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A RE-INVESTIGATION OF BOLIVARITE AND EVANSITE

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Abstract

The type specimen of bolivarite from Campo Lameiro, Pontevedra, in Spain, is shown to have physical and optical properties similar to those of the type specimen of evansite from Mt. Železník, Gömör, Slovakia. Both minerals are X-ray amorphous. DTA spectra of both minerals show a strong endothermic effect at 120°C and a weaker one at 399°C. IR spectra show absorption peaks at 3500, 1600 and 1000 cm^{-1}, which are attributed to OH, H_2O and PO_4, respectively. NMR spectra give a P signal centered at –10.7 ppm, typical of amorphous phosphates, and an Al signal centered at –4.2 ppm, which is typical of Al in octahedral coordination. Chemical analyses give the empirical formula $Al_2(PO_4)_{0.92}(OH)_{3.25}{\cdot}4.03H_2O$ for bolivarite and $Al_3(PO_4)_{1.09}(OH)_{5.73}{\cdot}7.77H_2O$ for evansite. Analyses of other specimens of hydrous aluminum phosphates from the Pontevedra area give results that indicate a range of Al:P atomic ratios varying between 2.44 and 3.58. Because of the amorphous nature of these materials, it is difficult to know if these analytical data pertain to mixtures of hydrous aluminum phosphates or if bolivarite and evansite represent intermediate members of a wide solid-solution series in which PO_4 radicals are replaced by 3(OH).

Keywords: bolivarite, evansite, amorphous, Pontevedra, Spain, Mt. Železník, Slovakia.

Sommaire

L'échantillon type de bolivarite, provenant de Campo Lameiro, Pontevedra, en Espagne, fait preuve de propriétés physiques et optiques semblables à celles d'un échantillon type d'evansite provenant du mont Železník, Gömör, en Slovaquie. Dans les deux cas, il s'agit de minéraux amorphes aux rayons X. Les spectres d'analyse thermique différentielle montrent un effet endothermique marqué à 120°C, et un autre, plus faible, à 399°C. Les spectres d'absorption infra-rouge montrent des pics à 3500, 1600 et 1000 cm^{-1}, qui seraient dus à OH, H_2O and PO_4, respectivement. Les spectres de resonance magnétique nucléaire montrent un signal dû au P situé à –10.7 ppm, typique des phosphates amorphes, et un autre situé à –4.2 ppm, attribué à Al en coordinence octaédrique. Les analyses chimiques mènent à la formule empirique $Al_2(PO_4)_{0.92}(OH)_{3.25}{\cdot}4.03H_2O$ dans le cas de la bolivarite, et $Al_3(PO_4)_{1.09}(OH)_{5.73}{\cdot}7.77H_2O$ dans celui de l'evansite. L'analyse d'autres échantillons de phosphates hydratés d'aluminium provenant de la région de Pontevedra indique un rapport atomique Al:P variant entre 2.44 and 3.58. A cause de la nature amorphe de ces matériaux, il est difficile de savoir si ces résultats analytiques se rapportent à des mélanges de phosphates hydratés d'aluminium ou si bolivarite and evansite représentent des membres intermédiaires d'une série étendue de solutions solides dans laquelle les radicaux PO_4 seraient remplacés par 3(OH).

Mot-clés: bolivarite, evansite, amorphe, Pontevedra, Espagne, mont Železník, Slovaquie.

INTRODUCTION

The name *bolivarite* was introduced into the literature by Navarro & Barea (1921) for an amorphous hydrated aluminum phosphate from Campo Lameiro, Pontevedra, Spain, which occurs as pale greenish yellow fracture-fillings up to 1 cm thick in granite. This mineral was named for Ignacio Bolivar (1850–1944), well-known zoologist and, at the time, director of the National Museum of Natural Sciences in Madrid. A chemical analysis gave a formula close to $Al_2(PO_4)(OH)_3 \cdot H_2O$. A later chemical analysis of bolivarite from the type locality by Van Tassel (1960) produced a similar formula, $Al_2(PO_4)(OH)_3 \cdot 5H_2O$, except for the water content, which was much higher. This led Van Tassel to conclude that bolivarite was related to the amorphous aluminum phosphates evansite and vashegyite. A semiquantitative X-ray-fluorescence (XRF) analysis of the same material indicated the presence of 0.2% UO_3 in the mineral (Van Wambeke 1971). A similar mineral, but containing up to 1.9% UO_3, was reported from the Kobokobo pegmatite in Zaire, and also was called bolivarite (Van Wambeke 1971).

