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BENYACARITE, A NEW TITANIUM-BEARING PHOSPHATE MINERAL SPECIES FROM CERRO BLANCO, ARGENTINA

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ABSTRACT

The new phosphate mineral species benyacarite, $(H_2O,K)_2Ti\mathit{M}(1)_2\mathit{M}(2)_2(PO_4)_4(O,F)_2{\cdot}14H_2O$, closely related to paulkerrite and mantienneite, but poorer in Mg and K and richer in Mn^{2+} and Ti^{4+}, occurs in granitic pegmatites in Argentina (Cerro Blanco, Tanti, Córdoba). It is associated with other phosphates such as triplite, and fluorides such as pachnolite. The mineral is orthorhombic, biaxial (+), with $2V$ 60(3)°, $X \parallel b$, $Y \parallel c$, $Z \parallel a$. The indices of refraction are: α 1.612(3), β 1.621(3) and γ 1.649(3). The unit-cell parameters are: a 10.561(5), b 20.585(8), c 12.516(2) Å, space group *Pbca*, $Z = 4$, $D_x = 2.37$ g·cm^{-3}. The strongest seven lines in the powder-diffraction pattern [d in (Å)(I/I_o)(hkl)] are: 3.13(100)(004), 6.26(100)(002), 10.29(90)(020), 7.51(80)(111), 3.76(50)(222), 5.16(40)(040), and 3.96(40)(212). Benyacarite contains layers perpendicular to [010] composed of two kinds of octahedra. On both sides of these layers, there are PO_4 tetrahedra, with one face approximately parallel to the layers. The cavities existing within the network of octahedra and tetrahedra are occupied by K^+ and H_2O molecules.

Keywords: phosphates, benyacarite, new mineral species, paulkerrite, mantienneite, "matveevite", Cerro Blanco, Argentina.

SOMMAIRE

Nous décrivons ici la benyacarite, $(H_2O,K)_2Ti\mathit{M}(1)_2\mathit{M}(2)_2(PO_4)_4(O,F)_2{\cdot}14H_2O$, nouvelle espèce minérale étroitement liée à la paulkerrite et la mantiennéite; par rapport à ceux-ci, ce phosphate est appauvri en Mg et K, et enrichi en Mn^{2+} et Ti. Elle fait partie d'un assemblage de phosphates, dont la triplite, et de fluorures, dont la pachnolite, dans des massifs de pegmatite granitique dans la région de Cerro Blanco, Tanti, Córdoba, en Argentine. Elle est orthorhombique, biaxe positive, avec un angle $2V$ égal à 60(3)°, et l'orientation $X \parallel b$, $Y \parallel c$, $Z \parallel a$. Les indices de réfraction sont: α 1.612(3), β 1.621(3) et γ 1.649(3). Les paramètres réticulaires sont: a 10.561(5), b 20.585(8), c 12.516(2) Å, groupe spatial *Pbca*, $Z = 4$, $D_x = 2.37$ g·cm^{-3}. Les sept raies les plus intenses du spectre de diffraction X (méthode des poudres) [d en (Å)(I/I_o)(hkl)] sont: 3.13(100)(004), 6.26(100)(002), 10.29(90)(020), 7.51(80)(111), 3.76(50)(222), 5.16(40)(040), et 3.96(40)(212). La benyacarite contient des couches perpendiculaires à [010] faits de deux sortes d'octaèdres. De part et d'autre de ces couches se trouvent des tétraèdres PO_4, dont une des faces est sensiblement parallèle à ces couches. Les cavités formées au sein de cette trame d'octaèdres et de tétraèdres contiennent des ions K^+ et des molécules de H_2O.

(Traduit par la Rédaction)

Mots-clés: benyacarite, phosphates, nouvelle espèce minérale, paulkerrite, mantienneite, "matveevite", Cerro Blanco, Argentine.

