

Lakebogaite, $\text{CaNaFe}_2^{3+}\text{H}(\text{UO}_2)_2(\text{PO}_4)_4(\text{OH})_2(\text{H}_2\text{O})_8$, a new uranyl phosphate with a unique crystal structure from Victoria, Australia

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ABSTRACT

Lakebogaite, ideally $\text{CaNaFe}_2^{3+}\text{H}(\text{UO}_2)_2(\text{PO}_4)_4(\text{OH})_2(\text{H}_2\text{O})_8$, is a new Ca–Na–Fe uranyl phosphate mineral from a quarry in Upper Devonian granite near Lake Boga, northern Victoria, Australia. It is associated with Na-analogue of meurigite (IMA 2007-024), torbernite, and saléeite on a matrix of microcline, albite, smoky quartz, and muscovite. Lakebogaite occurs as bright lemon-yellow transparent prismatic crystals up to 0.4 mm across. The crystals have a vitreous luster and a pale yellow streak. Mohs hardness is about 3. The fracture is even to conchoidal. In transmitted light, the mineral is pale yellow with very weak pleochroism: X = yellow, Y = grayish yellow, Z = grayish yellow; dispersion $r > v$, strong. Lakebogaite crystals are biaxial (+), with slightly variable refractive indices within the ranges: $n_\alpha = 1.650(2)$ – $1.652(2)$, $n_\beta = 1.660(4)$ – $1.664(3)$, $n_\gamma = 1.681(3)$ – $1.686(2)$, measured using white light, and with $2V_{\text{meas}} = 80$ – 85° and $2V_{\text{calc}} = 70$ – 74° . Orientation: Y = **b**; crystals are elongated along [010], resulting in straight extinction. The empirical chemical formula (mean of nine electron microprobe analyses) calculated on the basis of 30 anions is $(\text{Ca}_{1.00}\text{Na}_{0.80}\text{Sr}_{0.10})_{\Sigma 1.90}(\text{Fe}_{1.85}\text{Al}_{0.30})_{\Sigma 2.15}(\text{UO}_2)_{1.80}(\text{PO}_4)_{4.07}(\text{OH},\text{H}_2\text{O})_{10.12}$. Lakebogaite is monoclinic, space group *Cc*, $a = 19.6441(5)$, $b = 7.0958(2)$, $c = 18.7029(5)$ Å, $\beta = 115.692(1)^\circ$, $V = 2349.3(7)$ Å³, $Z = 4$. The seven strongest reflections in the powder X-ray diffraction pattern are [d_{obs} in Å (*I*) (*hkl*): 6.60 (100) (110), 3.16 (40) (514, 604), 4.07 (20) (404), 3.80 (20) (314), 3.56 (20) (020, 312), 3.31 (20) (114, 220), 2.797 (20) (006)]. The crystal structure was solved from single-crystal X-ray diffraction data and refined to $R_1 = 0.038$ on the basis of 5222 unique reflections with $F > 4\sigma F$. It comprises pairs of edge-shared UO_7 pentagonal bipyramids that are inter-linked via corner-sharing with PO_4 tetrahedra, to form chains parallel to the **c**-axis. Each UO_7 polyhedron also shares one of its edges with another PO_4 tetrahedron. The $(\text{UO}_2)_2(\text{PO}_4)_4$ chains are cross-linked via corner-sharing between the PO_4 tetrahedra and $\text{Fe}^{3+}\text{O}_4(\text{OH})_2$ octahedra. The octahedra join together by corner-sharing via OH anions to form chains parallel to **b**. The Na^+ and Ca^{2+} cations, and 4 water molecules occupy eight-sided channels along [010]. The remaining water molecules occupy large ten-sided channels directed along [001] and intersecting the [010] channels. The mineral is named for the nearest township.