The name *evansite* was introduced by D. Forbes in 1864 (Woodward 1883) for a secondary mineral from Mt. Železník, Gömör, Slovakia; it has subsequently been reported from a substantial number of other localities. It has a vitreous luster, inclining to resinous or waxy, and is colorless to milky white, locally tinged with blue, green, red or yellow. Its chemical composition has been well characterized, the accepted formula approximating $Al_3PO_4(OH)_6 \cdot 6H_2O$. Like bolivarite, it is amorphous to X rays.

Because of the similarity between bolivarite and evansite, we decided to re-investigate some of their properties to determine if they might represent the same mineral.

BOLIVARITE

The specimen of bolivarite investigated in this study is part of the type specimen from Campo Lameiro, Pontevedro, Spain, described by Navarro &

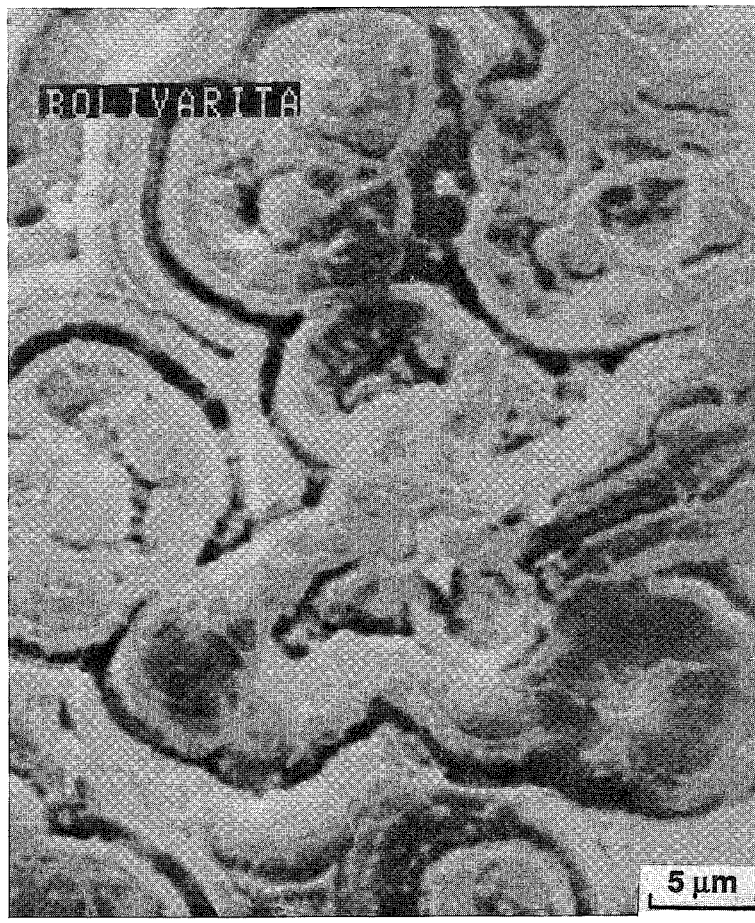

FIG. 1. SEM micrograph of bolivarite.

