

The uranium-bearing mineral bolivarite: new data and a second occurrence

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SUMMARY. A second occurrence of the mineral bolivarite has been found in the Kobokobo pegmatite, Kivu, Republic of Congo (Kinshasa). This amorphous mineral was previously considered to be evansite. Its physical properties are: weak birefringence; biaxial to uniaxial positive; $n = 1.50-1.51$; specific gravity 1.97-2.05; hardness 3 to $3\frac{1}{2}$.

Three chemical analyses have been performed on the Congolese material. The general formula of the mineral is $Al_2(PO_4)(OH)_{3.4-5} \cdot H_2O$. Both known bolivarites from Spain and Congo contain abnormal amounts of U. The bright green UV fluorescence is due to the presence of U. The DTA curve of the Congolese bolivarite is given. Its genesis is discussed. This uranium-bearing mineral may be an indicator of uranium mineralization in Spain.

THE ill-defined amorphous mineral bolivarite from Pontevedra in Spain first described by Navarro and Barea in 1921 was restudied by Van Tassel in 1960. This last author has shown that the first chemical analysis was incorrect and that the formula of bolivarite is $Al_2(PO_4)(OH)_3 \cdot 5H_2O$.

In 1957 an amorphous green mineral found in the pegmatite of Kobokobo, Kivu, Republic of Congo (Kinshasa), was determined independently as evansite by Melon *et al.* (1957) and by us (1957). However, its refractive indices were somewhat higher than those of the known evansites, which themselves show large variations in the refractive indices, ranging from 1.44 to 1.49 (Palache *et al.*, 1957). Moreover, as outlined by Melon *et al.*, the Al/P atomic ratio was much nearer 2 than 3 as found in evansite. Variable amounts of uranium up to 6% U_3O_8 have been found in some Congolese specimens (Van Wambeke, 1957). Because some doubts remained about the determination of this hydrated aluminium phosphate of Kobokobo, the mineral has been completely investigated. Three chemical analyses have been performed on this amorphous material, and from this study it emerges that the so-called evansite of Kobokobo is in fact a bolivarite.

Physical properties. The Congolese bolivarite generally occurs in botryoidal masses as a coating on other minerals and is located especially in the weathering zone and in the phosphate-rich zone of the pegmatite of Kobokobo. Sometimes it also forms veinlets (Safiannikoff *et al.*, 1967). Its colour varies from bright and yellowish green to greenish white, the green material being in general richer in uranium. Bolivarite has a vitreous lustre and a conchoidal fracture. Its colour and lustre are characteristic and permit a quick distinction between bolivarite and the other aluminum phosphates

or oxides of the Kobokobo pegmatite, such as coeruleolactite, gibbsite, and also a probably new hydrated aluminum phosphate in microscopic laths.

Under the microscope, the bolivarite of Kobokobo shows concentric shells and is generally colourless. The mineral locally contains brown undeterminable inclusions, unevenly distributed and considered tentatively by Melon (1957) as xenotime. A fairly common inclusion is quartz and, more rarely, autunite and phosphuranylite are found in the richest uraniumiferous specimens. The physical properties of the mineral of Kobokobo match closely those of the bolivarite of Pontevedra, Spain (Van Tassel 1960).

	<i>Mineral of Kobokobo</i>	<i>Bolivarite, Pontevedra</i>
Optics	—Very weakly to weakly birefringent —Biaxial to uniaxial+ $n = 1.50-1.51$ —Mosaic texture —Strongly fluorescent in both UV wavelengths (bright green similar to U compounds)	—Very weakly birefringent $n = 1.506$ —Mosaic texture —Strongly fluorescent with bright green colour
X-rays	Amorphous to 1050 °C	Amorphous
Specific gravity	1.97-2.05 (pycnometric method)	2.04 (Berman balance)
Hardness	3 to 3½	—

Chemical composition. Three chemical analyses (table I) have been performed on the Kobokobo material by the Department of Chemistry of the Ispra Research Establishment on samples that do not contain secondary uranium minerals as impurities. The element Mg has not been detected.

The mineral of Kobokobo is thus essentially a hydrated aluminium phosphate of general formula $Al_2(PO_4)(OH)_3 \cdot 4H_2O$. It differs from evansite [$Al_3(PO_4)(OH)_6 \cdot 6H_2O$] by its general formula and by its atomic ratio Al/P. Its chemical composition is similar to that of bolivarite, restudied in 1960 by Van Tassel: $Al_2(PO_4)(OH)_3 \cdot 5H_2O$. The difference in the H_2O content may well be due to the fact that the Congolese mineral loses or absorbs moisture quickly, as was observed before the analyses. The formula of bolivarite is thus: $Al_2(PO_4)(OH)_3 \cdot 4$ to $5H_2O$. The chemical analysis of the 'evansite' of Kobokobo reported by Melon *et al.* (1957) agrees also very well with the present results. However, owing to the lack of sufficient data concerning bolivarite, it was impossible at that time to determine the mineral as bolivarite.