Keywords: Lakebogaite, new mineral, uranyl phosphate, Lake Boga quarry, north-western Victoria, Australia, crystal structure, $(\text{UO}_2)_2(\text{PO}_4)_4$ chains

INTRODUCTION

Uranyl minerals are widespread and locally abundant in weathering zones, reflecting their insolubility under most ambient conditions (Fronzel 1958; Finch and Ewing 1992). Phosphate-bearing members of the autunite group (Finch and Murakami 1999) dominate these assemblages and are commonly present as well-formed millimeter-sized crystals showing spectacular colors. While these secondary minerals are generally not considered as uranium ore, they are attractive to mineral collectors for their aesthetic qualities and to crystal chemists for their novel structures (e.g., Burns et al. 1997; Burns and

Klingensmith 2006). Of the many localities yielding secondary uranyl species, a large quarry in the Lake Boga Granite, northern Victoria, Australia, is unique for being the type locality for two new uranyl phosphates, ulrichite (Birch et al. 1988; Kolitsch and Giester 2001) and the new species lakebogaite, the subject of this paper. Along with torbernite, saléeite, and metanatroautunite (sodium autunite) (Mills 2004), ulrichite and lakebogaite occur as well-formed crystals in miarolitic cavities and on joint planes. Although all five species have resulted from the alteration of primary uraninite in the granite by oxidizing groundwaters, the crystallization of ulrichite and lakebogaite appears to have required novel and restricted geochemical conditions.

The first specimen of lakebogaite was collected in 2000 by John Carey, a member of a local mineral-collecting club, which pays regular visits to the Lake Boga quarry. Other collectors have

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since found more material, so that there are now six specimens containing about 35 crystals of lakebogaite. The mineral data and name were approved by the IMA Commission on New Minerals, Nomenclature and Classification in March 2007 (IMA 2007-001). The name is for the locality, in turn derived from the Bogan tribe of Australian aboriginal people, who were the original inhabitants of the region. Due to the small amount of material available, there is no holotype specimen, but three co-types are housed in the mineralogical collections at Museum Victoria (M46722 for crystal structure and optics; M47678 for microprobe analysis; M50194 for microprobe analysis and crystal structure).

Occurrence

The host rock for the lakebogaite crystals is a pegmatitic phase of the Lake Boga Granite, a large Upper Devonian S-type pluton within the Lachlan Fold Belt of southeastern Australia (VandenBerg et al. 2000). The bi-lobate outline of the pluton is known only from geophysical interpretation, as its entire natural exposure is covered by Cenozoic Murray Basin sediments that are up to several hundred meters thick. The only window into the granite for sampling purposes is a quarry located about 10 km SSW of the township of Lake Boga (35°33'8"S, 143°34'31"E). Textures exposed in the uppermost levels of the quarry include miarolitic cavities, pegmatitic veins and patches, and quench features suggestive of the pluton's roof zone, although no contact rocks are exposed (Mills 2003; Mills et al. 2008). At deeper levels (40–60 m) the granite is uniform and porphyritic in K-rich feldspar. The uppermost 10 m of the granite have undergone light to moderate weathering, and prominent vertical and horizontal jointing has provided access for groundwater.

Mineralogically, the Lake Boga Granite is distinctive for abundant, centimeter-sized, hydrothermal fluorapatite crystals in miarolitic cavities, sporadic patches of magmatic copper sulfides (mainly chalcopyrite), and accessory uraninite microcrystals, mainly as inclusions in biotite (Mills 2003). This assemblage has been particularly fertile when subjected to the influx of groundwater under the semi-arid conditions of the region. Alteration associated with weathering has provided locally high concentrations of soluble species of Cu, P, U, Bi, Fe, Mg, Ca, Sr, Al, K, and Na in the groundwater solutions that saturate the rock and migrate along joint planes. Strong seasonal climatic fluctuations have resulted in periodic crystallization of suites of phosphates, such as turquoise-chalcociderite, libethenite, pseudomalachite, an unnamed polymorph of sampleite (Giester et al. 2007), Na-analogue of meurigite (IMA 2007-024) (Birch et al. 1996; Kampf et al. 2007), and the uranyl phases, in fractures and miarolitic cavities throughout the weathered zone. The occurrence of assemblages and individual species is sporadic and unpredictable, although the uranium phosphates tend to be concentrated along joint planes encrusted with iron-oxyhydroxides.

