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Peprossiite-(Ce), a new mineral from Campagnano (Italy): the first anhydrous rare-earth-element borate

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Abstract : Peprossiite-(Ce) occurs as light yellow platy and well cleaved grains filling the open spaces between sanidines, in a "sanidinite" ejectum within the pyroclastics of the Sacrofano volcanic centre, Sabatini complex, Roman perpotassic province, at Campagnano (Latium, Italy). Associated minerals are sanidine, aegirine-augite, a hellandite-group mineral, zircon, titanite and magnetite. Peprossiite-(Ce) is optically uniaxial, n_E 1.711(5) and n_O 1.703(2), non pleochroic. The empirical formula derived from ion probe analysis for B and WDS microprobe analysis is $(Ce_{0.40}La_{0.32}Pr_{0.09}Nd_{0.05}Th_{0.02}Ca_{0.09})_{\Sigma 0.97}Al_{2.04}[B_{3.00}O_{8.97}(OH)_{0.03}]$, or ideally $(Ce,La)Al_2B_3O_9$. D_{meas} 3.45(5) g•cm^{-3}, D_{calc} 3.47 g•cm^{-3}. The mineral is hexagonal, $P\bar{6}2m$, with a = 4.610(1), c = 9.358(7)Å, Z = 1. The most intense lines of the powder pattern (Gandolfi camera) are [as *d* in Å - I/I_o (*hkl*)] 3.67 - 100 (101), 3.04 - 100 (102), 2.458 - 75 (103), 2.308 - 50 (110), 2.020 - 50 (104), 1.953 - 50 (201), 1.855 - 50 (113), 1.835 - 50 (202). The crystal structure consists of boron-oxygens tetrahedral sandwiches geometrically similar to those present in micas with REE as interlayer cation. The genesis is related to a final stage of deposition from pneumatolytic to hydrothermal fluids circulating through the trachytic mother-rock prior to its explosive ejection into pyroclastics.

Key-words : new mineral, peprossiite-(Ce), borate, rare earths, Roman perpotassic province, Italy.

Introduction

The Sacrofano eruptive centre of the Sabatini volcanic complex, in the Roman perpotassic province of central Italy, is a well-known source for rare minerals, including new species. Most of them occur in the blocks within the pyroclastic rocks deposited during the first phase of strombolian explosive activity of the volcano, prior to the calderic collapse, and are characteristically associated to two types of ejecta.

Sacrofanite (Burragato *et al.*, 1980), a feldspathoid of the cancrinite group, occurs in association with andraditic garnet, diopsidic clinopyroxene, haüyne and sanidine in the dark-green ejecta of the "skarn type", namely those where latiumite, the first new mineral found in Latium during this century, has been discovered (Tilley & Henry, 1953). On the other hand giuseppettite (Mazzi & Tadini, 1981), also a feldspathoid of the cancrinite group, occurs in an ejectum which consists mainly of K-feldspar with

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minor nepheline, haüyne, biotite and kalsilite, and so belongs to the "sanidinite type".

The finding of giuseppettite prompted an extensive research on "sanidinite" ejecta, which resulted in numerous discoveries of rare minerals, mostly U-, Th-, REE-bearing silicates and borosilicates (De Casa *et al.*, 1986; Della Ventura *et al.*, 1986a,b, 1990), among which a few possibly new ones are still under investigation. All these rare minerals are found in "sanidinites" containing coarse sanidine showing an advanced degree of order ("type-A sanidinite" of Della Ventura *et al.*, 1992) and with trachytic bulk composition. They are believed to derive from disruption of dykes intruded and equilibrated at hypabyssal depth before being explosively brought to surface during the earliest stage of the strombolian activity (Della Ventura *et al.*, 1992).

We describe here a new mineral, the first essentially anhydrous borate of rare-earth elements. It was found by the mineral collector Mr. Giorgio Penco in 1986 while working out a "type-A sanidinite" ejectum at Monte Cavalluccio, community of Campagnano, province of Rome, at the northern internal edge of the Sacrofano caldera. A second sample was later found at the same locality by another distinguished mineral collector, Mr. Salvatore Fiori.

The mineral has been approved by the Commission on New Minerals and Mineral Names, I.M.A., in March 1990. We dedicate it to Giuseppe Rossi ("Pep" to his friends), mineralogist and crystallographer, Director of the C.N.R. Centre for Structural Crystallography at Pavia, Italy, and Vice-President of the European Mineralogical Union. Pep died of lung cancer on January 17, 1989, when he was at the peak of his scientific activity and in the prime of his life (he was barely 50, having been born on September 3, 1938, at Bressanone, Italy).