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INTRODUCTION

In the year 1984, two new titanium-bearing phosphate minerals, paulkerrite and mantienneite, were discovered almost simultaneously. Paulkerrite was found in the 7U7 Ranch granitic pegmatite, Arizona (Peacor *et al.* 1984), together with other phosphates typical of such rocks. A similar occurrence of this mineral at Bendada, Portugal, was also reported (Schnorrer-Köhler & Rewitzer 1991). Contrary to the case for paulkerrite, mantienneite is not typical of pegmatites, but comes instead from a sedimentary deposit at Anloua, Cameroun (Fransolet *et al.* 1984).

The crystal-chemical analogy between paulkerrite and mantienneite was already pointed out at the time of their discovery on the basis of the close similarity in unit-cell data, space group, and chemical composition (Tables 1, 2). Particularly interesting is the presence of titanium, an element rarely found in natural phosphates.

About one year later, another titanium-bearing phosphate was observed for the first time by one of us (H.D.G.) in a granitic pegmatite at Cerro Blanco, near Tanti, Córdoba, Argentina, together with other phosphates and with species particularly rich in fluorine, such as fluellite and pachnolite. On the basis of the similarity in powder-diffraction patterns, the mineral was recognized to be isostructural with paulkerrite and mantienneite; chemical analysis showed, however, significant differences in composition, thereby suggesting the possibility of a new species. This mineral, for which the name *benyacarite* is proposed, could be considered as the Mn^{2+}-rich member of the paulkerrite group; unfortunately, the preliminary analytical data obtained by electron microprobe were affected by systematic errors due to extensive dehydration of the sample under the electron beam, and were considered insufficient for complete characterization. Moreover, the only single crystal then available was of poor quality, and no definite conclusion about the space group could be drawn: the symmetry seemed to be monoclinic (with a β angle of 90.9°) rather than orthorhombic as for paulkerrite and mantienneite (Gay 1990). Therefore, in order to confirm the status of a new mineral species, an accurate crystal-structure determination using suitable material was considered to be essential. Furthermore no structure determinations had been performed yet on any of these minerals, and a definite basis for establishing the crystal-chemical relationships among the members of this group was needed. After several attempts, a crystal fragment of good quality was selected out of a considerable number of samples of benyacarite, and the crystal structure was determined and refined accurately (Demartin *et al.* 1993). Besides confirming the orthorhombic symmetry, space group *Pbca*, consistent with that of paulkerrite and mantienneite, the new refined data permitted a consistent interpretation of the results of the chemical analysis. Consequently, our proposal of benyacarite as a new species was submitted to the IMA Commission on New Minerals and Mineral Names (CNMMN) (proposal 95–002) and was approved. The mineral was named in honor of Maria Angelica R. de Benyacar (b. 1928), a researcher with a long affiliation with the Comision Nacional de Energia Atomica, Buenos Aires, Argentina, for her contribution to mineralogical studies. The type material is deposited at the Mineralogical Museum of the Department of Earth Sciences, University of Milano.

TABLE 1. UNIT-CELL DATA FOR MINERALS RELATED TO BENYACARITE

	Paulkerrite*	Mantienneite#	Benyacarite†	"Matveevite"‡
a [Å]	10.49(7)	10.409(2)	10.561(5)	10.52
b [Å]	20.75(13)	20.330(4)	20.585(8)	20.52
c [Å]	12.44(2)	12.312(2)	12.516(2)	12.42
Space group	*Pbca*	*Pbca*	*Pbca*	*Pmcn*(?)

Sources of data: * Peacor *et al.* (1984), # Fransolet *et al.* (1984), † Demartin *et al.* (1993), ‡ Kydryashova & Rohzdestvenskaya (1991).

