Kobokoboite, Al₆(PO₄)₄(OH)₆·11H₂O, a new mineral from the Kobokobo pegmatite, Democratic Republic of the Congo

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Abstract: Kobokoboite, ideally Al₆(PO₄)₄(OH)₆·11H₂O, is a new mineral (IMA2009–057), from the Kobokobo pegmatite, South Kivu Province, Democratic Republic of the Congo. Kobokoboite forms 0.1 to 0.15-mm thick crusts and coatings of pearly white, glistening, platy crystals, usually on a matrix of frondelite and keckite. Other associated minerals reported include a fine-grained mixture of planerite, variscite and wavellite ("coeruleolactite"), as well as muscovite-2*M*₂, evansite and apatite-(CaOH). Individual crystals of kobokoboite are rectangular plates or flattened blades on (001). The dominant form observed is {001}. The crystals have a pearly lustre, are translucent but transparent on edge, have a white streak and are non-fluorescent. Mohs hardness is about 2 (estimated). The fracture is irregular and the tenacity is brittle. Measured density is 2.21(3); calculated density is 2.287 gcm⁻³. Kobokoboite crystals are biaxial (-), with the indices of refraction $\beta = 1.558(2)$ and $\gamma = 1.562(2)$ measured in white light and with $2V_{\text{meas.}} = 60-80^{\circ}$. Orientation: $X \approx c$; *Y* and *Z* could not be determined. Crystals are non-pleochroic. The empirical formula (based on (O + OH + F) = 33) is: (Al_{5.85}Fe³⁺0.14</sub>Ca_{0.03}Na_{0.02})_{2.6.04}(PO₄)_{3.97}[(OH)_{5.80}F_{0.34}]_{2.6.14}·10.98H₂O. Kobokoboite is triclinic, space group *P*1 or *P*1, *a* = 7.460(1), *b* = 7.737(1), *c* = 12.385(5) Å, $\alpha = 102.79(2)$, $\beta = 90.20(3)$, $\gamma = 116.33(2)^{\circ}$, V = 620.6(3) Å³ and Z = 1. The five strongest lines in the powder X-ray diffraction pattern are [*d*_{obs} in Å, (*I*]]: 11.990, (100); 6.868, (45); 3.552, (39); 6.006, (33); 3.081, (29). The chemistry and cell parameters of kobokoboite suggest a structural relationship with planerite and the new mineral IMA2005–025a, where the same sheet of octahedra and tetrahedra parallel to {001} are responsible for *a*, *b* and γ . The name is in reference to the type locality.

Key-words: Kobokoboite, new mineral, aluminium phosphate, optical properties, Kobokobo pegmatite, Democratic Republic of the Congo.

1. Introduction

The Kobokobo pegmatite in South Kivu Province, Democratic Republic of the Congo (formerly Zaïre), was at one time the largest source of beryl in Africa. It outcrops in the Kamituga region, about 100 km southwest of Bukavu, within the Archaean to Proterozoic Kibaran Metallogenic Province of Central Africa (Pohl, 1994). The pegmatite occupies the anticlinal axis of a recumbent fold formed within micaceous schists and amphibolites, and is strongly and asymmetrically zoned (Safiannikoff & van Wambeke, 1967). The principal minerals present are albite, microcline and Li-bearing micas, and these host a wide variety of accessory minerals, including significant concentrations of beryl, columbite-group minerals and cassiterite. The Kobokobo pegmatite is classified as belonging to the LCT family, rare-element class, Li subclass, beryl type, beryl-columbite/beryl-phosphate subtype, after Černý & Ercit (2005). An upper branch of the pegmatite contained Th-rich uraninite, apatite-(CaF) and primary Li–Fe–Mn phosphates (van Wambeke, 1987). Late-stage hydrothermal activity and supergene reactions have strongly altered this assemblage and remobilised elements such as Al, Ca, P and U to form a suite of rare minerals, including thirteen new species, mostly U(\pm Al) phosphates (Deliens *et al.*, 1981, 1984, 1990; van Wambeke, 1987). Here we report the 14th new mineral from the Kobokobo pegmatite.

The type specimen of kobokoboite and associated material were discovered during extensive prospecting trips to the Kobokobo pegmatite ($3^{\circ} 5' S, 27^{\circ} 8' E$) in the 1960s by one of the authors (LVW). The name of the new mineral is derived from the name of the locality. Both the mineral and name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2009–057). The type specimen is preserved in the collections of Museum Victoria (PO Box 666,

Melbourne, Victoria 3001, Australia), registered number M49194.

2. Occurrence and paragenesis

About 20 specimens carrying possible kobokoboite have been collected, but on many of these, admixture with other fine-grained white minerals, such as apatite-(CaOH), muscovite- $2M_2$, "coeruleolactite" (a mixture of planerite, wavellite and variscite) (Foord & Taggart, 1998) and evansite (="bolivarite") (van Wambeke, 1971) have in the past made it difficult to obtain pure samples for investigation. Two small specimens have been preserved in the collections of the Museum Victoria, but the current location of the remaining samples is unclear.