Lakebogaite crystals have been found in small cavities in pegmatoidal and leucocratic quench-textured varieties of the granite, with the matrix consisting mainly of smoky quartz, microcline, albite, and muscovite. The precise discovery locations of the lakebogaite-bearing samples in the quarry are not known. Na-analogue of meurigite (IMA 2007-024), minor torbernite, and saléeite may be associated with the lakebogaite.

Physical and optical properties

Lakebogaite occurs as well-formed, lustrous, blocky to short prismatic (along [010]) crystals up to 0.4 mm across (Fig. 1) and as clusters of finer crystals up to 0.5 mm across. Forms observed are pedions: {101}, { $\bar{1}01$ }, { $\bar{1}0\bar{1}$ } and {10 $\bar{1}$ } with possibly additional pedions {001} and {00 $\bar{1}$ }, and domes {110} and { $\bar{1}10$ }. Crystals are bright lemon-yellow, transparent, and have a vitreous luster. Some crystals show a milky to cloudy off-white core, which appears to be caused by very fine-grained brownish inclusions. The streak is pale yellow. There is a possible indistinct cleavage direction normal to [010], fracture is even to conchoidal, and tenacity is brittle. No macroscopic or microscopic twinning is observed, although the crystal-structure solution demonstrated the presence of racemic twinning. The Mohs hardness is estimated to be about 3. The density was not determined precisely but crystals sink in tetrabromoethane (2.955 g/cm³) and float in Clerici solution (~4.3 g/cm³). A density of 3.485 g/cm³ was calculated based on the empirical formula and unit-cell parameters from the single-crystal refinement.

Crystals are biaxial (+), with slightly variable refractive indices within the ranges: $\alpha = 1.650(2)$ – $1.652(2)$, $\beta = 1.660(4)$ – $1.664(3)$, $\gamma = 1.681(3)$ – $1.686(2)$, measured using white light, and with $2V_{\text{meas}} = 80$ – 85° and $2V_{\text{calc}} = 70$ – 74° . Orientation: Y = **b**; crystals are elongated along [010], resulting in straight extinction and variable character of optical elongation (e^+ and e^- , depending on crystal orientation). In transmitted light, lakebogaite is pale yellow, with very weak pleochroism: X = yellow, Y = grayish yellow, Z = grayish yellow; absorption: X slightly stronger than Z; and dispersion: $r > v$, strong. The Gladstone–Dale compatibility index is 0.054, categorized as good.

Chemical composition

Chemical analyses (9) of lakebogaite were carried out by means of an electron microprobe (WDS mode, 20 kV, 5 nA, 20 μm defocused beam diameter) at CSIRO Minerals, Melbourne. The results, as well as the standards used, are shown in Table 1. The mineral is extremely difficult to analyze with a microprobe, due to a rapid reaction under the electron beam. Even with a very low beam current and defocused beam, analytical totals were variable and hence so were water contents “by difference.” Due to the very small number of crystals available there was not enough material available for direct water determination, but the presence of H₂O was confirmed by the crystal-structure solution.

The mean composition of lakebogaite corresponds to the empirical formula (calculated on the basis of 30 apfu):

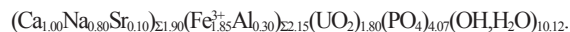


TABLE 1. Electron microprobe analyses (wt%) of lakebogaite

Constituent	Mean wt%	Range	Stand. dev.	Probe standard
Na ₂ O	2.01	1.27–2.76	0.65	NaCl
CaO	4.55	4.37–4.65	0.16	wollastonite
SrO	0.87	0.62–1.08	0.19	SrTiO ₃
Fe ₂ O ₃	11.98	11.00–12.92	0.73	hematite
Al ₂ O ₃	1.23	0.80–1.76	0.42	MgAl ₂ O ₄
P ₂ O ₅	23.44	22.90–23.70	0.34	fluorapatite
UO ₃	41.74	40.70–42.99	0.81	uraninite
H ₂ O _{diff}	14.18	12.30–15.89	–	–
Total	100.00			



FIGURE 1. Lakebogaite crystal with Na-analogue of meurigite (IMA 2007-024) globules on a quartz matrix. Crystal is 0.4 mm across.