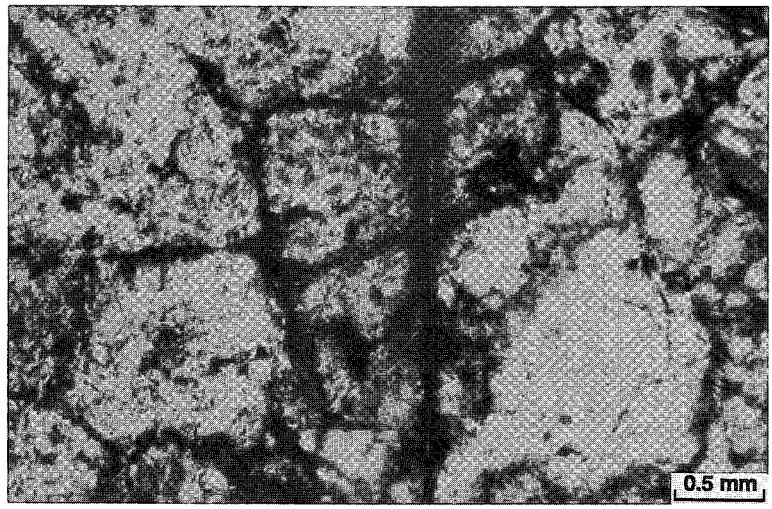

FIG. 2. Optical micrograph of thin section of bolivarite.

Barea (1921) and preserved in the National Museum of Natural Sciences in Madrid as specimen BOLI–E–1.

Under the scanning electron microscope, the bolivarite is seen to have a spherulitic texture (Fig. 1). Measurement of the mineral's specific gravity with a hydrostatic balance gave a value of 2.04, which conforms with Van Tassel's (1960) determination. However, the heterogeneous nature of the bolivarite, as shown in Figure 1, renders this finding highly suspect.

The Vickers hardness (VHN) of bolivarite was found to be between 111 and 114, which corresponds roughly to a Mohs hardness of 3; Navarro & Barea (1921) estimated the hardness to be 2½. The mineral fluoresces strongly bright green under both long-wave (365 nm) and short-wave (254 nm) ultraviolet (UV) radiation, which may be attributed to its UO_3 content (see below).

Optically, the mineral is weakly birefringent, with an index of refraction of 1.48, slightly lower than the values reported by Van Tassel (1960) and Manly

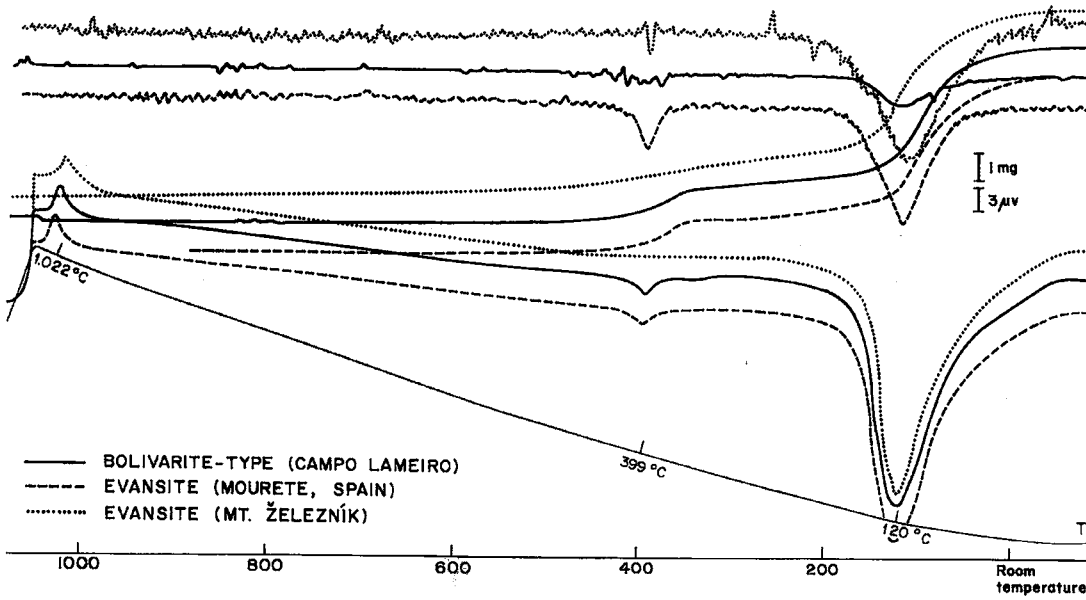

FIG. 3. DTG (top), TGA (middle), and DTA (bottom) spectra of bolivarite and evansite.

