic ejectum, as very rare, transparent, light-blue, hexagonal-prismatic euhedral crystals, up to 0.5 mm in length. It is optically uniaxial (-), and shows a weak pleochroism from colourless to very light blue. The refraction indices are: $\epsilon = 1.619(3)$ and $\omega = 1.625(3)$; the density is: $D_{\text{obs}} = 2.79(3) \text{ g/cm}^3$, $D_{\text{calc}} = 2.811 \text{ g/cm}^3$. Stoppaniite is hexagonal, s.g. $P6/mcc$, with $a(\text{\AA}) = 9.397(1)$, $c(\text{\AA}) = 9.202(2)$. Strongest X-ray powder diffraction lines (Gandolfi camera) are (d in $\text{\AA}$, intensities visually estimated): 3.278 (νS), 8.12 (S), 2.903 (S), 4.00 (m), 2.553 (mw), 1.752 (mw).

The empirical crystal-chemical formula is:

$(\text{Fe}^{3+}_{2.70}\text{Mg}_{0.64}\text{Al}_{0.42}\text{Mn}_{0.06}\text{Ti}_{0.02}\text{Sc}_{0.02})(\text{Be}_{6.88}\text{Si}_{11.60})\text{O}_{36} \cdot 2\text{H}_2\text{O}(\text{Na}_{0.94}\text{K}_{0.02}\text{Cs}_{0.02})$
compatible with the simplified formula:

$(\text{Fe}^{3+})_3(\text{Mg,Fe}^{2+})\text{Na}(\text{Be}_6\text{Si}_{12}\text{O}_{36}) \cdot 2\text{H}_2\text{O}$, or ideally $\text{Fe}^{3+}_4\text{Be}_6\text{Si}_{12}\text{O}_{36}$.

A rational classification of beryl group minerals based on the octahedral occupancy is proposed.

Key-words: new mineral, stoppaniite, beryl group, Vico volcanic District, Italy.

Introduction

The volcanic ejecta, scattered at random in the pyroclastic formations widespread throughout the Roman Comagmatic Region of central Italy, are an unexhausted source of rare or new minerals. Most of them occur in the vugs of holocrystalline to

hypocrystalline rocks of syenitic composition, consisting mostly of sanidine, and locally known as "sanidinites" (Della Ventura *et al.*, 1992). This paper relates the occurrence of a new mineral belonging to the beryl group from one of these rocks. The ejectum was collected in the Vico Volcanic District, north of Rome, at Capranica

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(Viterbo). The name stoppaniite is in honour of Dr. Francesco Saverio Stoppani (born in 1947), a distinguished mineral amateur active in the volcanic regions of Latium. Both name and species have been approved by the Commission for new minerals and mineral names of I.M.A. (April 1996). The type and cotypes materials are deposited at Museo di Mineralogia, Università di Roma "La Sapienza" number MMUR-29900/1 and in the mineralogical collection of the Museum National d'Histoire Naturelle of Paris (catalog no. 198.14). Note that the species fully described here is the same for which Ferraris *et al.* (1998) recently gave structural details.

Occurrence

The ejectum where stoppaniite was found was collected by one of us (Paolo Rossi) inside an explosive breccia belonging to the so called "C" pyroclastic flow unit (Locardi, 1965). Stoppaniite occurs inside the miarolitic cavities of the ejectum as very rare transparent, light-blue, hexagonal prismatic euhedral crystals, up to 0.5 mm in length (Fig. 1). Other minerals typically associated in the vugs where stoppaniite occurs are: biotite, quartz, sanidine, hematite, danburite, helvite, hellandite, allanite-(Ce) and a not yet completely characterized gadolinite-like mineral.

Physical properties

Stoppaniite has a white streak and a vitreous lustre. It shows the usual {001} basal parting of the beryl-group minerals. The density was measured by immersion in Clerici solution at 25°C; the density of the liquid was then determined with a micropipnometer. It is $D_{\text{obs}} = 2.79(3) \text{ g/cm}^3$. This value is in good agreement with the density calculated from the chemical formula (see later), $D_{\text{calc}} = 2.811 \text{ g/cm}^3$. Stoppaniite is optically uniaxial (-), and shows a weak pleochroism from colourless to very light blue. The refraction indices, measured with $\lambda = 589 \text{ nm}$ light, are: $\epsilon = 1.619(3)$ and $\omega = 1.625(3)$. The compatibility index (Gladstone-Dale), calculated according to Mandarino (1981), is 0.05, indicating a good agreement between the physical and chemical properties.