The simplified formula is $\text{CaNaFe}_3^{3+}\text{H}(\text{UO}_2)_2(\text{PO}_4)_4(\text{OH})_2(\text{H}_2\text{O})_8$, which requires Na_2O 2.43, CaO 4.40, Fe_2O_3 12.54, P_2O_5 22.28, UO_3 44.91, H_2O 13.44, total 100.00 wt%. In the formula of lakebogaite, there is an additional negative charge, which has been formally compensated by the addition of a hydrogen atom. It is possible that one of the water molecules in lakebogaite is a hydronium ion, or that an additional hydrogen exists within the structure (see further discussion below). There was insufficient material to investigate this by infrared spectroscopy. There is no evidence for protonation of any of the phosphate ions, as shown by the bond-valence sums of the oxygen atoms (see below).

CRYSTAL STRUCTURE

Experimental methods

The $0.4 \times 0.4 \times 0.1$ mm prismatic crystal shown in Figure 1 was dissected with a scalpel to give a smaller, more equi-dimensional fragment for crystallographic studies. Precession photographs showed that the crystal fragment was of a good quality (no twinning or diffuse features) and it displayed *C*-centered monoclinic symmetry, with approximate cell parameters $a = 19.6$, $b = 7.1$, $c = 18.7$ Å, and $\beta = 115.6^\circ$. The precession photographs displayed a pronounced sub-cell with a halved *c*-axis of length 9.35 Å. Reflections with $\ell = 2n + 1$ were generally very weak. Single-crystal intensity data were collected at room temperature using a Nonius Kappa CCD diffractometer (Monash University, Melbourne). The data collection and refinement details are summarized in Table 2. The CCD intensity data sets were processed to produce absorption-corrected data files, which were analyzed in WinGX (Farrugia 1999). The structure refinement was made using SHELXL-97 (Sheldrick 1997).

An analysis of the full reflection data set confirmed the *C*-centered monoclinic symmetry and identified an additional extinction condition, for $(h0l)$ reflections with $l = 2n + 1$. This restricted the possible space groups to *C2/c* or *Cc*. Initially, the centrosymmetric space group was used. The coordinates of the U atoms were determined from a Patterson map and all other atoms were located in successive Fourier and difference Fourier maps. However, the *C2/c* model could not be refined below an *R* value of 10%. Lowering of the space group symmetry to *Cc* allowed the structure refinement to converge satisfactorily, and demonstrated the presence of racemic twinning [refined twin ratio 0.43(1):0.57]. Refinement in the non-centrosymmetric space group showed that one of the two independent U atom sites was incompletely occupied. The large-cation site, which had a statistical distribution of Ca and Na in *C2/c*, separated into two sites in *Cc* and distinct ordering of Na and Ca in separate sites was found.

The final refinement was made with anisotropic displacement parameters for all metal atom sites and isotropic displacement parameters for the O atoms. The H atoms associated with hydroxyl ions and water molecules were not located. The final

TABLE 2. Summary of data collection conditions and refinement parameters for lakebogaite