TABLE 2. CHEMICAL COMPOSITION OF MINERALS RELATED TO BENYACARITE, $(H_2O,K)_2TiM(1)_2M(2)_2(PO_4)_4(O,F)_2 \cdot 14H_2O$

	Paulkerrite*		Mantienneite#		Benyacarite†		"Matveevite"‡		
Na	-		0.06		0.07		-		
K	0.90		0.53		0.32		0.43		
Fe^{2+}	-	2.07	0.45	1.95	0.42	2.00	-	1.94	M(1) site
Mn	0.97		0.02		1.50		1.10		
Mg	1.10		1.43		0.07		0.84		
Ca	-		0.05		0.01		-		
Al	0.30	1.95	1.83	2.00	0.14	2.06	0.81	1.99	M(2) site
Fe^{3+}	1.47		0.17		1.36		1.15		
Ti	0.18		-		0.56		0.03		
Ti	1.00		1.00		1.00		1.00		
P	4.00		4.00		4.00		4.00		
F	0.50		-		0.80		-		

Atomic proportions are based on 4 atoms of P. Sources of data: * Peacor *et al.* (1984), # Fransolet *et al.* (1984), † Demartin *et al.* (1993), ‡ Kydryashova & Rohzdestvenskaya (1991).

OCCURRENCE AND PARAGENESIS

The Cerro Blanco mining district is located in the Sierra Grande of Córdoba Province, Argentina, near the locality of Tanti (on the Route N. 20), 45 km west of Córdoba (Fig. 1). Bedrock in the district includes a group of granitic pegmatites related to a pink monzogranite of the Achala batholith. The age of batholith emplacement is Silurian (Rb/Sr, 399 ± 25 Ma: Rapela