Kobokoboite formed as a result of supergene weathering of the upper branch of the albite-beryl-microcline pegmatite. Strong alteration has resulted in the remobilisation of Al, P, U and Ca, and has created a rich secondary Alphosphate assemblage. Kobokoboite is interpreted as one of the latest forming minerals in the Kobokobo assemblage.

3. Appearance and physical properties

On the two small samples available for study (both provided to WDB by LVW in 1993), kobokoboite occurs as crusts and coatings of pearly white, glistening, platy crystals. The crusts are 0.1–0.15 mm thick and line small cavities in a matrix of frondelite (\pm keckite) and may also encrust prisms of apatite-(CaOH). SEM investigations show that individual crystals are pseudo-hexagonal plates or flattened blades on (001). The dominant form observed is {001}; other forms could not be identified. Crystals range up to about 50 μ m across and of the order of a few micrometers thick (Fig. 1 and 2).

Kobokoboite crystals show a pearly lustre, are translucent but transparent on edge, have a white streak and are



Fig. 2. Compact crusts of white intergrown blades of kobokoboite

Fig. 2. Compact crusts of white intergrown blades of kobokoboite overgrowing keckite and frondelite. Field of view approximately 3 mm across. Museum Victoria specimen M49194.

non-fluorescent in shortwave or longwave ultraviolet light. Mohs hardness is estimated to be about 2, the tenacity is brittle, fracture is irregular and no cleavage or parting or twinning was observed. The density measured by the sink–float method in an aqueous solution of sodium polytungstate is 2.21(3) gcm⁻³, whilst the calculated density from the empirical formula and unit cell is 2.287 gcm⁻³. Kobokoboite is not soluble in concentrated HCl acid.

Crystals of kobokoboite are biaxial negative, with the indices of refraction $\beta = 1.558(2)$ and $\gamma = 1.562(2)$ measured in white light; it was not possible to measure α due to the unfavourable orientation of the kobokoboite crystals. 2V ranges between 60 and 80°. Using an intermediate 2V (70°), the calculated α is 1.556. Kobokoboite is non-pleochroic and the optical orientation is $X \approx c$; Y and Z could not be determined.

4. Chemical composition

Quantitative wavelength-dispersive electron-microprobe analyses (nine points) were carried out using a Cameca SX 50 electron microprobe at the University of Melbourne. Operating conditions were 15 kV, 20 nA with a 10 μ m defocussed beam. The ZAF correction method was used. No other elements were detected by energy dispersive spectroscopy. H₂O was determined using a Carlo Erba 1106 automatic CHN analyser in the Microanalytical Unit of the Research School of Chemistry, Australian National University on 0.728 mg of kobokobite. The results, as well as the standards used, are shown in Table 1.

The mean composition of kobokoboite yields an empirical formula, based on (O + OH + F) = 33, of: $(Al_{5.85}Fe^{3+}_{0.14}Ca_{0.03}Na_{0.02})_{\Sigma 6.04}(PO_4)_{3.97}[(OH)_{5.80}F_{0.34}]_{\Sigma 6.14} \cdot 10.98H_2O$. The simplified formula of kobokoboite is $(Al,Fe)_6(PO_4)_4(OH)_6 \cdot 11H_2O$ and the end-member formula is $Al_6(PO_4)_4(OH)_6 \cdot 11H_2O$, which requires Al_2O_3 36.33, P_2O_5 33.71, H_2O 29.96, total 100 wt%.





Table 1. Electron-microprobe analyses (9) of kobokoboite.

Table 2. X-ray powder diffraction data for kobokoboite.

Constituent	Wt%	Range	Stand. dev.	Probe standard
Na ₂ O	0.06	0.02-0.09	0.02	Albite
CaO	0.18	0.07-0.26	0.07	Wollastonite
MnO	0.01	0-0.04	0.02	Mn metal
Fe ₂ O ₃	1.31	0.40-4.74	1.34	Hematite
Al_2O_3	35.16	33.46-37.61	1.67	Corundum
P_2O_5	33.25	29.62-36.30	1.92	Apatite-(CaF)
F	0.76	0-1.05	0.32	Apatite-(CaF)
H_2O^*	29.52			
F=O	-0.32			
Total	99.93			

*Measured using the CHN method.

The Gladstone-Dale compatibility, using an intermediate 2V of 70°, is $1 - (K_p/K_c) = -0.024$ (excellent).