Formula (idealized)		$\text{CaNaFe}_3^{3+}\text{H}(\text{UO}_2)_2(\text{PO}_4)_4(\text{OH})_2(\text{H}_2\text{O})_8$
Crystal data		
Cell parameters		$a = 19.6441(5)$ Å $b = 7.0958(2)$ Å $c = 18.7029(5)$ Å $\beta = 115.692(1)^\circ$ $V = 2349.3(7)$ Å ³
Z		4
Space group		<i>Cc</i> (no. 9)
Data collection		
Temperature (K)		293
λ (MoK α)		0.71073
Crystal shape, size		prism, $0.08 \times 0.08 \times 0.05$ mm
Collection mode		φ scan, $0-360^\circ$, $\Delta\varphi = 0.5^\circ$ plus ω scans
Count time per frame		40 s
$2\theta_{\text{max}}$ ($^\circ$)		60
Reflection range		$-27 \leq h \leq 27$; $-9 \leq k \leq 9$; $-26 \leq l \leq 25$
Total no. reflections		24108
Data completeness		99.3%
No. unique reflections		6306
No. reflections, $F > 4\sigma(F)$		5222
Absorption correction		$\mu = 37.2$ mm ⁻¹
(Multi-scan)		$T_{\text{min}}/T_{\text{max}} = 0.60$
R_{merge} on F^2		0.034
Refinement		
No. parameters refined		221
R_1 , $F > 4\sigma(F)$		0.038
R_1 , all data		0.051
wR_2 (F^2)*, all data		0.080
GOF		1.04
$\Delta\sigma_{\text{min}}, \Delta\sigma_{\text{max}}$ (e/Å ³)		-1.6, 2.9
* $w = 1/[\sigma^2(F_o^2) + (0.024P^2 + 50.1P)]$, $P = [2F_o^2 + \text{Max}(F_o, 0)]/3$.		

R_1 factors were 0.038 for 5222 observed reflections with $F > 4\sigma(F)$ and 0.051 for all 6306 unique reflections (see Table 2). The refined structure model corresponds to the formula $(\text{Ca}_{0.85}\text{Na}_{0.15})\text{NaFe}_3^{3+}(\text{Fe}_{0.90}\text{Al}_{0.10})\text{H}(\text{UO}_2)_2(\text{PO}_4)_4(\text{OH})_2(\text{H}_2\text{O})_{7-8}$.

The refined atomic coordinates, site occupancies and equivalent displacement parameters are given in Table 3. Anisotropic displacement parameters for the metal atoms are reported in Table 4, polyhedral bond distances in Table 5, and a bond-valence analysis in Table 6. A list of observed and calculated structure factors is available from the authors. Note that Table 3 reports O_w positions corresponding to seven water molecules, while the electron microprobe analyses suggest closer to eight water molecules per formula unit. A peak in the final difference Fourier map close to (0.57, 0.51, 0.32) has nearest neighbors that are consistent with it being a water molecule. However, the peak was very diffuse, indicating positional disorder or possible high mobility. Addition of an O atom at the site did not significantly improve the *R* factors.

A second fragment from a different crystal was measured at room temperature using a Nonius Kappa CCD diffractometer at the University of Vienna ($2\theta_{\text{max}} = 60^\circ$, full Ewald sphere, crystal size $0.05 \times 0.05 \times 0.07$ mm). Refined unit-cell parameters are $a = 19.714(4)$, $b = 7.120(1)$, $c = 18.744(4)$ Å, $\beta = 115.60(3)^\circ$, $V = 2372.7(8)$ Å³. The space group *Cc* was confirmed, as was the presence of racemic twinning [twin ratio 0.496(9):0.504]. The refined model ($R_1 = 0.029$) indicates the chemical formula:



therefore suggesting that the chemical composition of lakebogaite is slightly variable. The second crystal has a slightly larger unit cell, in agreement with a refined composition reflecting a slightly higher Fe/Al ratio, a somewhat different Ca/Na ratio (no Na on Ca site, but instead some Ca on Na site) and water content (see below). The two U-site occupancies, if refined, yield values of 0.942(4) for U1 and 0.973(3) for U2; it is unknown if these values are artifacts. The above-mentioned peak/site at approximately (0.57, 0.51, 0.32) in the model of the first crystal was less diffuse in the second crystal and could be refined as a water molecule with $U_{\text{eq}} = 0.039(2)$ Å² (refined occupancy ~ 1.05). Since the accurate chemical composition of the second crystal was not determined, the discussion below is restricted to the results from the first crystal. Measurement and structural details of the second crystal may be obtained from the authors.

