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Barberiite, NH_4BF_4, a new mineral from Vulcano, Aeolian Islands, Italy

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ABSTRACT

Barberiite, ammonium tetrafluoroborate, occurs as a fumarolic encrustation at Fossa crater on Vulcano, Aeolian Islands, Italy. Associated minerals are sulfur, malladrite, realgar, salammoniac, cannizzarite, galenobismutite, and bismuthinite. The mineral is orthorhombic and occurs as minute crystals tabular to platy on {001} and sometimes elongated [010] or [100], forming globular aggregates (average diameter 1–2 mm). It is admixed with sulfur and sometimes with malladrite, salammoniac, and realgar. The very thin crystals (about 1 μm in thickness) range from about 50 to 300 μm in length and are very unstable in air. The mineral is colorless, transparent to translucent, nonfluorescent, with a vitreous luster and a white streak. $VHN_{25} = 14.2$ kg/mm^2 (range: 13.0–15.4), cleavage {100} perfect, {010} and {001} good, fracture not observed. $D_{calc} = 1.90$, $D_{meas} = 1.89(3)$ g/cm^3. Barberiite is biaxial, $2V_{meas} = 90 \pm 2°$; the mean n, calculated from the Gladstone-Dale relationship, is 1.308. It has $a = 9.0615(7)$, $b = 5.6727(6)$, $c = 7.2672(6)$ Å, $V = 373.5(1)$ Å^3, $a{:}b{:}c = 1.5974{:}1{:}1.2811$, $Z = 4$, space group $Pnma$. The strongest six lines in the X-ray powder diffraction pattern are [d in ångströms (I/I_0) hkl]:3.183(100)211, 3.540(90)210, 2.8982(80)112, 4.472(75)011, 2.1631(70)113, 2.5362(65)121. On the basis of chemical analysis, IR spectroscopy, and X-ray data, barberiite corresponds to the synthetic compound NH_4BF_4. The mineral is named after Franco Barberi, professor of volcanology at Pisa University.

INTRODUCTION

The island of Vulcano is part of the Aeolian Archipelago and lies off the northern coast of Sicily. It has been shaped by various volcanoes and in recent times its geological, volcanic, and structural features have been the subject of many detailed investigations (e.g., Barberi et al., 1974; Keller, 1980; Frazzetta et al., 1983). The Fossa crater, one of the most recent volcanoes of Vulcano, is a 391-m cone, with a base diameter of 1 km (Fig. 1). Since the last explosive eruption, which occurred at the Fossa crater from 1888 to 1890 (Mercalli and Silvestri, 1890), Vulcano has been in a dormant state characterized by fumarolic activity of varying intensity. After a peak value of 615 °C, recorded in 1924 (Sicardi, 1973), the average temperatures have been below 400 °C. Since 1987 there has been a progressive increase in activity at the Fossa crater, where the maximum temperature of the fumaroles has increased from 330 to 700 °C (October 1992).

In order to contribute to the understanding of the genesis and evolution both of fluids and depositional environments of sublimates at Vulcano, since 1988 we have been studying the fumarolic products and encrustations at La Fossa crater from a mineralogical, chemical, and morphological point of view, carrying out two to three field studies each year.

In 1988 sulfur, salammoniac, and sassolite were found to be present throughout the fumarolic area of the Fossa cone. Since 1990, as well as the above-mentioned minerals, some sulfides and sulfosalts were also found (Di Chio et al., 1991) around the hottest fumaroles (FF and FA in Fig. 1). In October 1992, when the maximum temperature of the crater fumaroles increased to 700 °C, we found barberiite on the ground around the FF and FA vents. The mineral was recognized as a new species on the basis of its powder pattern and cell parameters, which closely resembled those for synthetic NH_4BF_4 (JCPDS 15-745). Chemical analyses, IR spectroscopy, and density confirm the identity of barberiite with the synthetic compound.

The mineral NH_4BF_4 has been named barberiite after Franco Barberi, professor of volcanology at the University of Pisa, who, as president of the Gruppo Nazionale per la Vulcanologia (National Group for Volcanology, Italy), has promoted volcanological, geochemical, and mineralogical research on the island of Vulcano. Both the mineral and the name have been approved by the Commission on New Minerals and Mineral Names, IMA. The holotype is deposited in the mineralogical museum of Bari University (N. 4/nm).

OCCURRENCE AND PARAGENESIS

The Fossa volcano, for which documentation is available dating back to about 500 B.C., is characterized by eruptions, generally lasting a few years, interspaced by a few decades of calm, with intensive fumarolic activity. The last eruption began at the Fossa crater in 1888 and ended in 1890; since then the volcano has remained in a fumarolic stage.