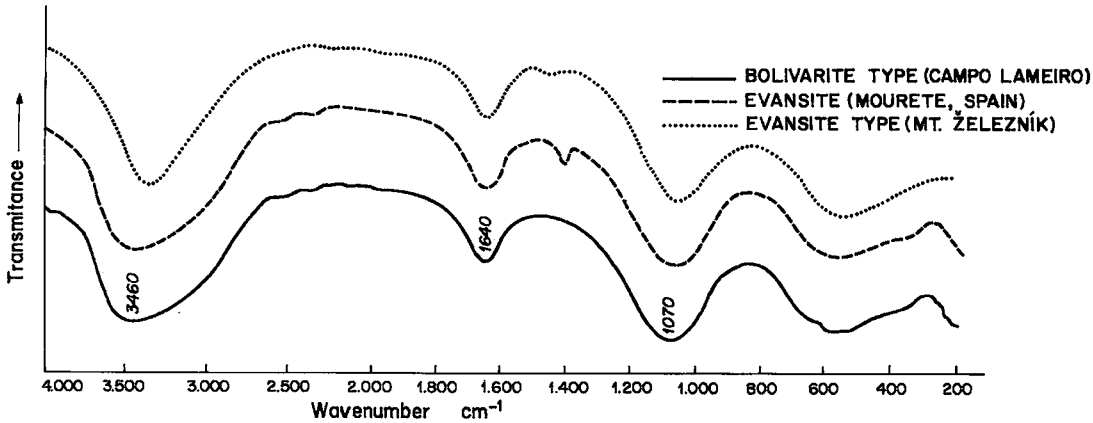

FIG. 4. Infrared spectra of bolivarite and evansite.

(1950). Between crossed nicols, bolivarite is seen to have a mosaic texture, with microfissures containing opaque material (Fig. 2) shown to contain mainly Al and P, possibly with some additional organic material.

The differential thermal analysis (DTA), thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) spectra of bolivarite (Fig. 3), were obtained on a 10 mg pulverized sample, in a static air atmosphere at 10°/min. The DTA spectrum shows a strong endothermic effect at 120°C, attributed to loss of water, and a weaker one at 399°C, which may be due to the presence of small amounts of another phase, possibly an aluminum oxyhydroxide. The exothermic peak at 1022°C is probably due to the recrystallization of an anhydrous phosphate phase. These results are somewhat different from those reported for bolivarite by Manly (1950), who recorded a strong broad endothermic reaction at 220°C, a sharp secondary endothermic reation at 430°C, and a weak exothermic reaction at 950°C. The differences between the two sets of results may be due to different heating regimes.

The infrared (IR) absorption spectrum of bolivarite, obtained by means of a Nicolet–60 SX spectrophotometer, is shown in Figure 4. The following assignments of the absorption peaks can be made: 3500 cm^{-1}: OH; 1600 cm^{-1}: H_2O; 1000 cm^{-1}: PO_4 stretching mode (Arlidge *et al.* 1963). All the absorption peaks are poorly defined, presumably owing to the poor degree of crystallinity.

Bolivarite is largely amorphous to X rays, giving a broad peak in the region of 30° 2θ (Fig. 5), enabling the radial distribution function to be calculated (Fig. 6) according to the method of Wignall *et al.* (1977). On heating, the residue gives an X-ray powder-diffraction pattern corresponding to a mixture of cubic and orthorhombic polymorphs of $AlPO_4$ (ICDD nos. 31–28 and 26–34, respectively).

High-resolution nuclear magnetic resonance (NMR) spectra of bolivarite were obtained by means of a

