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Zeophyllite from Monte Somma, Vesuvius, Italy

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ABSTRACT. Zeophyllite, a rare calcium silicate, occurs at Monte Somma, Italy, as milky-white, slightly fibrous spherules associated with apophyllite on the surface of pumice in a welded tuff dated 472 AD. The chemical analysis and the indexed powder pattern, along with the chemical formula and unit cell dimensions calculated from these data, are given. The deficiency of Ca and Si cations and the abundance of (OH) and F anions in the chemical formula calculated on the basis of 38 anions (O + F) is interpreted as due to the presence of (O_4H_4) substituting for (SiO_4) tetrahedra and of fluorine instead of oxygen atoms in two anionic sites.

ZEOPHYLLITE is a calcium silicate discovered by Pelikan (1902*a*, *b*) at Litoměřice (= Leitmeritz), Bohemia. Hibsch (1917) reported its presence at Radejšín (= Radzein), Bohemia. Associated with pyrite, epidote, and chlorite, it was described by Fairbanks (1926) in the fractures of a dolomite at Riggins, Salmon River District, Idaho. Chalmers *et al.* (1958) gave a complete crystal-chemical description of zeophyllite from Leitmeritz and, on the basis of both a new chemical analysis and dehydration curve, suggested the chemical formula $Ca_{12}Si_9O_{24}(OH)_6F_6 \cdot 6H_2O$, which differs from that proposed by Pelikan (1902*a*, *b*) for the O and H content. From a crystal structure analysis, Merlino (1972) gave the schematical formula $Ca_{13}Si_{10}O_{28.6}F_{7.4}(OH)_2 \cdot 6H_2O$ for the zeophyllite from Radzein and suggested the existence of substitution of the type (O_4H_4) for SiO_4 in the zeophyllite from Leitmeritz.

This paper describes the first find of zeophyllite in Italy, thereby broadening the crystal-chemical knowledge of this very rare silicate.

Occurrence

In the NW sector of the Somma-Vesuvius volcano, near the town of Pollena Trocchia, is a quarry presently mining pozzolanic ash and sands. Some pyroclastic deposits have accumulated as welded tuffs and lahars and have been described by Di Girolamo (1968) and Franco and Rolandi (1978). Among them, two deposits have been ascribed to the eruptions dated 79 and 472 AD respectively (Delibrias *et al.*, 1979): the first is partially welded by chabazite; the second shows phenocrysts of leucite, clinopyroxenes, and biotite in a finely vesicular glassy groundmass and locally welded by phillipsite and chabazite. The latter deposit is characterized by very friable light brown pumices ranging in size from a few mm to several cm. Most of their surfaces are covered by a very thin transparent crust of phillipsite and K-rich chabazite (De Gennaro *et al.*, 1980). Frequently large leucite crystals rest on these crusts and recently, on some samples collected by one of us (C.P.) from the deposit dated 472 AD, milky-white spherules with a radiating fibrous structure have been observed (fig. 1*a*). The spherules range from 0.1 to 0.5 mm and the largest show a compact nucleus in cross-section. The morphology of the spherules is demonstrated by SEM photographs: in fig. 1*b* a cross-section of a spherule shows lamellar radiating crystals; the lamellar shape of the crystals is clearly visible under high magnification on the surface of the spherule (fig. 1*c*).

The X-ray powder patterns obtained with a Gandolfi camera showed apophyllite to be the constituent of the compact nucleus and zeophyllite as the lamellar crystals.

Crystal chemistry

Chemistry. The chemical composition of zeophyllite was obtained as a combination of microprobe data and TG analyses. The electron microprobe analysis was carried out in the wavelength dispersive mode on an ARL-SEMQ instrument operated at 15 kV and 20 nA probe current and a defocused beam (spot size *c.* 15 μm). On-line

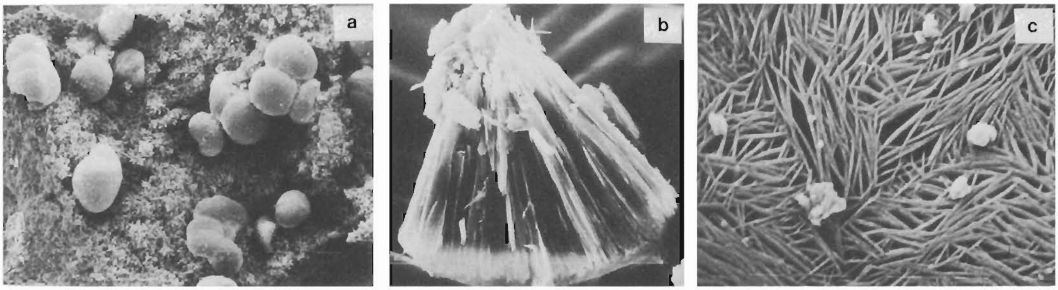

FIG. 1. SEM photographs: (*a*) Zeophyllite spherules on a crust of phillipsite and K-chabazite (35 ×); (*b*) Cross-section of a zeophyllite spherule showing the radiating lamellar crystals (50 ×); (*c*) The surface of a zeophyllite spherule showing the lamellar shape of the crystals (4000 ×).