The geochemistry of bolivarite. The bright green UV fluorescence of bolivarites from both Spain and the Democratic Republic of Congo (Kinshasa) has led us to a more detailed analysis of the minor elements present in both materials.

The bolivarite of Kobokobo contains small amounts of U, alkali metals, As, Si, Fe, Ca, and Sc, as well as traces of Ba, Pb, and Y. Large variations in the contents are observed especially for U and Sc.

A semi-quantitative X-ray fluorescence analysis was performed on a small quantity of the Spanish material kindly provided by Van Tassel (ref. no. 21-703—order no. B 7176). The minor elements present in the Spanish material are very similar to those

found in the Congolese bolivarites. The Spanish bolivarite also contains U (0.2 % UO_3), besides small amounts of Si, Ca, K, and Sb. Trace amounts of Ba, Pb, and Sc are also present.

The most characteristic feature of the geochemistry of the bolivarites is certainly the presence of appreciable amounts of U. At Kobokobo the other hydrated aluminium phosphates, and in particular coeruleolactite, also contain U but in smaller amounts than the bolivarites (up to 0.5 % U_3O_8). The uraniferous coeruleolactites

TABLE I. *Chemical analyses of some bolivarites of Kobokobo*

	Ko/300/1 veinlet	Ko/307/1 coating*	Ko/315 coating*	Atomic ratios to (P, As, Si) $\text{O}_4 = 1$		
				Ko/300/1	Ko/307/1	Ko/315
Na_2O	0.15	0.50	0.40	0.014	0.045	0.036
K_2O	0.30	0.06	0.15	0.019		
Li_2O	<0.007	0.007	0.007			
CaO	0.05	0.02	0.05			
MnO_2	—	0.01	0.01			
UO_3	0.40	0.70	1.9	0.011	0.015	0.036
Sc_2O_3	0.01	0.02	0.03			
Fe_2O_3	0.10	0.10	0.15			
Al_2O_3	36.60	35.70	34.80	1.959	1.940	1.895
P_2O_5	25.65	25.30	25.40	0.988	0.99	0.993
As_2O_5	0.25	0.20	0.10	0.012	0.010	0.007
SiO_2^\dagger	0.54	0.47	0.10			
H_2O^+	13.60	16.40	13.90	3	3	3
H_2O^-	22.1	20.6	23.1	3.93	4.21	4.20
Total	99.75	100.087	100.097‡			

* The samples Ko/307/1 and Ko/315 contain very low amounts of lithiophorite.

† SiO_2 is mainly quartz: 0.4 % in sample Ko/300/1 and 0.37 % in sample Ko/307/1.

‡ Sr is present as a trace element in sample Ko/315.

also have the typical green UV fluorescence but the intensity is lower than in the bolivarites. These observations indicate that the homogeneous green fluorescence is essentially due to the presence of uranium in these hydrated aluminium phosphates, either amorphous or crystallized. However, the bolivarites can accommodate several per cent of U, but when the U content exceeds about 3 % UO_3 secondary uranium minerals such as autunite or phosphuranylite are generally present as microscopic inclusions.

Another interesting geochemical feature of the Congolese bolivarites is the presence of Sc, which occurs only as a trace element in the Spanish material examined (10 to 20 ppm Sc). Large variations in the Sc contents, from 50 to more than 500 ppm, are observed in the Congolese bolivarites. The causes of these variations are not well explained but may be due to the presence of indeterminate brown inclusions unevenly distributed in the mineral. The bolivarite of Kobokobo is also the richest scandium-bearing mineral of this pegmatite. Activation analyses performed on a large number of different minerals of this pegmatite have shown that the Sc content does not exceed

60 ppm of Sc. The presence of Sc in hydrated aluminium phosphate is not exceptional. In the Fairfield deposit in the U.S.A., Mrose and Weppner (1959) have shown that the mineral sterretite, previously regarded as a hydrated Al phosphate, was in fact a hydrated Sc phosphate and that the mineral kolbeckite also contains large amounts of Sc. Moreover, Borisenko (1961) has found about 200 ppm of Sc in the pseudowavelite and the crandallite of Fairfield. Most probably Sc partly replaces Al in these phosphates.

Differential thermal analysis of bolivarite

A differential thermal curve of the Spanish bolivarite was published by Manly in 1950. The upper curve in fig. 1 gives the differential thermal curve for the Kobokobo bolivarite. The mineral shows an important endothermic reaction with a maximum at 205 °C and a second weaker endothermic peak at 458 °C. An exothermic reaction occurs only at 1056 °C. Compared with Manly's data there are only small differences of temperature for the endothermic reactions (220 and 430 °C). This last author found a weak exothermic reaction at 95 °C which was not detected in the Congolese bolivarite. The DTA curve of Manly only goes up to 1000 °C. The Kobokobo bolivarite remains amorphous up to the exothermic reaction at 1056 °C. Above this temperature an X-ray diffraction pattern showing only three lines is obtained. The *d*-values are 4.15 Å (100), 4.37 Å (35), and 2.533 (15). The DTA curve is different from that for evansite and other hydrated aluminium phosphates (Manly, 1950), so DTA seems to be one of the best methods for the determination of these phosphates. The lower curve in fig. 1 shows loss of weight v. temperature for the Kobokobo mineral.