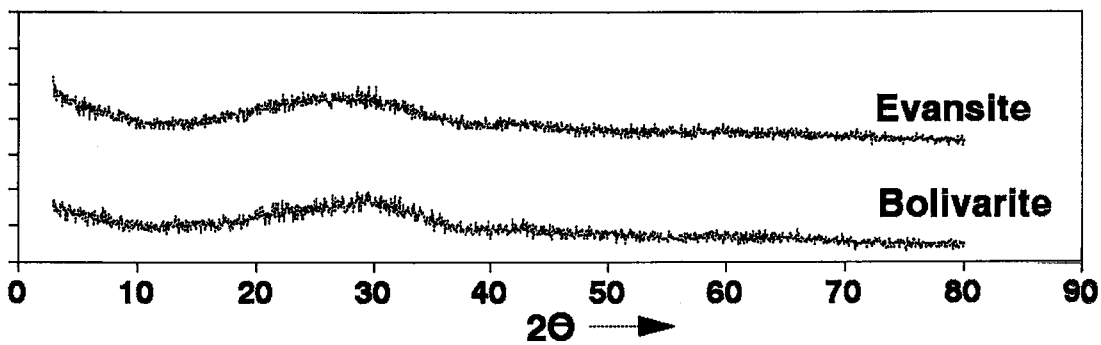

FIG. 5. X-ray-diffraction spectra of bolivarite and evansite.

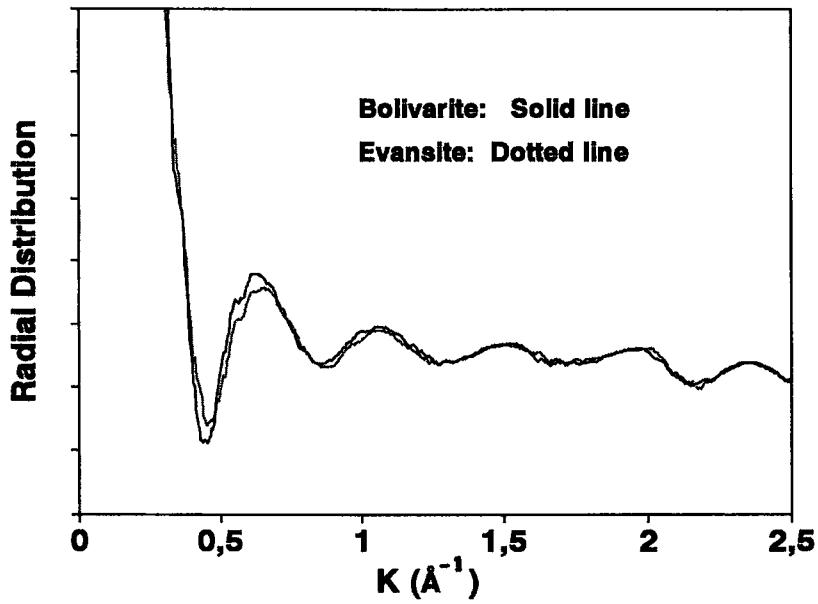

FIG. 6. Radial distribution function of electron density around the aluminum ion in bolivarite.

Bruker MSL–400 instrument with Magic Angle spinning of 54°44′. The ^{31}P spectrum (Fig. 7), analyzed to 161.9 MHz, gives a wide signal centered at –10.7 ppm, typical of amorphous phosphates with P in tetrahedral coordination. The ^{27}Al spectrum (Fig. 7), analyzed to 104.26 MHz, also gives a wide signal characteristic of amorphous structures, with resonance at –4.2 ppm, which is typical of Al in octahedral coordination. The side bands shown in the NMR spectra are due to sample rotation.

The bolivarite from Campo Lameiro was analyzed by XRF spectrometry, with the water content equated with the weight loss at 120°C. The results of the analyses are shown in Table 1, together with the results reported by Navarro & Barea (1921) and Van Tassel (1960) . The new composition is similar to that of Van Tassel (1960) and, as found by him, it contains far more H_2O than reported by Navarro & Barea (1921). We are inclined to agree with Van Tassel that the original analysis was probably done on partially dehydrated material.

The new chemical analysis of type bolivarite gives the empirical formula $Al_{2.00}P_{0.92}H_{11.31}O_{10.95}$, or $Al_2(PO_4)_{0.92}(OH)_{3.25}\cdot 4.03H_2O$, on the basis of two atoms of Al, and with the H distributed between OH and H_2O to give charge balance. This formula has a somewhat lower PO_4:OH ratio than the generally accepted idealized formula, $Al_2(PO_4)(OH)_3\cdot 5H_2O$, but this condition is not entirely unexpected from a structurally disordered mineral. Chemical analyses also were made of bolivarite specimens from other occurrences in the Pontevedra area. The results, shown in Table 2, gave a range of atomic Al:P ratios from 2.44 to 3.58.