The type specimen of peprossiite-(Ce) supplied by G. Penco is deposited at Museo di Mineralogia, University of Rome, Italy. Part of the holotype is deposited at the Museum National d'Histoire Naturelle, Paris, France. The co-type found by S. Fiori has been distributed to several museums in Italy and in Canada.

Physical properties

Peprossiite-(Ce) occurs as minute light-yellow flakes, translucent to transparent, with a vitreous luster. Streak is white. Mohs' hardness is 2 or slightly more, but it could not be determined exactly due to the small grain size. The crystals exhibit a hexagonal contour and a platy habit, and are usually arranged as books, only occasionally as rosettes (Fig. 1). The largest cluster is 2 mm in diameter. Twinning was not observed. Cleavage is perfect on {0001}, and distinct on {11.0}; the latter simulates the crossing cleavage typical of carbonates.


Fig. 1. Platy hexagonal crystals of peprossiite-(Ce) arranged as a rosette in a vug among sanidine crystals. Monte Cavalluccio, Campagnano di Roma, Italy. Sample and photograph of Mr. Salvatore Fiori. Horizontal field of view 2.5 mm.

The specific gravity, measured at room temperature by suspension in Clerici solution, is 3.45(5) g•cm^{-3}. This compares favourably with a calculated value of 3.476 g•cm^{-3} from unit cell and chemical analysis as given in Table 2.

Optically, peprossiite-(Ce) is uniaxial positive. The refractive indices, measured at room temperature in white light, but corrected for D light and 20°C, are $n_O = 1.703(2)$, $n_E = 1.711(5)$. While n_O can be measured easily, the determination of n_E is made difficult by the preferred orientation shown by the cleavage flakes. Consequently it was established indirectly by measuring the extraordinary refraction index of flakes showing the optic axis inclined to the perpendicular to the stage by an angle which could be determined from the interference figure (Tobi's method as modified in Bloss, 1961 p. 135). The birefringence calculated as difference between the two indices measured in this way (0.008 ± 0.003) is in excellent agreement with that measured in thin section (0.009 ± 0.003) using a Berek compensator. In thin section peprossiite-(Ce) is colourless and non-pleochroic. Under crossed polarizers, the cleavage flakes appear dark grey, but rarely completely extinct, most probably because of the stresses undergone during preparation. In the conoscopic set-up, these flakes always show the emergence of a sligthly off-centred optic axis.

X-ray crystallography

The X-ray data (Table 1) have been obtained by the Gandolfi method using a cluster of few grains. The observed pattern can be fitted with the hexagonal unit-cell $a = 4.610(1)$, $c = 9.358(7)$ Å, $V = 172.2(2)$ Å^3, in close agreement with the unit-cell dimensions $a = 4.611(1)$, $b = 9.372(7)$ Å, $V = 172.60$ Å^3, $Z = 1$, preliminarily determined on a single crystal by Prof. L. Ungaretti (Pavia) to whom peprossiite-(Ce) has been supplied for structure determination (in progress). The space-group symmetry determined by him is $P\overline{6}2m$. The crystal structure has been determined and refined to $R = 1.5\%$. It consists of boron-oxygens tetrahedral sandwiches geometrically similar to those present in micas, with REE as interlayer cation. The tetrahedral sandwiches contain a cation layer incompletely occupied by Al in five-fold coordination; the vacancy at the Al site is accompanied by a corresponding vacancy at one oxygen site (at the middle of two opposite tetrahedral six-fold rings). In this rather complicated and disordered situation, minor amounts of OH cannot be ruled out on the basis of XRD only.

Table 1. X-ray powder diffraction data of peprossiite-(Ce).

I	d_{meas}	d_{calc}	hkl
20	9.37	9.358	001
20	4.68	4.679	002
10	3.98	3.992	100
100	3.67	3.672	101
100	3.04	3.037	102
75	2.458	2.4579	103
50	2.308	2.3048	110
20	2.239	2.2379	111
20	2.068	2.0676	112
50	2.020	2.0184	104
35	1.994	1.9960	200
50	1.953	1.9521	201
50	1.855	1.8537	113
50	1.835	1.8358	202
20	1.696	1.6945	105
20	1.641	1.6418	114
20	1.559	1.5596	006
20	1.517	1.5184	204
35	1.490	1.4896	211
35	1.454	1.4529	115
35	1.437	1.4360	212
30	1.358	1.3583	213
30	1.331	1.3307	300
20	1.280	1.2799	302
35	1.269	1.2680	214

Gandolfi camera 114.7 mm, Cu/Ni, 50 kV 30 mA. Intensities visually estimated.