Occurrences and genesis of bolivarite. The Pontevedra bolivarite occurs as a coating in a granite and is believed to be of hydrothermal origin (Navarro *et al.*, 1921). Particularly interesting is the presence of abnormal amounts of U in this mineral, which indicates that uranium mineralization may exist in the granites of the Campo Lameiro area, Spain.

In the Kobokobo pegmatite, bolivarite is one of the last minerals to be formed. Its formation begins during the final stage of hydrothermal activity, particularly as veinlets cutting other minerals. However, bolivarite has been deposited mainly during the supergene stage as a coating on several minerals located either in the phosphate or in the weathering zones. Bolivarite as a supergene mineral is often associated with lithiophorite. In the weathering zone the associated minerals are lithiophorite, limonite, coeruleolactite, and clay minerals (L. Van Wambeke, 1957).

The genesis of the Kobokobo bolivarite can readily be explained. This mineral, together with the other hydrated aluminium phosphates and in particular coeruleolactite, was formed after the deposition of the Li-Fe-Mn-Ca phosphates. Primary alteration of the thorian uraninite and also of the feldspars begins locally during the main phosphate deposition, giving rise to an enrichment of the residual solutions in Al, U, and Si, besides Ca and P. The result was the formation of the hydrated aluminium phosphates, quartz, and clay minerals, which occur locally as veins. During the

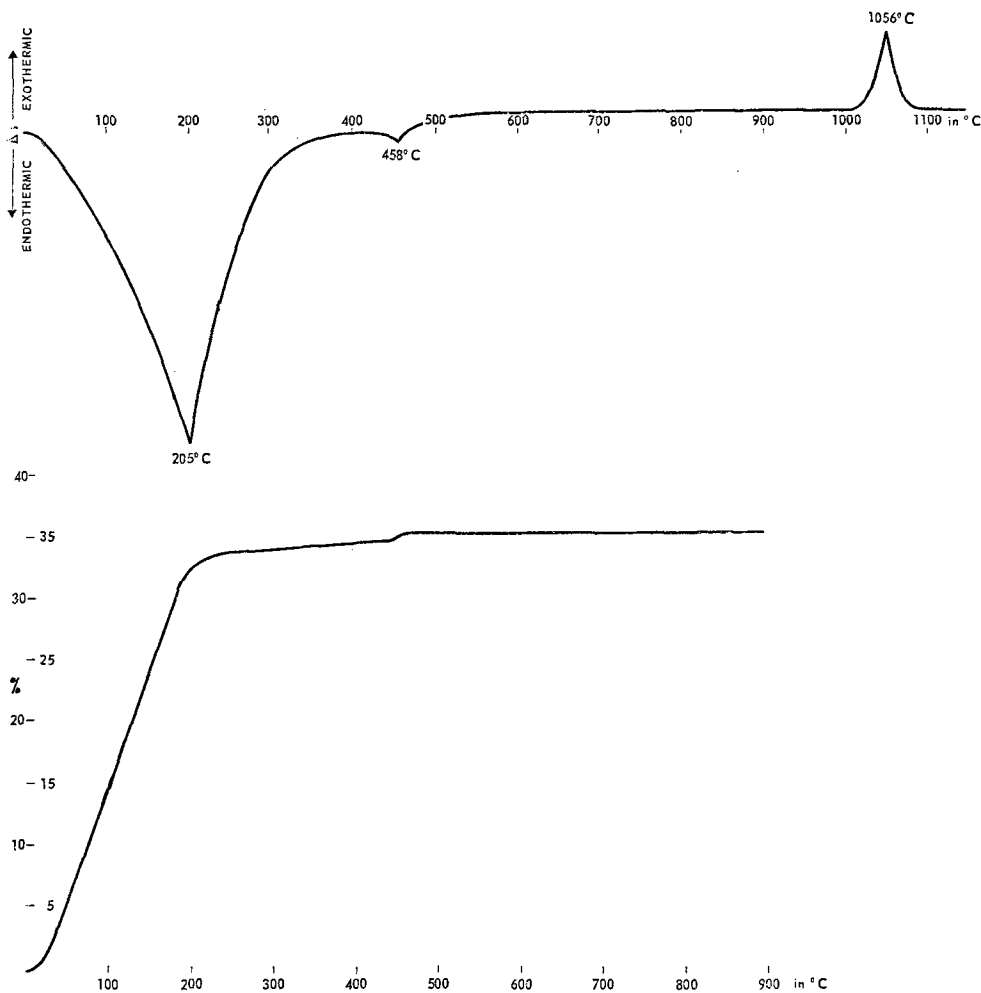


FIG. 1. D.t.a. (top) and thermogravimetric curves for Kobokobo bolivarite.

weathering, the solutions had about the same chemical composition as the residual solutions but most probably with a higher P:Si ratio, due mainly to the partial secondary alteration of the Li-Fe-Mn phosphates. U was again remobilized also. The result was the particular mineral assemblage with the bolivarite found in the weathering zone.

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