X-ray crystallography

Single-crystal XRD refinement (Ferraris *et al.*,



Fig. 1. Euhedral crystal of stoppaniite in the vug of the ejectum. Field-width ~ 2 mm.

1998) confirms that stoppaniite has the $P6/mcc$ space-group symmetry of beryl (Gibbs *et al.*, 1968) and bazzite, the Sc-analogue of beryl (Peyronel, 1956; Armbruster *et al.*, 1995). The X-ray powder-pattern of stoppaniite (Table 1), obtained with a Gandolfi camera (114.7 mm

Table 1. X-ray powder diffraction data for stoppaniite.

Iobs	Icalc	dmeas	dcalc	hkl
S	65	8.12	8.14	0 1 0
w	10	4.60	4.60	0 0 2
m	38	4.00	4.00	0 1 2
vS	100	3.278	3.287	-1 2 2
vw	7	3.043	3.048	0 2 2
S	64	2.903	2.917	-1 3 1
vw	10	2.702	2.713	0 3 0
mw	18	2.553	2.557	-1 3 2
w	9	2.304	2.301	0 0 4
vw	5	2.178	2.192	-1 4 1
			2.172	-1 3 3
vw	6	2.023	2.026	-1 4 2
vw	8	2.000	2.003	0 2 4
vw	8	1.812	1.818	-1 4 3
w	16	1.766	1.776	-1 5 0
mw	18	1.752	1.754	0 3 4
vw	5	1.735	1.744	-1 5 1
w	17	1.642	1.644	-2 4 4
w	10	1.535	1.537	-1 5 3
w	16	1.459	1.459	-2 6 2
			1.458	-1 2 6
vw	12	1.296	1.303	-2 7 0
			1.301	0 6 2

Intensities visually estimated: S = strong; m = medium, w = weak; v = very.

radius, $\text{CuK}\alpha$, Ni-filtered radiation), was indexed on the basis of single-crystal XRD intensities. Cell dimensions were refined using the Appleman & Evans (1973) least-squares program. They are given in Table 2 and compared with the data of other beryl-group minerals from the literature.

Chemistry

The grain used for single-crystal X-ray data collection was embedded in epoxy resin and analyzed at the CAMPARIS, University of Paris VI (Pierre et Marie Curie), on a CAMECA SX50 microprobe, in the WD mode with operating voltage 15 kV and beam current 10 nA. Natural minerals were used as standards, except MnTiO_3 (for Mn, Ti) and metallic Sc (Sc). Data were corrected according to Pouchou & Pichoir (1984). Analytical conditions for Be were: synthetic BeO as standard (BeO has the same $\text{BeK}\alpha$ peak form as silicates in order to eliminate possible chemical effects like peak shift); Mo/ B_4C (2d = 200 Å) as monochromator; 10 kV and 100 nA beam current; counting time: 20 s on peak ($\text{BeK}\alpha$) and 20 s on background. The peak/background intensity ratio was $\cong 2.5$. Possible interferences between $\text{BeK}\alpha$ and $\text{SiL}_{\text{II,III}}$ peaks was verified both on the BeO standard and on the stoppaniite sample. In

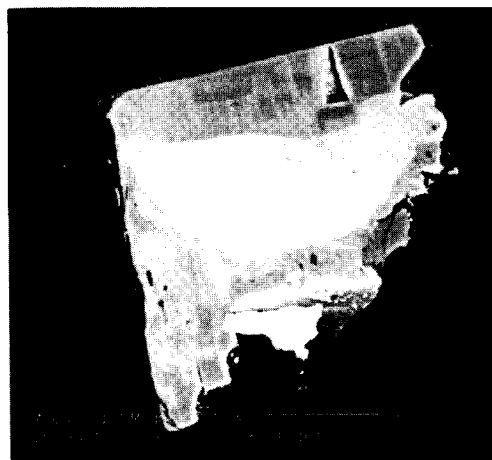


Fig. 2. Back-scattered-electron image of the analysed grain.

order to eliminate them, choice of the background was made, after a profile peak study, at -7000 and +19000 steps (1 step = 25.10^{-5} Bragg sine angle).