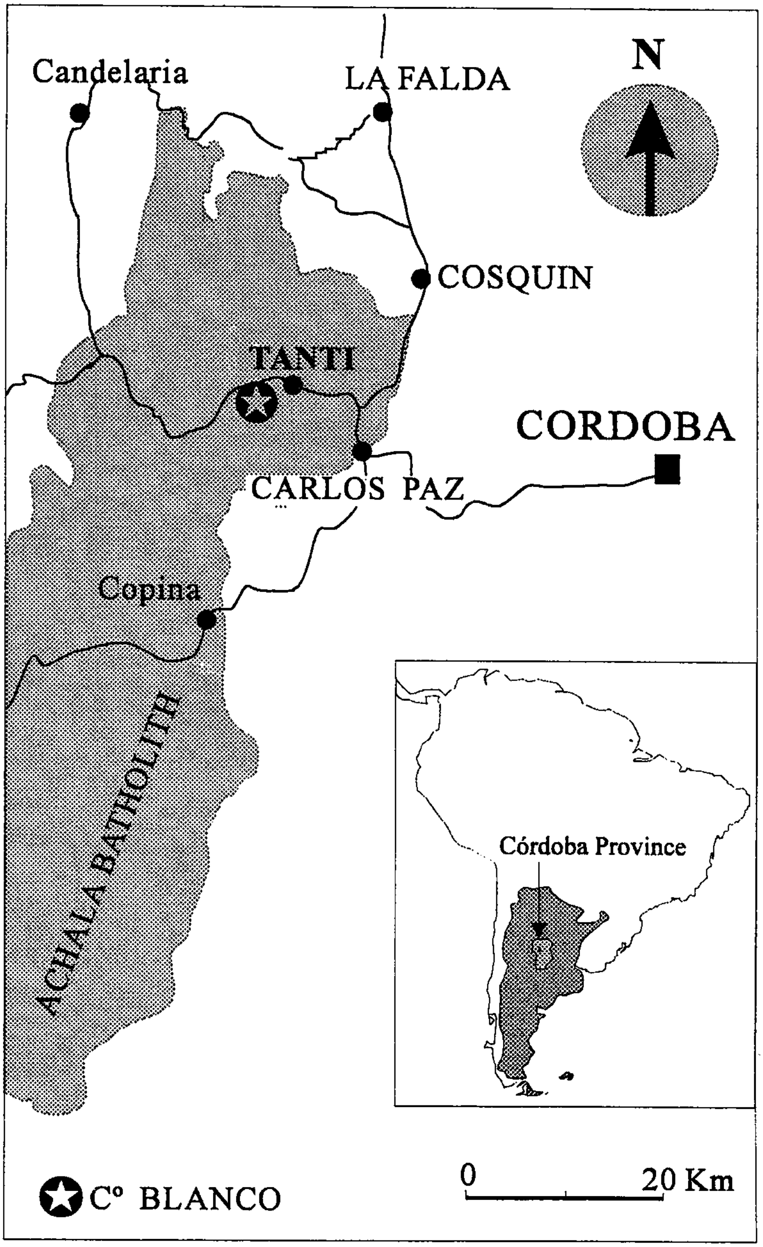

FIG. 1. The Cerro Blanco area.

1982); Linares & Latorre (1969) determined a K/Ar age of 350 ± 30 Ma for the pegmatites. Benyacarite was found in one of these pegmatites, in the El Criollo mine. The main body of the pegmatite is elongate (150 m) with a north–south orientation and a 60-m-wide oval section (Gallager & Jutoràn 1971). Galliski (1994) classified these pegmatites as Rare Elements Class, Beryl–Columbite–Phosphate type, hybrid to the NYF family, based on the classification of Černý (1991). Feldspar, quartz, beryl and minor columbite–tantalite are mined from these pegmatites. As reported by Hurlbut & Aristarain (1968), Gay (1968, 1973, 1990, 1993), Schalamuk (1970), and Gay & Lira (1987), they are characterized by high contents of phosphate minerals, both primary (triplite and apatite) and secondary. Triplite is the most common primary phosphate mineral: it occurs in nodules, some of them quite large (up to 4 m in diameter), commonly showing alteration along the surface and fractures. Together with the triplite relics, there are considerable amounts of secondary phosphates, such as phosphosiderite, strengite, and rockbridgeite, together with minor quantities of lipscombite, dufrénite, libethenite, bermanite and hentschelite; some fluorine-rich species such as fluellite and pachnolite have also been observed, suggesting that a fluorine-rich paragenesis might be essential for the formation of benyacarite and of the paulkerrite-group minerals in general. The most common secondary phosphate is phosphosiderite, a mineral mainly pink in color that occurs both as idiomorphic crystals and in massive form, and also as porous bluish-purple masses in a matrix to the benyacarite. Small crystals of benyacarite have also been observed implanted on strengite and pachnolite in a mineral association dominated by secondary apatite, in some cases accompanied by scarce dark purple phosphosiderite and torbernite. Massive benyacarite was identified in continuity with phosphosiderite; it can be distinguished by its green color in contrast to the pink coloration of the earlier-formed phosphosiderite.

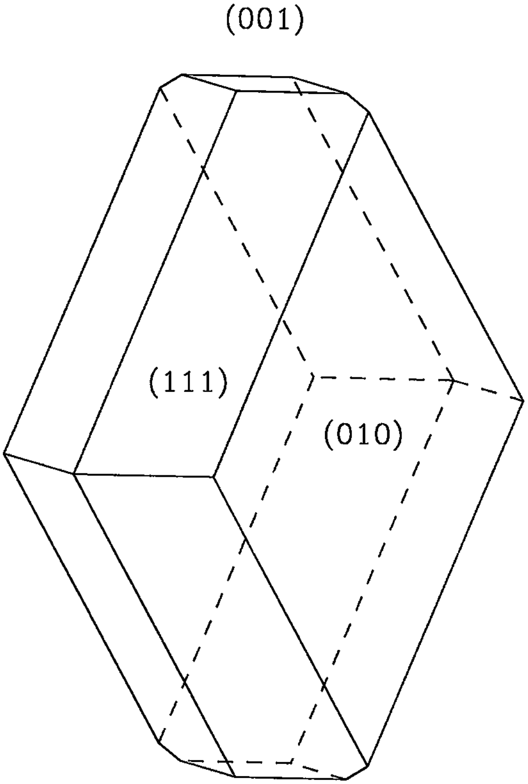

FIG. 2. SHAPE drawing of a benyacarite crystal.