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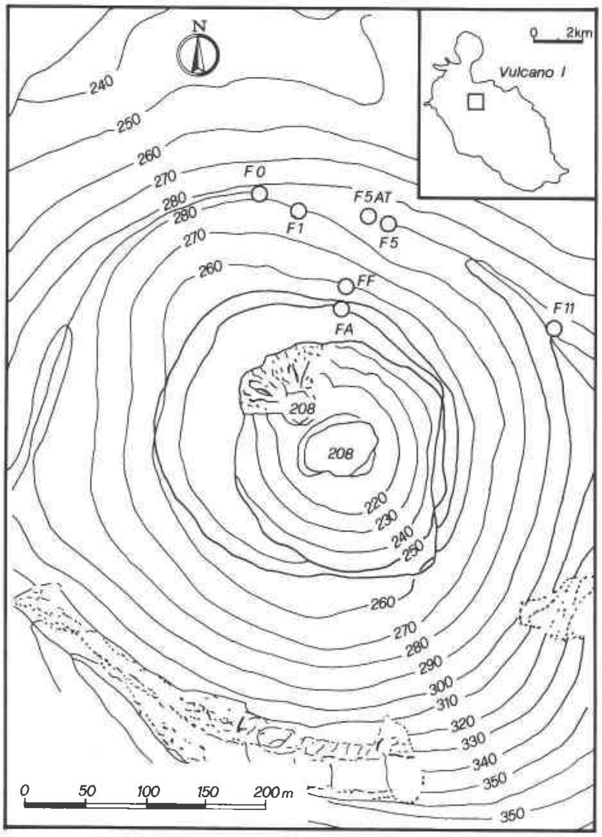

Fig. 1. Location of the Fossa crater fumaroles at Vulcano (redrawn from Gruppo Nazionale per la Vulcanologia, 1988).

In 1987, when the maximum temperature of the fumaroles was below 400 °C, sulfur, salammoniac, and sassolite were the only phases present in the fumarolic area of the Fossa cone. Since 1990, when the maximum temperature of the hottest fumaroles (FF and FA in Fig. 1), situated on the inner slope of the crater, increased to 607 °C, bismuthinite (Bi_2S_3), cannizzarite ($Pb_4Bi_{5+x}S_{11.5+1.5x}$), galenobismutite ($PbBi_2S_4$), and sphalerite (ZnS) have been collected, in addition to the minerals mentioned above. These phases were also observed in 1991 and 1992; in 1992 barberiite was collected. Other associated minerals are malladrite (Na_2SiF_6) and realgar (AsS). The ground temperature where we collected barberiite ranged from 200 to 600 °C.

Barberiite occurs as globular aggregates (average diameter 1–2 mm) admixed with sulfur; salammoniac (where the temperature of the ground is below 300 °C), malladrite, and realgar are admixed as well. Very thin crystals of barberiite (about 1 μm in thickness) range from about 50 to 300 μm in length (Fig. 2).

Tetrafluoroborate ions can be formed only in a strongly acid solution containing more F than B (see references in Onishi, 1969). Barberiite can be formed by the reaction between boron trifluoride and ammonium fluoride, according to Berzelius (in Mellor, 1924).

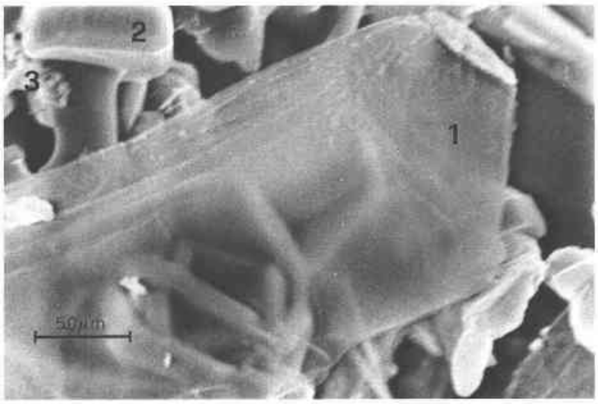

Fig. 2. Scanning electron photomicrograph of a platy and very thin crystal of barberiite (1) on malladrite (2) and realgar (3). Scale bar = 5.0 μm.

Barberiite in the sampling area reacts with HCl present in fumarolic fluids (about 0.5 vol%) to form NH_4Cl, BF_3, and HF; in damp air, as the synthetic NH_4BF_4, it decomposes partially, yielding perhaps NH_3BF_3OH and HF (Pascal, 1961; Bonadeo and Silberman, 1969), and so we conserve the mineral in a covered filter weighing bottle made of a transparent plastic material.