Chemical composition

Electron microprobe analysis of three grains (10 points) was carried out using the Camebax wavelength-dispersive microprobe at the Museum National d'Histoire Naturelle (Paris) for the elements with $Z > 9$, using as standards Drake and Weil's glasses (Ce, La, Pr, Nd, Dy, Y, Sm), thorianite (Th), wollastonite (Ca), and albite (Al, Si). The precautions suggested by Reed (1986) were used for REE peak overlap. Experimental conditions were the following: acceleration voltage 15 kV, current intensity 10 nA, counting time on peak and background 10 s, beam diameter 5 μm.

Boron was determined with an IMS 3F ion microprobe at C.R.P.G. (Nancy). Samples were polished and coated with gold, and sputtered by an O^- primary beam of 0.1-0.5 nA intensity, 10 keV energy, and ≈ 2 μm diameter. The secondary positive ions were accelerated at + 4.5 keV, and analyzed with a centred energy bandpass of ± 40 V and at a mass resolution (M/DM) of 2000. The two isotopes of boron were measured and the $^{11}B/^{10}B$ ratio was used to check the absence of any significant interference or instrumental problem. Boron peak intensities were normalized to the Al peak intensity, Al being the major element common to the sample and the standards. Standards used were synthetic and natural glasses (containing 15 wt% Al_2O_3 and between 0.03 and 0.62 wt% B_2O_3) and a natural tourmaline (containing 31.94 wt% Al_2O_3 and 10.2 wt% B_2O_3). The measurements of the $^{11}B/^{27}Al$ ratios were reproducible to ± 1% on both the standards and the sample. No significant matrix effects (< 1% relative difference) on the emissivity of B was observed between the standard glasses and tourmaline. However, since the B content found in

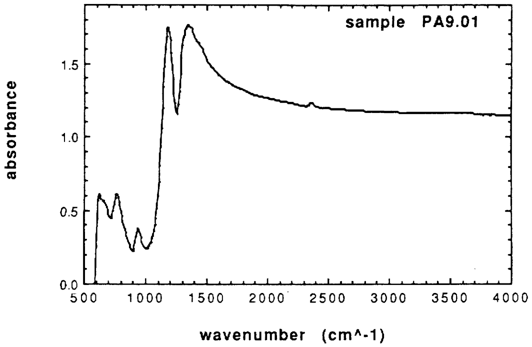

Fig. 2. Reflectance spectrum of peprossiite-(Ce) obtained by FTIR microscopy on one of the grains analyzed by electron microprobe.

Table 2. Chemical analysis and empirical formula of peprossiite-(Ce).

	wt%	e.s.d.				
Ce_2O_3	18.62	0.62	Ce	0.40		
La_2O_3	14.53	0.66	La	0.32		
Pr_2O_3	4.37	0.18	Pr	0.09		
Nd_2O_3	2.11	0.0	Nd	0.05	ΣX	0.97
Dy_2O_3	0.06	0.01	Dy	0.00		
ThO_2	1.68	0.47	Th	0.02		
CaO	1.34	0.09	Ca	0.09		
Al_2O_3	29.40	0.22	Al	2.04	ΣY	2.04
B_2O_3	29.56	0.17	B	3.00	ΣZ	3.00
$[H_2O]$	0.08	calc	[OH]	0.03		
Sum	101.75		O	8.97	ΣA	9.00

Microprobe analysis: Y, Sm and Fe below detection limits. Ion probe analysis for B. Formula on the basis of 9 anions. E.s.d. are the standard deviations of the means of ten points over three grains.

peprossiite-(Ce) is three times larger than that of the tourmaline standard, and since it is calculated using the measured Al content, the B content is given with an incertitude of ± 5%, whereas the analytical relative accuracies estimated from measurement statistics and possible matrix effects are on the order of ± 3% for oxides determined with the electron microprobe. Enough H_2O was then calculated to give (O+OH) = 9 with 3 B in the formula, but it proved to be practically negligible.

A Raman microprobe spectrum on the same grains has been recorded with the Jobin- Yvon spectrometer of C.R.S.C.M. (Orléans, courtesy of J.-M. Bény) equipped with an argon-ion laser of wavelength 488 nm. It rules out the presence of anionic groups such as CO_3, PO_4, SO_4, and NO_3, which characteristically show intense absorptions in the region 1100-1000 cm^{-1}.