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for lakebogaite

	x	y	z	U_{eq}
U1*	322(1)	5094(1)	1651(1)	6(1)
U2	9593(1)	5014(1)	8378(1)	16(1)
Fe1	2471(2)	7326(4)	5022(2)	13(1)
Fe2*	2459(2)	2302(4)	5032(2)	11(1)
Al2*	2459(2)	2302(4)	5032(2)	11(1)
P1	3711(3)	9773(5)	4742(3)	13(1)
P2	6225(3)	9882(4)	5323(3)	11(1)
P3	1521(2)	4703(5)	3417(3)	11(1)
P4	8385(3)	4940(4)	6595(3)	17(1)
Ca1*	2678(2)	2311(3)	2990(2)	14(1)
Na1*	2678(2)	2311(3)	2990(2)	14(1)
Na2	7159(4)	7405(8)	6913(4)	36(2)
O1	3370(5)	1460(11)	4967(5)	19(2)
O2	4463(4)	9223(11)	5409(4)	16(2)
O3	3165(5)	8069(10)	4528(5)	18(2)
O4	3798(5)	352(11)	3975(5)	17(2)
O5	6102(5)	9406(12)	6038(5)	18(2)
O6	6537(5)	8158(11)	5098(5)	23(2)
O7	6750(5)	1568(10)	5499(5)	16(2)
O8	5460(5)	415(12)	4624(5)	27(2)
O9	1645(5)	4920(9)	2675(5)	13(2)
O10	1749(4)	6433(9)	3953(4)	14(1)
O11	1981(4)	2967(10)	3868(4)	17(2)
O12	650(4)	4359(11)	3097(4)	14(1)
O13	8188(5)	3206(11)	6110(5)	22(2)
O14	7908(5)	6620(10)	6195(5)	19(2)
O15	9251(4)	5329(10)	6925(4)	15(1)
O16	8321(5)	4603(12)	7399(5)	19(2)
O17	360(5)	7502(12)	1870(5)	25(2)
O18	292(5)	2606(11)	1454(5)	21(2)
O19	9526(6)	7509(13)	8460(6)	36(2)
O20	9656(6)	2492(13)	8259(6)	33(2)
OH1	2918(7)	4809(11)	5284(7)	18(3)
OH2	1971(7)	9798(11)	4733(6)	17(2)
OW1	3490(6)	4715(14)	3907(6)	48(2)
OW2	2112(5)	9241(13)	3021(5)	31(2)
OW3	2958(6)	4679(14)	2152(6)	46(3)
OW4	1706(5)	1125(14)	1614(6)	44(2)
OW5	5519(4)	4796(9)	4587(4)	11(1)
OW6	4546(7)	5083(16)	5248(7)	57(3)
OW7	4160(4)	4894(10)	6819(4)	24(2)

Note: U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

* Refined site occupancies are U1 0.888(4), Fe2 0.91(1), Al2 0.09(2), Ca1 0.87(2), Na1 0.13(3).

TABLE 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for lakebogaite

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U1	3(1)	11(1)	4(1)	-1(1)	1(1)	0(1)
U2	14(1)	25(1)	12(1)	-2(1)	8(1)	-1(1)
Fe1	12(1)	19(1)	11(1)	-1(1)	7(1)	-1(1)
Fe2	9(1)	16(1)	10(1)	-1(1)	5(1)	3(1)
Al2	9(1)	16(1)	10(1)	-1(1)	5(1)	3(1)
P1	11(2)	24(2)	4(2)	0(1)	5(2)	3(1)
P2	7(2)	20(2)	7(2)	2(1)	4(2)	3(1)
P3	4(2)	25(2)	4(2)	-5(1)	2(1)	-2(1)
P4	15(2)	22(2)	14(2)	-3(1)	6(2)	-2(1)
Ca1	16(1)	17(1)	17(1)	0(1)	13(1)	5(1)
Na1	16(1)	17(1)	17(1)	0(1)	13(1)	5(1)
Na2	32(3)	35(3)	48(4)	19(3)	24(3)	12(2)

Note: The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$.

Description of the structure

The crystal structure of lakebogaite is unique among those of U^{6+} minerals and synthetic uranyl compounds. A polyhedral representation of the structure, viewed in projection along the **b**-axis, is shown in Figure 2. It comprises pairs of edge-shared UO_7 pentagonal bipyramids that are inter-linked via corner-sharing with PO_4 tetrahedra, to form chains parallel to the **c**-axis.