CHEMISTRY

Barberiite is very soluble in H_2O; 100 parts of H_2O at 16 and 100 °C dissolve 25 and 95–98 parts of NH_4BF_4, respectively (Stolba, 1870; Mellor, 1924). A preliminary qualitative analysis was made by atomic absorption spectroscopy for B and by the Nessler method for NH_4. Since no electron probe analysis was possible because of the chemical composition of the mineral, quantitative analyses of barberiite were carried out by wet methods. Because of the small amounts of the collected mineral available, analytical methods were tested many times on synthetic 99.99% NH_4BF_4 from Aldrich Chemical Co.

A small amount of purified material, dissolved in deionized H_2O, was analyzed by means of a Dionex ion chromatograph. For the cations, column CS 10 was used with 25 mM of HCl and 0.25 mM of 2–3 diamino propionic acid monohydrochloride as eluents. For the anions, column AS 5A-5 μm was used with 2 mM of Na_2CO_3, 1 mM of NaOH, and 1 mM of p-cyanophenol as eluents. The analytical results (in weight percent) are Na = 0.4, K = 2.2, NH_4 = 16.6, F = 0.3, Cl = 0.6, Br = 0.1, BF_4 = 79.8, total = 100.0. The F, Cl, and Br and an appropriate amount of NH_4 were deducted as admixed salammoniac. The empirical formula (based on BF_4 = 1) is $[(NH_4)_{0.96}K_{0.06}Na_{0.02}]_{\Sigma=1.04}BF_{4.00}$. The simplified formula can be written as NH_4BF_4 and requires NH_4 = 17.21, BF_4 = 82.79, total 100.00 wt%.

X-RAY CRYSTALLOGRAPHY

An X-ray single-crystal study would have been desirable but proved impossible owing to the very platy habit of the crystals and the unstable nature of the mineral. In

TABLE 1. X-ray powder pattern for barberiite and synthetic NH_4BF_4

	Barberiite			Synthetic NH_4BF_4		JCPDS 15-745	
hkl	d_{calc}	d_{obs}	I/I_0	d_{obs}	I/I_0	d_{obs}	I/I_0
101	5.6693	5.669	25	5.677	22	5.668	30
200	4.5308	4.531	30	4.534	40	4.528	60
011	4.4717	4.472	75	4.480	75	4.482	100
201	3.8448	3.843	50	3.850	40	3.844	50
002	3.6337	3.634	45	3.639	50	3.635	50
210	3.5402	3.540	90	3.544	100	3.542	85
102	3.3726	3.374	10	3.377	10	3.376	12
211	3.1826	3.183	100	3.187	80	3.186	85
112	2.8989	2.8982	80	2.9033	50	2.902	60
202	2.8346	2.8346	50	2.8372	30	2.839	35
301		—	—	2.7936	2	2.792	4
121	2.5366	2.5362	65	2.5394	35	2.541	45
311	2.5030	2.5030	20	2.5047	12	2.505	12
220	2.4041	2.4037	20	2.4074	12	2.409	12
103	2.3403	2.3404	55	2.3433	18	2.341	25
302		—	—	—	—	2.324	35
221	2.2825	2.2822	65	2.2855	35	2.286	35
400	2.2654	2.2651	15	2.2662	6	2.266	10
022	2.2358	2.2358	40	2.2397	13	2.238	18
013	2.2278	2.2275	17	2.2304	13	2.232	
122	2.1707	2.1716	40	2.1746	35	2.176	45
113	2.1634	2.1631	70	—	—	2.165	
312	2.1496	2.1493	30	2.1525	12	2.151	12
203	2.1363	2.1358	10	2.1384	4	2.138	6
410	2.1038	2.1037	20	2.1054	14	2.104	12
411	2.0208	2.0207	4	2.0230	2	2.022	4
222	2.0050	2.0043	5	2.0069	2	2.008	4
303	1.8898	1.8900	4	1.8921	2	1.891	2
031		—	—	—	—	1.834	2
412	1.8207	1.8209	12	1.8233	4	1.821	6
123	1.8051	1.8054	15	1.8079	7	1.808	8
104		—	—	—	—	1.782	2
501		—	—	—	—	1.759	<1
230		—	—	—	—	1.749	<1
421	1.7198	1.7201	12	1.7216	5	1.721	6
223		—	—	—	—	1.708	2
114		—	—	—	—	1.701	<1
511		—	—	1.6815	3	1.680	4
132		—	—	1.6513	12	1.653	20
502		—	—	1.6235	2	1.622	4
	$a = 9.0615(7)$ Å $b = 5.6727(6)$ Å $c = 7.2672(6)$ Å			$a = 9.0701(8)$ Å $b = 5.6803(7)$ Å $c = 7.2776(9)$ Å		$a = 9.063$ Å $b = 5.686$ Å $c = 7.272$ Å	