The reflectance IR spectrum (Fig. 2) was recorded using a Nicolet model 800 FTIR spectrometer equipped with a IR-Plan infrared microscope on the polished section previously used for the microchemical analyses. The spectrum was obtained with a 100-μm-diameter spot, with an MCT detector cooled with liquid nitrogen, KBr beamsplitter, 4 cm^{-1} nominal resolution, averaging 100 scans on the sample and the background. No detectable bands are observed in the OH-stretching region, supporting that peprossiite-(Ce) is essentially anhydrous. The little noise around 3700 cm^{-1} (Fig. 2) can be related to H_2O vapour in air.

The composite analysis, with mean results and standard deviations, is reported in Table 2. The empirical formula satisfactorily fits the simple stoichiometric ratio X:Y:Z:A = 1:2:3:9, where X is filled predominantly by trivalent rare-earth cations. The little deficit of X can be made up by the excess of Y (Al, another trivalent cation), while the partial substitution of tetravalent Th for REE is largely compensated by divalent Ca. Ce is the prevailing REE cation, and Levinson's rule (1966) has been applied accordingly. The simplified formula calculated according to the analytical data of Table 2 is: $(Ce,La)Al_2B_3O_9$, which (with all REE as Ce) requires: Ce_2O_3 44.30, Al_2O_3 27.52, B_2O_3 28.19. However, it must be noted that the formula resulting from the structural refinement is somewhat different: REE $Al_{2.14}$ B_4 $O_{10.72}$ (Ungaretti pers. comm.). The density calculated from the latter formula is 3.94 g·cm^{-3} in disagreement with the observed one (see preeceding paragraph). The Gladstone-Dale coefficient calculated according to the formula resulting from microprobe analyses is = 0.082, while the same coefficient calculated according to the formula resulting from the crystal-structure refinement is = 0.051, the latter one corresponding to a better agreement between chemical and physical properties. It must be noted, however, that both values were calculated using the same data set of refaction indexes. Several reasons may be taken into consideration to explain this discrepancy: (i) the notorious problems for REE and light elements analysis, and (ii) the constant presence of thin coating of amorphous silica around the grains (see later). This last point, coupled with the small dimension and pronounced platy morphology of the samples could account in particular for the errors in the density measurements. Detailed discussion on this point will be deferred until additional data are available on other peprossiite-(Ce) samples.

None of the 144 REE minerals compiled by Miyawaki & Nakai (1987, 1988, 1989) is an essentially anhydrous borate. The only REE-borate known at all, braitschite, $(Ca,Na_2)_7(Ce,La)_2B_{22}O_{43}\cdot 7H_2O$ (Raup *et al.*, 1968) or $6(Ca,Na_2)O\cdot RE_2O_3\cdot 12B_2O_3\cdot 6H_2O$ (Strunz, 1978), albeit poorly characterized, contains abundant molecular water and is chemically quite different. Thus peprossiite-(Ce) is the first compound of a new mineral series.

The mineral is insoluble in water, in diluted and concentrated HCl, and in organic liquids.

Conditions of formation

As all the rare minerals occurring in the vugs among sanidines in the ejecta of Latium, peprossiite-(Ce) formed by late-stage deposition from pneumatolytic to hydrothermal fluids circulating through the already solid igneous mother-rock.

From the composition and degree of order attained by their K-feldspar, the minimum equilibration conditions of "type-A sanidinites" have been established to be 550°C and less than 1 kbar, or 1500 - 2500 m depth (Della Ventura *et al.*, 1992). These are the maximal conditions at which peprossiite-(Ce) could form, since the mineral fills the space among the already solid sanidines and grew freely under unconstrained conditions (Fig. 1).

The minimum conditions at which peprossiite-(Ce) may have formed cannot be established with certainty. However, as most Latian minerals in ejecta, peprossiite-(Ce) is often coated by a thin film of hydrous amorphous silica, which is probably related to circulation of very late warm waters - at most 100°C. Thus, the formation of peprossiite-(Ce) can be bracketed in temperature between 550° and 100°C, but it is probably in excess of 350°C, otherwise a water-bearing mineral such as braitschite could have been stable and would have been found in the assemblage.

The growth of peprossiite-(Ce) can also be bracketed in time, since the timing of the eruptive development of the Sacrofano caldera is known (De Rita *et al.*, 1983). Peprossiite-(Ce) occurs in "type-A ejecta" which are found *in situ* only in the "lower pyroclastic flow" of the Sacrofano sequence, dated ca. 0.4 Ma. Consequently it formed just before that age, within the trachyte dykes injected into the basement rocks. The age of the trachytes is unknown, but it cannot be much older, since the entire volcanic evolution of the Sacrofano eruptive centre began 0.86 Ma ago (Fornaseri, 1985).

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