A backscattered SEM image (Fig. 2) of the analyzed grain shows two well-defined zones, with different bulk average atomic numbers. 19 point-analyses were done on each part. The micro-chemical analyses show that the sample consists of a Fe-rich "core" (S part, "stoppaniite") and a (Fe,Al)-rich "rim" (B part, "beryl"). Table 3 gives the average data for both the S and B portions of the grain. The S/(S+B) bulk mass-ratio, according to the XRD structural refinement (Ferraris *et al.*, 1998) is estimated to be = 0.75. The empirical formulae, also given in Table 3, were calculated assuming 36 oxygens in the anhydrous part of the structure. Note that Ferraris *et al.* (1998) give a different calculation basis (22 M + T cations) for the stoppaniite formula to account for the probable presence of OH in the structure. However, both their and our calculation procedures give very similar results. The major chemical differences between parts B and S (Table 3) are in the Al_2O_3 vs FeO_{tot} and in the BeO contents. The total alkali contents are constant around 1 apfu, and Na is for both parts the dominant occupant of the channel site(s).

In calculating the crystal-chemical formulae, all iron was converted into Fe^{3+} . With this procedure, the cation sums at the octahedral sites are close but slightly less than the ideal value 4, suggesting that most, if not all, iron is in fact in the

Table 2. Cell parameters of stoppaniite and related minerals.

	$a(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$	c/a
1	9.346(3)	9.213(6)	697.0	0.986
2	9.397(1)	9.202(2)	703.7	0.979
3	9.254(1)	9.195(1)	681.9	0.994
4	9.292(1)	9.193(1)	687.4	0.989
5	9.30	9.20	689.1	0.989
6	9.212(4)	9.187(6)	675.2	0.997
7	9.56	9.16	725.0	0.958

- 1) Stoppaniite, this work, powder pattern.
- 2) Stoppaniite, Ferraris *et al.* (1998), single-crystal.
- 3) Blue beryl from Ariege (Fontan & Fransolet, 1982).
- 4) Blue beryl from Ireland (Sanders & Doff, 1991).
- 5) "Femag beryl" (Schaller *et al.*, 1962).
- 6) Synthetic Al-beryl (Gibbs *et al.*, 1968).
- 7) Synthetic Sc-beryl (Frondel & Ito, 1968)

Table 3. Chemical analyses and crystal-chemical formulae for S and B parts of the stoppaniite crystal.

	S	range	B	range
SiO ₂	59.13	58.31-59.77	61.60	0.86-62.22
Al ₂ O ₃	1.80	1.45- 2.16	7.99	6.36- 9.09
Fe ₂ O ₃	18.36	17.50-19.30	8.51	6.93-10.56
Sc ₂ O ₃	0.08	0.05- 0.09	0.04	0.01- 0.06
TiO ₂	0.11	0.05- 0.18	0.52	0.25- 0.94
MgO	2.21	2.04- 2.40	2.76	2.38- 3.02
MnO	0.41	0.28- 0.50	0.14	0.04- 0.19
SnO ₂	0.03	0.00- 0.06	0.07	0.01- 0.25
Na ₂ O	2.47	2.04- 2.70	2.50	2.24- 2.68
K ₂ O	0.08	0.04- 0.13	0.03	0.01- 0.04
Cs ₂ O	0.19	0.14- 0.26	0.34	0.24- 0.48
BeO	14.59	12.81-15.88	13.16	11.60-14.56
H ₂ O	(2.98)		(3.08)	
Tot	102.44		100.74	

	Formulae based on 36 O		W.M.
Si	11.60	11.92	11.72
Be	0.88	0.12	0.58
ΣT ⁺	12.48	12.04	12.30
Be	6.00	6.00	6.00
Al	0.42	1.82	0.98
Fe ³⁺	2.70	1.24	2.12
Mg	0.64	0.80	0.70
Mn	0.06	0.02	0.04
Ti	0.02	0.08	0.04
Sc	0.02	0.00	0.02
ΣOct	3.86	3.96	3.90
Na	0.94	0.94	0.94
Cs	0.02	0.02	0.02
K	0.02	0.00	0.02
ΣCh	0.98	0.96	0.98

W.M. = weighted mean according to Ferraris *et al.* (1998).

trivalent state, in agreement with the work of Duchi *et al.* (1993) which shows that iron occurs as Fe³⁺ in Fe-rich beryls from Alpi Apuane (Italy).

The B part of the grain has Al apfu > Fe³⁺ apfu (Table 3). However, almost all point-analyses in part B show Al apfu to be less than 2.0, thus part B has a composition different from the one of a "normal" beryl (Fig. 3), which should, in principle, have Al apfu > 2.0 in the octahedral site. Part B is indeed an extreme case of what has been called "femag-beryl" (Schaller *et al.*, 1962), *i.e.* a beryl with extensive Mg-Fe substitution at the Al site. The S part has Fe³⁺ >> Al apfu and represents what we describe here as stoppaniite.