APPEARANCE AND PHYSICAL PROPERTIES

Benyacarite occurs in euhedral crystals ranging from 0.2 to 0.3 mm in size. The observed forms are {010}, {111} and {001}, with {100} less common. The habit is commonly tabular, with prevalence of {010} (Fig. 2); in some crystals, {111} is better developed, thereby attaining an almost equidimensional habit (Fig. 3). Its color is greenish yellow, in some cases light brown, probably owing to partial alteration. Other properties are: transparent to translucent, colorless streak, vitreous luster, no fluorescence under ultraviolet radiation, hardness 2.5–3, cleavage perfect on {010}, very brittle, uneven fracture, and tendency to break along {101} owing to parallel growth.

Benyacarite is pale yellow in thin section, without pleochroism, biaxial (+), $2V = 60(3)°$ (measured in thin section using a universal stage), with orientation X ∥ b, Y ∥ c, Z ∥ a. The indices of refraction, measured on euhedral crystals using an uniaxial stage, are: α 1.612(3), β 1.621(3) and γ 1.649(3). Application of the Gladstone–Dale rule (Mandarino 1981) gives a calculated average index of refraction n_{calc} equal to 1.628, and the compatibility index is accordingly "superior".

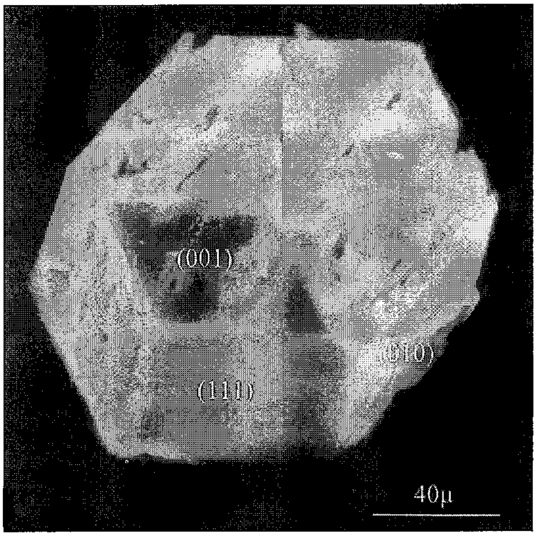

FIG. 3. SEM micrograph of a benyacarite crystal showing an almost equidimensional habit.

X-RAY-DIFFRACTION STUDIES AND CHEMICAL ANALYSIS

The X-ray powder-diffraction pattern, recorded using a Gandolfi Camera (114.59 mm in diameter, Si as internal standard) with Ni-filtered Cu*K*α radiation, is reported in Table 3, where observed and calculated d_{hkl} are compared. A comparison with corresponding data for paulkerrite and mantienneite clearly shows that all these minerals are isostructural. The indexation proposed for the benyacarite spectrum differs only in a few lines from that of paulkerrite and, at least for the largest d_{hkl} values, is the same as for mantienneite. The unit-cell parameters obtained from refinement of the powder-diffraction data [*a* 10.55(1), *b* 20.49(4), *c* 12.52(1) Å] are in good agreement with those obtained from the single-crystal data.

A full description of the determination of the crystal structure and of the chemical composition has been reported elsewhere (Demartin *et al.* 1993). The unit-cell data for all minerals related to benyacarite, and the compositional relationships among these species, are summarized in Tables 1 and 2, respectively. The empirical formula of benyacarite, calculated on the basis of four P atoms, is $(H_2O_{0.78}K_{0.16}Na_{0.03})_2Ti(Mn^{2+}V_{0.75}Fe^{2+}{}_{0.21}Mg_{0.04})_2(Fe^{3+}{}_{0.68}Ti^{4+}{}_{0.28}Al_{0.07})_2(PO_4)_4(O_{0.6}F_{0.4})_2 \cdot 14H_2O$.