data reduction was based on the program MAGIC IV (Colby, 1968). Natural albite (Si) and fluorite (Ca and F) were used as standards. A preliminary qualitative test excluded appreciable amounts of Ti, P, Mn, Mg, Sr, Ba, and Fe. The microprobe data were obtained by averaging several point-analyses of various spherulitic grains as the percentage variations among the values thus obtained were within the experimental uncertainty (2–3 % relative). The water content was determined on about 6 mg of material carefully selected under a binocular microscope and separated if necessary from the apophyllitic nuclei. The instrument used was a Du Pont thermal analyser operated in air and with a heating rate of 10 °C/min. From the TG curve it can be seen that zeophyllite begins to lose weight at a very low temperature (40 °C). At higher temperatures the following reactions were observed; a faster reaction rate between 150 °C and 300 °C followed by a slow and gradual weight loss up to 700 °C; a rapid weight loss between 700 °C and 900 °C followed by a slow weight loss until the final temperature of the experiment (*c.* 1100 °C) was reached. The curve shape is in good agreement with that reported for the same mineral by Chalmers *et al.* (1958). Previous crystal-chemical (Chalmers *et al.*, 1958) and structural (Merlino, 1972) work, along with the microprobe analysis, enable the weight loss up to 300 °C (8 %) to be attributed to zeolitic water, between 300 °C and 900 °C (6.4 %) to (OH) groups and after 900 °C to F ions. The chemical analysis is reported in Table I. The F content determined by microprobe analysis was considered reliable, the value obtained by TG being slightly lower.

Due to the very small size of pure grains, the density could not be experimentally determined. Following the suggestions by Merlino (1972) the chemical formula has been calculated on the basis of 38 anions (O + F) (Table I). As previously stated, a temperature of 300 °C has been assumed as distinguishing between zeolitic water and hydroxyl loss; assuming a slightly different temperature only creates a minimal change in the cation content of the chemical formula.

Table I. Chemical analysis, and formula on the basis of 38 (O + F), and unit-cell dimensions of zeophyllite from Monte Somma.

SiO_2	35.47	Si	8.63
Al_2O_3	0.22	Al	0.07
F	11.04	F	8.50
CaO	42.96	Ca	11.18
Na_2O	0.02	Na	0.01
K_2O	0.03	K	0.01
H_2O^-	8.00	H	10.38
H_2O^+	6.40	O	29.50
	104.14	H_2O	6.50
Less O for F	4.65		
Total	99.49		

a(Å) = 9.359(6) ; c(Å) = 36.67(6)

V(Å)^3 = 2782(5) ; D_{calc}(g/cm^3) = 2.60

Error in brackets.

X-ray crystallography. X-ray diffraction data (Table II) have been obtained on a pure zeophyllite spherule using a Gandolfi camera (114.59 mm in diameter) and Cu-*K*α Ni-filtered radiation (λ = 1.54051 Å). A few powdered grains of $Pb(NO_3)_2$ attached to the sample-holder have been used as an internal standard. As some lines of the standard overlap some lines of zeophyllite, a powder pattern without internal standard was also obtained. The data reported in Table II are therefore the combination of the two powder patterns. The reflections have been indexed on a hexagonal cell as the structure factors of the mineral (Merlino, 1972) are based on this cell. Cell dimensions from the powder pattern were determined by a least-squares refinement program using an indexing method (Alberti, 1976) which takes the structure factors (Merlino,

Table II. X-ray powder pattern of zeophyllite from Monte Somma.