Regarding the 0.2% UO_3 reported by Van Wambeke (1971), we obtained a value of 2840 ppm UO_3 using a ZnS scintillation counter, thereby confirming the mineral's radioactivity.

EVANSITE

The type specimen of evansite from Mt. Železník, Gömör, Slovakia (specimen 1935–26572) was kindly provided by Dr. Petr Korbel, Narodni Museum, Prague. It was investigated by procedures similar to those used in the study of bolivarite.

The specific gravity of evansite has been given as 1.8 to 2.2 (Palache *et al.* 1951), a range that encompasses that of bolivarite. The hardness is given as 3–4, somewhat greater than that of bolivarite. Like bolivarite, evansite is isotropic or weakly birefringent, and has a similar index of refraction (Palache *et al.* 1951). However, unlike bolivarite, it does not exhibit fluorescence under either long-wave or short-wave UV illumination.

The thermal spectra (Fig. 3) of evansite and bolivarite are very similar, as are their IR and NMR spectra (Figs. 4 and 7, respectively). The X-ray

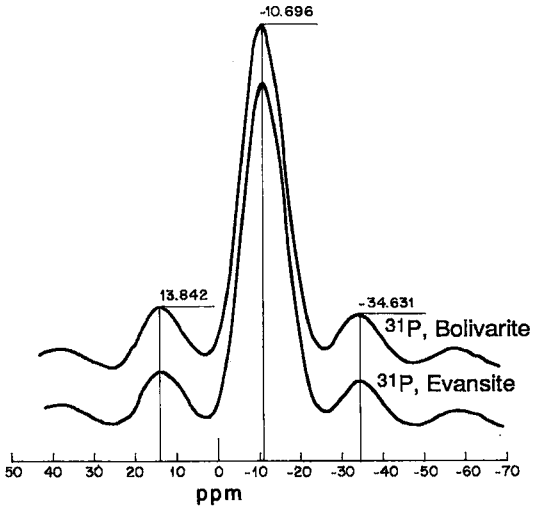

TABLE 1. RESULTS OF CHEMICAL ANALYSES OF TYPE SPECIMENS OF BOLIVARITE FROM CAMPO LAMEIRO, PONTEVEDRA, SPAIN

	Navarro & Barea(1921)	Van Tassel (1960)	$Al_2PO_4(OH)_3$·$5H_2O$	This study **	This study (at. props.)
Al_2O_3 (wt %)	44.07	36.2	35.16	36.12	Al 2.00
P_2O_5	34.93	24.9	24.47	23.00	P 0.92
H_2O	20.60	39.5*	40.37	36.10	H 11.31
$FeO+Fe_2O_3$	nd	nd	nd	00.04	
SiO_2	nd	nd	nd	00.02	
Na_2O	nd	nd	nd	00.14	Na 0.01
Total	99.60	100.6	100.0	95.53	

* Loss on ignition. ** X-ray fluorescence analysis, with H_2O equated with weight loss at 120°C. nd = not determined

TABLE 2. CHEMICAL DATA ON SPECIMENS FROM OTHER OCCURRENCES IN THE PONTEVEDRA AREA

	Al_2O_3 (wt %)	P_2O_5 (wt %)	Al/P (at. props.)
Quinteiro-Geve	34.71	13.50	3.58
Teis-Vigo	36.45	16.50	3.07
Louros-Muros	34.71	19.80	2.44
Campo Lameiro 2	34.68	19.80	2.44

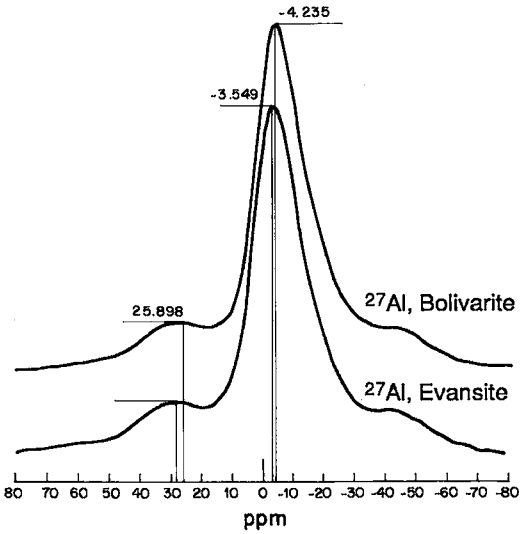

FIG. 7. NMR spectra of ^{31}P (top) and ^{27}Al (bottom) in bolivarite and evansite.