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR BENYACARITE

h	*k*	*l*	I/I₀	d_obs	d_calc
0	2	0	90	10.29	10.292
1	1	1	80	7.51	7.514
0	0	2	100	6.26	6.258
0	4	0	40	5.16	5.146
2	2	0	5	4.70	4.698
1	4	1	1	4.32	4.339
2	1	2	40	3.96	3.960
2	2	2	50	3.76	3.757
0	0	4	100	3.13	3.129
3	1	2	1	3.02	3.034
0	2	4	20	2.99	2.993
1	2	4	40	2.88	2.880
1	5	3	20	2.813	2.823
2	6	1			2.803
3	4	2	30	2.635	2.635
4	1	1	20	2.560	2.563
2	5	3			2.562
2	3	4	10	2.507	2.506
4	4	2	1	2.193	2.199
5	0	1	10	2.082	2.082
3	1	5	10	2.030	2.030
4	2	4	20	1.980	1.980
4	3	4	10	1.935	1.935

Gandolfi camera, 114.59 mm in diameter. Ni-filtered Cu*K*α radiation. The intensities were estimated visually.

CRYSTAL-CHEMICAL RELATIONSHIPS TO OTHER SPECIES

On the basis of the structure determination carried out on benyacarite, and of detailed discussion of the subject reported by Demartin *et al.* (1993), the following general chemical formula for the paulkerrite-like minerals can be derived: $(H_2O,K)_2TiM(1)_2M(2)_2(PO_4)_4(O,F)_2 \cdot 14H_2O$. The *M*(1) site is mostly occupied by Mn^{2+} and some Fe^{2+} in benyacarite, by Mg and Mn^{2+} in paulkerrite, and by Mg and some Fe^{2+} in mantienneite. In the *M*(2) site, Fe^{3+} prevails in paulkerrite and in benyacarite, whereas in mantienneite, this site is essentially occupied by Al. In spite of the lack of crystal-structure information, the interpretation of the chemical analysis for both paulkerrite and mantienneite given by Peacor *et al.* (1984) and by Fransolet *et al.* (1984) is close to our inferences. The differences mostly concern the role of potassium, which can be extensively replaced by H_2O molecules, and the possibility that some Fe^{2+}, as well as the dominant Fe^{3+}, may occur in mantienneite.

Another mineral recently reported in the literature is the so-called "matveevite", not approved as a new species (Kydryashova & Rohzdestvenskaya 1991, Puziewicz 1993). The chemical composition as given by these authors and recalculated on the basis of 4 P atoms is reported in Table 2, and compared with the other minerals of this group. On the basis of these data, together with the similarity of the unit-cell parameters, crystal habit, and X-ray-diffraction pattern, there seems little doubt that "matveevite" belongs to the paulkerrite series. The only relevant difference is the space group (*Pmcn* or *P*2₁*cn* instead of *Pbca*), which may, however, be incorrect. On considering the ideal formula of benyacarite, where Mn^{2+} and Fe^{3+} prevail in the *M*(1) and *M*(2) sites, respectively, "matveevite" can be described as a Mg- and Al-rich variety of benyacarite, occurring in a similar paragenesis. The extensive substitution of Mn^{2+} and Fe^{3+} by lighter elements accounts for the lower values of its indices of refraction.

The structure of these minerals is characterized by the presence of layers perpendicular to [010] containing two kinds of octahedra, $M(2)O_5(O,F)$ and $TiO_5(O,F)$; the fluorine atom, whose presence may be essential, is shared between such different octahedra. On both sides of these layers are PO_4 tetrahedra, with one face approximately parallel to the layers. The three corners of this face are shared with octahedra centered on Ti and *M*(2), whereas the remaining corner is shared with $M(1)O_6$ octahedron. The network of octahedra and tetrahedra results in cavities occupied by K^+ and H_2O molecules.

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