Regarding the composition of the tetrahedral sites, part S systematically shows the presence of significant amounts of Be at the T⁺ tetrahedral site (≈ 0.45 apfu). All microprobe data of part B show a Be content very close to the ideal value of 6 apfu and a Si content very close to the ideal value of 12

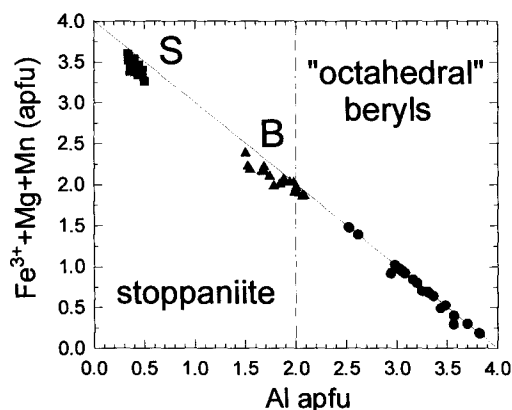


Fig. 3. Relationship between the Al content versus octahedral substitutions at the Al-site. S = stoppaniite (19 points); B = beryl (19 points). Filled dots: beryl data from the literature (source: Bakakin *et al.*, 1970 and Aurisicchio *et al.*, 1988).

apfu, whereas all analyses of part S show Be apfu significantly higher than 6 and Si lower than 12. When discussing the data for Be in terms of beryl crystal-chemistry, analytical uncertainties must be taken into account. However this difference cannot be assigned to systematic errors in the analysis of two fragments of the same crystal, and suggests that significant amounts of Be do indeed substitute for Si into the T'' site of stoppaniite. The presence of Be at T'' is also confirmed by single-crystal XRD (Ferraris *et al.*, 1998).

The microRaman spectrum of stoppaniite (Parodi *et al.*, 1996) shows that there is a fairly similar amount of H₂O in both the B and S zones of the crystal. The spectrum consist in a well-defined doublet centered at 3595-3588 cm⁻¹ and is similar to all other Raman spectra measured on water-bearing beryls (Hagemann *et al.*, 1990; Charoy *et al.*, 1996). This doublet is assigned, in analogy with IR spectra, to type II water molecules.

Cell parameters

The complex crystal-chemistry of beryls was re-evaluated by Aurisicchio *et al.* (1988) on the basis of well-characterized chemical and structural data on samples with different compositions and from different sources. It is well known (Bakakin *et al.*, 1966) that all natural beryls belong to two solid-solution series: (i) octahedral-substituted beryls and (ii) tetrahedral-substituted beryls. Both series are characterized by well-defined ranges of *c/a* values. In particular, the *a* cell-edge is very sensitive to octahedral substitutions, while the *c* cell-edge is very sensitive to tetrahedral substitutions (Bakakin *et al.*, 1966; Aurisicchio *et al.*, 1988).

Fig. 4(a) shows the relationships between the *a* parameter and the mean radius at the octahedral site for stoppaniite, plotted next to several synthetic and natural beryls from the literature. It is apparent that the *a* parameter of the beryl structure is a linear function of the aggregate size of the octahedral cation. Synthetic bazzite (Table 2; Fig. 4a) has the *a* edge 0.35 Å longer than synthetic Al-beryl, and this value is close to the difference in ionic diameter between Sc and Al (0.42 Å, from Shannon, 1976). All data for octahedrally substituted beryls from the literature show a well defined linear relationship between *a* and $\langle r_{\text{oct}} \rangle$ (Fig. 4a). Such an ideal behaviour for the *a* parameter is also evident for stoppaniite. Note that the $\langle r_{\text{oct}} \rangle$ for stoppaniite used in Fig. 4 has been calcu-

lated on the basis of the crystal chemical formula of Table 3, with all Fe as Fe³⁺. The almost perfect correspondance between *a* and $\langle r_{\text{oct}} \rangle$ calculated for stoppaniite supports our inference that most if not all Fe is indeed trivalent. The same kind of linear trend is also observed for the cell volume (Fig. 4b).