TABLE 3. RESULTS OF CHEMICAL ANALYSES OF EVANSITE FROM MT. ŽELEZNÍK, SLOVAKIA

	Lacroix (1910)	$Al_3PO_4(OH)_6$·$6H_2O$	This study *	This study (at. props.)
Al_2O_3 (wt%)	39.31	39.60	36.25	Al 3.00
P_2O_5	19.05	18.40	18.34	P 1.09
H_2O	39.95	42.00	45.41*	H 21.27
Total	98.31	100.00	100.00	

* Analysis by X-ray–fluorescence spectrometry; H_2O by difference.

powder-diffraction pattern of evansite is also very similar to that of bolivarite (Fig. 5).

The chemical composition of evansite (Table 3) gives the empirical formula $Al_{3.00}(PO_4)_{1.09}H_{21.27}O_{17.86}$ or, approximately, $Al_3(PO_4)(OH)_6$·$8H_2O$. The Al_2O_3 content is similar to that of bolivarite, but the P_2O_5 content is substantially lower, and the H_2O content much higher. The composition can therefore not be accommodated in the bolivarite formula, which has Al:P:OH = 2:1:3. Instead, this ratio approximates 3:1:6.

CONCLUSIONS

The type specimens of bolivarite and evansite have virtually identical physical properties. However, their chemical compositions are sufficiently dissimilar to preclude them from being the same mineral species if they had been well crystallized. Analysis of other specimens of hydrous aluminum phosphates from the Pontevedra area (Table 3) shows that they have broadly similar Al_2O_3 contents, but their P_2O_5 contents are more variable. This suggests a substitution of the type $PO_4 \rightleftharpoons 3(OH)$, with the Al content remaining more-or-less constant. Such a substitution in phosphates, not previously reported, may be analogous to the substitution of SiO_4 by 4(OH) in hydrogarnets. The Al:P atomic ratios observed in the samples of

bolivarite from Pontevedra not only encompass that of evansite (3:1), but also exceed it. Because the minerals are X-ray amorphous, it seems impossible to determine whether such compositions represent mixtures of different hydrated aluminum oxides and phosphates or whether bolivarite and evansite should be considered as intermediate members of one compositionally variable series. To our knowledge, there have been no studies of the low-temperature relationships in the system Al_2O_3–P_2O_5–H_2O that might shed light on this question.

Are bolivarite and evansite both valid mineral species? Should they be regarded as the same mineral? There are differences in opinion among members of the mineralogical fraternity on the question of whether naturally occurring amorphous substances should be considered as minerals; the term "mineraloid" has sometimes been used for such substances. Some years ago, the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association (IMA) canvassed the opinions of members of the Commission on the question of naturally occurring amorphous substances, but there was no clear consensus. At the 1986 General Meeting of the IMA, approval was given to the establishment of a working group to investigate this matter but, to our knowledge, no report by this working group has been tabled. Finally, it seems to come down to a matter of personal opinion as to whether such substances should be regarded as valid mineral species.

If amorphous inorganic substances like bolivarite and evansite are to be regarded as mineral species, is there justification for the two names? The results of the investigations reported herein make this doubtful. The name evansite has clear historical priority, so if one of the names is to be discarded, it should be bolivarite. Matters involving discreditation of mineral species are normally considered by the CNMMN, but in this case, lacking crystallographic data, the authors felt that an adequate case for discrediting bolivarite in favor of evansite could not be made. It seems, therefore, that in spite of our efforts, these names will continue to exist in the mineralogical limbo reserved for inadequately characterized minerals.

Acknowledgements

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