fact, the crystals of barberiite used for the experiment liquefy after 1–2 d under the combined effects of radiation and high room moisture. On the other hand, attempts to coat the crystalline materials were unsuccessful because they decompose when in contact with cellulose acetate. Finally, the rotation photograph spots obtained on a sample introduced into a Lindemann capillary tube are very broad, and so only one cell parameter could be determined, and that with poor precision [$c = 7.30(3)$ Å]. On the other hand, the structure of synthetic NH_4BF_4 is well known (Hoard and Blair, 1935; Clark and Lynton, 1969; Caron and Ragle, 1971). It is orthorhombic, space group *Pnma*; $Z = 4$.

Instead, X-ray powder diffraction patterns were obtained separately for barberiite and for the synthetic compound (Table 1). A PW 1800 Philips diffractometer (Cu*Kα* radiation, ¼° 2*θ*/min) was used. The examined samples were spread on the support surface of pure, powdered, and compressed NaF, allowing the NaF surface to remain exposed between sample grains. With this preparation technique, the NaF may also be used as an internal standard (Garavelli and Mazzi, 1957). Indexing was performed on the basis of lattice parameters obtained from the references above.

In Table 2 chemical, physical, and crystallographic data of barberiite are compared with those of the two other tetrafluoroborate minerals: avogadrite, $(K,Cs)BF_4$ (Zambonini, 1926), and ferruccite, $NaBF_4$ (Carobbi, 1933).

PHYSICAL AND OPTICAL PROPERTIES

Minute crystals of barberiite appear tabular to platy on {001}, pseudohexagonal, commonly elongated [010] or [100]. The observed forms are rhombic bipyramid; no twinning was observed. The very thin crystals (about 1 μm in thickness and 50–300 μm in length, Fig. 2), are colorless, with a vitreous luster and a white streak. They are transparent to translucent and nonfluorescent. A density of 1.89(3) g/cm³ was measured by flotation in a benzene-bromoform mixture. The calculated density for the

TABLE 2. Relationship of barberiite with other tetrafluoroborates

	Avogadrite	Ferruccite	Barberiite
Chemical formula	$(K,Cs)BF_4$	$NaBF_4$	NH_4BF_4
System crystal	orthorhombic	orthorhombic	orthorhombic
Space group	*Pnma*	*Cmcm*	*Pnma*
Unit-cell parameters	$a = 8.664$ Å $b = 5.480$ Å $c = 7.02$ Å $V = 333.3$ Å³	$a = 6.32$ Å $b = 6.25$ Å $c = 6.77$ Å $V = 267.4$ Å³	$a = 9.0615(7)$ Å $b = 5.6727(6)$ Å $c = 7.2672(6)$ Å $V = 373.5(1)$ Å³
Strongest lines	3.41 Å (100) 3.26 Å (80) 3.06 Å (75)	3.39 Å (100) 3.41 Å (85) 2.31 Å (40)	3.183 Å (100) 3.540 Å (90) 2.898 Å (80)
Optical data	biaxial (−) 2*V* very large $\alpha = 1.3239$ $\beta = 1.3245$ $\gamma = 1.3247$	biaxial (+) $2V = 11°25'$ $\alpha = 1.301$ $\beta = 1.3012_{calc}$ $\gamma = 1.3068$	biaxial (±) $2V = 90 \pm 2°$ $n_{calc} = 1.3081$

Note: data for avogadrite and ferruccite from JCPDS 16-378 and 11-671, respectively; optical data from Palache et al. (1951); barberiite lattice parameters refined from powder data.

ideal formula is 1.90 g/cm³. The microindentation hardness with a 25-g load (VHN_{25}) is 14.2 kg/mm² (range: 13.0–15.4).

Crystals of barberiite are biaxial. The value of 2*V*, measured in air with a universal stage, is 90 ± 2°. No indices of refraction are obtainable using the Becke line method because barberiite decomposes when in contact with the immersion medium. The mean index of refraction calculated from the Gladstone-Dale relationship, using the ideal formula and the constants given by Mandarino (1976), is 1.308.

The infrared spectra of barberiite and synthetic NH_4BF_4 are identical. The spectra show a broad band at 3250–3159 cm^{-1}, caused by NH stretching, and a sharp peak at 1400 cm^{-1}, caused by NH_2 deformation. Three bands at about 1300, 1750, and 2150 cm^{-1}, two peaks at 1000 and 1100 cm^{-1}, a weak peak at 770 cm^{-1}, and a doublet at 535 and 525 cm^{-1} constitute the vibrational spectrum of the BF_4^- ion, according to the data reported by Bonadeo and Silberman (1970).

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