5. X-ray diffractrometry

It was not possible to complete a full single-crystal investigation due to the poor quality of the crystals and the diffuse nature of the diffraction spots. A set of 36 images at 25 min exposures was collected for a crystal with dimensions 70 $\times 40 \times 7 \ \mu\text{m}$ using a Rigaku R-Axis Spider instrument. The approximate cell obtained was a = 7.4, b = 7.7, c = 12 Å, $\alpha = 100$, $\beta = 91$, $\gamma = 116^{\circ}$. This cell was used as the basis for the cell refinement of the powder data and reflections were indexed based upon the intensities of reflections observed in the single-crystal study. X-ray powder-diffraction data (Table 2) were collected using the same instrument and gave the unit cell a = 7.460(1), b = 7.737(1), c = 12.385(5) Å, $\alpha = 102.79(2)$, $\beta = 90.20(3)$, $\gamma = 116.33(2)^{\circ}$, V = 620.6(3) Å³ and Z = 1 (Table 3). We were unable to determine if kobokoboite is *P*1 or *P*1.

The unit cell of kobokoboite is unique and has no natural or synthetic analogues. The chemistry and cell parameters of kobokoboite suggest a structural relationship with the turquoise-group mineral planerite, $\Box Al_3(PO_4)_2(OH)_3 \cdot 2H_2O_4$ and an as-yet-unapproved new mineral IMA2005-025a, $Al_3(OH)_4(H_2O)_3(PO_4)(PO_3OH) \cdot H_2O$. All three have the same Al:P ratio (3:2) and share similar a and b cell lengths (7.4-7.5 Å, 7.7-7.8 Å) and the angle γ (115–116°) between them (Table 3). These parameters in IMA2005-025a (for which the crystal structure has been determined) and planerite (based upon it being isostructural with turquoise) are determined by the linkages of octahedra and tetrahedra forming the sheets parallel to $\{001\}$. It is very likely that the structure of kobokoboite is based upon the same sheet of octahedra and tetrahedra parallel to $\{001\}$ and that it differs in the linkage between sheets in the c direction.

I _{obs}	$d_{ m obs}$	hkl
100	11.990	0 0 1*
45	6.868	010*
33	6.006	0 0 2*
15	5.462	$1\ 0\ 1,\ \overline{1}\ 1\ 1$
19	5.135	0 1 2
18	4.719	ī 0 2*
16	3.894	$1\ 1\ 0,\ 1\ \overline{2}\ 1$
27	3.714	2 1 0
39	3.552	2 1 1*, 1 1 1
18	3.453	0 2 1
9	3.284	2 0 1*
18	3.202	2 2 0*, 2 2 1*
29	3.081	1 2 3*, 2 0 1
22	3.028	$\bar{2} 0 2^*, 2 \bar{2} 2$
17	2.908	ī 2 2*
19	2.556	1 3 1*
20	2.463	<u>3</u> 10*
21	2.365	2ī3*
15	2.301	$\bar{2}$ 3 1
14	2.271	Multiple
9	2.213	_ 3 0 1*
11	2.140	3 3 1*, 3 3 0*
10	2.077	Multiple
9	2.023	Multiple
14	1.974	Multiple
14	1.908	311
13	1.873	420
9	1.841	Multiple
6	1.783	Multiple
6	1.761	Multiple
4	1.740	Multiple
4	1.721	Multiple
6	1.659	Multiple
4	1.637	Multiple
5	1.564	Multiple
6	1.541	
16	1.509	3 5 2*, 3 5 1*
8 5	1.439	Multiple
3	1.428	Multiple
3	1.40/	Multiple
3	1.390	Multiple
3	1.302	wiutuple

Indexing is based on reflections observed from the single crystal study. "Multiple" indicates that several different *hkl* combinations are possible.

*Reflections used for unit-cell refinement.

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	Kobokoboite	IMA2005–025a	Planerite*
Ideal formula	$Al_6(PO_4)_4(OH)_6 \cdot 11H_2O$	$Al_3(OH)_4(H_2O)_3(PO_4)(PO_3OH) \cdot H_2O$	$\Box Al_3(PO_4)_2(OH)_3 \cdot 2H_2O$
Crystallography			
Space group	$P1$ or $P\overline{1}$	$P\bar{1}$	$P\bar{1}$
a(Å)	7.460(1)	7.386(3)	7.505(2)
$b(\mathbf{A})$	7.737(1)	7.716(3)	7.814(2)
c (Å)	12.385(5)	11.345(4)	9.723(3)
α (°)	102.79(2)	99.773(5)	111.43
β (°)	90.20(3)	91.141(6)	68.69
γ (°)	116.33(2)	115.58(5)	115.56
V (Å)	620.6(3)	571.6(3)	464.2(1)
Ζ	1	2	2

Table 3. Comparison of formulas and cell parameters for kobokoboite, IMA2005–025a and planerite.

*Foord & Taggart (1998); Anthony *et al.* (2000). No errors on the angles were reported. The cell has been transposed to correspond to the cells of turquoise, kobokoboite and IMA2005–025a.

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