Nomenclature of the beryl groups

The discovery of the natural Fe³⁺-beryl related here suggests that, in the beryl structure, the octa-

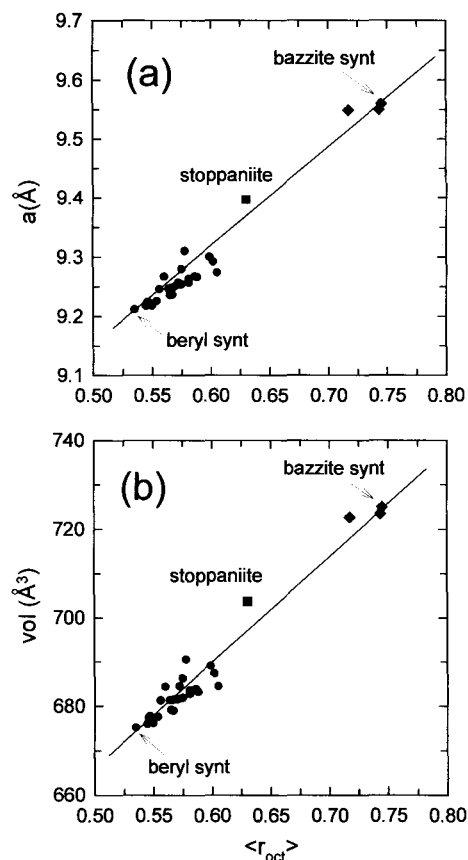


Fig. 4. Plot of (a) the *a* cell edge and (b) the unit-cell volume for stoppaniite and other synthetic and natural beryl-type minerals from the literature as a function of $\langle r_{\text{oct}} \rangle$. Data from Schaller *et al.* (1962), Frondel & Ito (1968), Gibbs *et al.* (1968), Bakakin *et al.* (1970), Fontan & Franolet (1982), Aurisicchio *et al.* (1988), Juve & Bergstøl (1990), Sanders & Doff (1991). Filled dots: beryls; filled square: stoppaniite; filled diamonds: bazzites).

hedral site can be extensively occupied by different trivalent cations. Substitutions at the tetrahedral site are limited (Aurischio *et al.*, 1988), while the channels sites can be randomly occupied by alkali cations $\pm$ water molecules ($\pm$ OH and CO₂), when needed to balance the overall charge neutrality of the structure.

For these reasons the beryl-group minerals should be classified according to the octahedral site occupancy. The data available in the literature and those reported here allow us to propose a classification diagram (Fig. 5) where all beryls can be grouped into three regions having Al (beryl), Sc (bazzite) and Fe³⁺ (stoppaniite), respectively, as their dominant octahedral cation. Note how the ternary solubility among the three end-members is limited within the triangle: there is some solubility along the Al - Fe³⁺ and Sc - Fe³⁺ binary joins, while there seems to be no Al-Sc exchange in the structure, as already suggested by Hänni (1980).

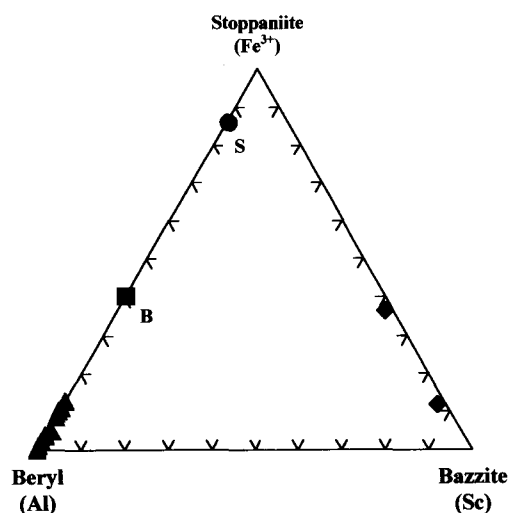


Fig. 5. Ternary classification diagram for natural beryl-group minerals. S and B are the different parts of the studied crystal. Triangles: beryls; diamonds: bazzites; data source as in Fig. 4.

Moreover, although beryl minerals have been extensively studied and a great number of chemical data is available in the literature, no ternary compositions have been reported so far. According to Fig. 5, almost all natural beryl-group minerals belong to the "normal", Al-rich, beryl type, whereas both bazzite and stoppaniite have to be considered as very rare minerals.