h k l	d_{calc}(Å)	d_{obs}(Å)	I/I_1
0 0 3	12.227	12.30	100
0 0 6*	6.112	6.13	50
1 1 0*	4.679	4.673	20
1 1 3*	4.370	4.344	20
2 0 1*	4.028	4.023	20
1 1 6	3.716	3.711	50
2 0 4*	3.707		
2 0 7*	3.205	3.198	40
0 0 12*	3.056	3.051	80
2 1 5*	2.827	2.822	30
2 0 10	2.719	2.694	30
3 0 0*	2.702		
3 0 3*	2.638	2.635	30
2 1 8*	2.547	2.547	40
2 2 0*	2.340	2.351	30
2 2 3*	2.298	2.301	20
3 0 9	2.252	2.236	50
3 1 1*	2.244		
2 2 6	2.185	2.182	30
3 1 4*	2.183		
1 0 17	2.085	2.072	40
3 1 7*	2.066		
2 2 9*	2.029	2.029	40
3 0 12	2.024		
3 1 10*	1.917	1.918	10
1 1 18	1.868	1.859	30
2 2 12*	1.858		
4 1 0*	1.769	1.770	70
2 1 17	1.764		
4 1 3*	1.750	1.755	30
4 1 6*	1.699	1.702	20
3 0 18	1.6267	1.6237	20
3 2 11	1.6239		
4 1 9	1.6224		
5 0 1	1.6194		
3 2 14	1.5163	1.5126	5
3 3 6	1.5114		
4 2 4*	1.5108		
3 1 19	1.4644	1.4571	5
3 3 9*	1.4567		
1 1 24	1.4526		

Indexing based on the hexagonal cell.
I/I_1 *visual. Reflections marked with * have been used in the refinement of the unit cell dimensions.*

1972) into account when assigning the indices. The reflections too far from the standard lines were discarded; therefore only the spacings marked with a star in Table II were used in this calculation. The unit cell dimensions so determined are reported in Table I along with the calculated density.

Conclusions

The chemical composition of the zeophyllite from Monte Somma confirms the possibility of substitution of (O_4H_4) for (SiO_4) in this rare silicate, as already suggested by Merlino (1972). On the basis of the structural data, Merlino recalculated the chemical formulae for zeophyllite samples known at that time. He proposed the schematical formula $Ca_{13}Si_{10}O_{28}[(OH)_3F_7]_{\Sigma 10}\cdot 6H_2O$ with the possibility (sample from Leitmeritz) of a 5% substitution of the type $SiO_4 \longleftrightarrow (OH)_4$ or $Si \longleftrightarrow H_4$. The chemical formula of the zeophyllite from Monte Somma (Table I) can be presented in the same way as:

$$(\square_{1.73}Ca_{11.27})_{\Sigma 13}[Si_{8.63}(H_4)_{1.37}]_{\Sigma 10}$$
$$[O_{24.6}(OH)_{3.4}]_{\Sigma 28}[(OH)_{1.5}F_{8.5}]_{\Sigma 10}\cdot 6.5H_2O.$$

The above-mentioned substitution of Si by H_4 is raised to 13%, and also Ca is vacant in the same frequency. The bond valences, estimated using the Donnay and Allman (1970) method, led Merlino to consider the following anion chemistry in his samples: the two-fold F(1) sites and the six-fold F(3) sites are occupied by fluorine ions with minor substitution by hydroxyl; the two-fold F(2) sites (surrounded by six Ca atoms) are occupied by fluorine and oxygen with a stoichiometric ratio of $F_{0.7}O_{0.3}$ because the valence sum of bonds joining this site is equal to 1.38. In our sample, vacancies on approximately two Ca sites probably refer to Ca(3) atoms; in this hypothesis the F(2) anions are surrounded by four instead of six Ca atoms and consequently no substitutions of fluorine by oxygens are to be invoked to balance the supersaturation found by Merlino in this site in his samples. So those ten sites are filled as follows in the mineral of Monte Somma: $[F]_2[F_{0.5}(OH)_{1.5}]\,[F]_6$.

The significant increase of the *c* parameter (36.67 Å) of zeophyllite from Monte Somma in comparison with the values reported from Radzein (*c* = 36.48 Å) and from Leitmeritz (*c* = 36.45 Å) may also be explained by the particular anion chemistry of this sample; by analogy with what happens in hydrogrossulars, substitutions of the type (O_4H_4) for (SiO_4) are suspected as the cause of this *c* increase.

The model now described obviously needs confirmation by structural analysis, which, in our opinion, is very difficult due to the small size of the crystals.

Finally, the paragenetic association observed in the samples suggests a progressive decrease of the K content in the solution permeating the tuff during crystallization resulting from the paragenetic order of crystal growth: phillipsite (a K-rich zeolite) and K-rich chabazite, apophyllite (K- and Ca-silicate) and, finally, zeophyllite (Ca-silicate).

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