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References

- Appleman, D.E. & Evans, H.T. (1973): Indexing and least-square refinement of powder diffraction data. Job 9412. *U.S. Geol. Survey Comp. Contrib.*, **20**, 62 p.
- Armbruster, Th., Libowitzky, E., Diamond, L., Auernhammer, M., Bauerhansl, P., Hoffmann, Ch., Irran, E., Kurka, A., Rosenstingl, H. (1995): Crystal chemistry and optics of bazzite from Furkabasistunnel (Switzerland). *Mineral. Petrol.*, **52**, 113-126.
- Aurischio, C., Fioravanti, G., Grubessi, O., Zanazzi, P.F. (1988): Reappraisal of the crystal chemistry of beryl. *Am. Mineral.*, **73**, 826-837.
- Bakakin, V.V., Rylov, G. M., Belov, N.V. (1966): Correlation between the chemical composition and unit cell parameters of beryls. *Doklady Akad. Nauk SSSR*, **173**, 129-132.
- , —, — (1970): X-ray diffraction data for identification of beryl isomorphs. *Geochemistry Int.*, **1970**, 924-933.
- Charoy, B., de Donato, F., Barres, O., Pinto-Choelo, C. (1996): Channel occupancy in an alkali-poor beryl from Serra Branca (Goiás, Brasil): Spectroscopic characterization. *Am. Mineral.*, **81**, 395-403.
- Della Ventura, G., Di Lisa, G.A., Marcelli, M., Mottana, A., Paris, E. (1992): Composition and structural state of alkali feldspars from ejecta in the Roman potassic province, Italy; petrological implications. *Eur. J. Mineral.*, **4**, 411-424.
- Duchi, G., Franzini, M., Giamello, M., Orlandi, P., Riccobono, F. (1993): The iron-rich beryls of Alpi Apuane. Mineralogy, chemistry and fluid inclusion. *N. Jb. Miner. Mh.*, **H. 5**, 193-207.
- Ferraris, G., Prencipe, M., Rossi, P. (1998): Stoppaniite, a new member of the beryl group: crystal structure and crystal-chemical implications. *Eur. J. Mineral.*, **10**, 491-496.
- Fontan, F. & Fransolet, A.M. (1982): Le beryl bleu rich en Mg, Fe et Na de la mine de Lassur, Ariège, France. *Bull. Minéral.*, **105**, 615-620.
- Fron del, C. & Ito, J. (1968): Synthesis of the scandium analogue of beryl. *Am. Mineral.*, **53**, 942-953.
- Gibbs, G.V., Breck, D.W., Meagher, E.P. (1968): Structural refinement of hydrous and anhydrous

- synthetic beryl, $\text{Al}_2(\text{Be}_3\text{Si}_6)\text{O}_{18}$ and emerald, $\text{Al}_{1.9}\text{Cr}_{0.1}(\text{Be}_3\text{Si}_6)\text{O}_{18}$. *Lithos*, **1**, 275-285.
- Hagemann, H., Lucken, A., Bill, H., Gysler-Sanz, J., Stalder, H.A. (1990): Polarized Raman spectra of beryl and bazzite. *Phys. Chem. Mineral.*, **17**, 395-401.
- Hänni, H.A. (1980): Mineralogische und mineral-chemische Untersuchungen an Beryll aus alpinen Zerrklüften. Dissertation, Universität Basel.
- Juve, G. & Bergstøl, S. (1990): Caesian bazzite in granite pegmatite in Tordal, Telemark, Norway. *Mineral. Petrol.*, **43**, 131-136.
- Locardi, E. (1965): Tipi di ignimbrite di magmi mediterranei: le ignimbrite del vulcano di Vico. *Atti Soc. Tosc. Sc. Nat., ser. A.*, **72**, 55-173.
- Mandarino, J.A. (1981): The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. *Can. Mineral.*, **19**, 441-450.
- Parodi, G.C., Smith, D.C., Della Ventura, G. (1996): The Raman spectrum of the new mineral stoppaniite: the Fe^{3+} equivalent of beryl. *Terra Abstracts*, **8**, 21.
- Peyronel, G. (1956): The crystal structure of Baveno bazzite. *Acta Cryst.*, **9**, 181-186.
- Pouchou, J.L. & Pichoir, F. (1984): Un nouveau modèle de calcul pour la microanalyse quantitative par spectrométrie de rayons X. *La Recherche Aéronautique*, **3**, 167-192.
- Sanders, I.S. & Doff, D.H. (1991): A blue sodic beryl from southeast Ireland. *Mineral. Mag.*, **55**, 167-172.
- Schaller, W.T., Stevens, R.E., Jahns, R.H. (1962): An unusual beryl from Arizona. *Am. Mineral.*, **47**, 672-699.
- Shannon, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.*, **A32**, 751-767.

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