TABLE 5. Polyhedral bond distances ($\text{\AA}$) in lakebogaite

M-O	Distance	M-O	Distance
U1-O17	1.745(9)	U2-O19	1.792(10)
U1-O18	1.798(8)	U2-O20	1.819(11)
U1-O2	2.253(8)	U2-O8	2.235(9)
U1-O5	2.308(9)	U2-O4	2.291(9)
U1-O15	2.393(8)	U2-O16	2.393(10)
U1-O9	2.471(9)	U2-O12	2.390(8)
U1-O12	2.547(8)	U2-O15	2.510(8)
mean	2.22	mean	2.20
Fe1-OH1	1.969(10)	Fe2-O1	1.943(9)
Fe1-OH2	1.967(9)	Fe2-OH1	1.958(10)
Fe1-O10	1.996(8)	Fe2-O6	1.964(9)
Fe1-O13	2.003(9)	Fe2-OH2	1.967(10)
Fe1-O3	2.023(9)	Fe2-O11	2.026(8)
Fe1-O7	2.045(9)	Fe2-O14	2.015(9)
mean	2.00	mean	1.98
P1-O1	1.512(10)	P2-O5	1.491(10)
P1-O2	1.517(10)	P2-O6	1.510(9)
P1-O3	1.544(9)	P2-O7	1.525(9)
P1-O4	1.575(10)	P2-O8	1.545(11)
mean	1.54	mean	1.52
P3-O9	1.517(10)	P4-O13	1.477(10)
P3-O10	1.522(8)	P4-O14	1.498(9)
P3-O11	1.541(9)	P4-O15	1.562(10)
P3-O12	1.568(9)	P4-O16	1.580(12)
mean	1.54	mean	1.53
Ca1-O16	2.43(1)	Na2-OW2	2.42(1)
Ca1-OW1	2.45(1)	Na2-O14	2.45(1)
Ca1-OW2	2.46(1)	Na2-O5	2.46(1)
Ca1-OW3	2.51(1)	Na2-OW3	2.51(1)
Ca1-O4	2.577(9)	Na2-OW4	2.64(1)
Ca1-O11	2.597(9)	Na2-O9	2.81(1)
Ca1-OW4	2.59(1)	Na2-O16	2.86(1)
Ca1-O9	2.619(9)	Na2-O6	3.12(1)
mean	2.53	mean	2.66

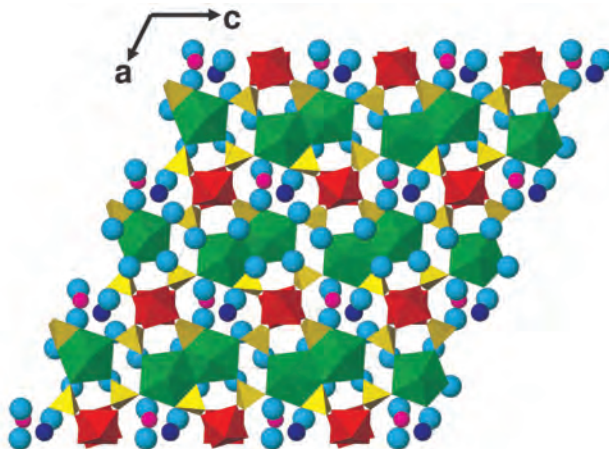


FIGURE 2. Polyhedral representation of the structure of lakebogaite, projected along [010]. Pentagonal bipyramids are UO_7 , sky-blue spheres are oxygen atoms of water molecules, dark-blue spheres are Ca, and red spheres are Na.

Each UO_7 polyhedron also shares one of its edges with another PO_4 tetrahedron. The chains, with composition $(UO_2)_2(PO_4)_4$, are topologically identical to those in the synthetic selenite compound $Sr[(UO_2)(SeO_3)_2] \cdot 2H_2O$ (Almond et al. 2002). The $(UO_2)_2(PO_4)_4$ chains are cross-linked via corner-sharing between the PO_4 tetrahedra and $FeO_4(OH)_2$ octahedra. The octahedra join together by corner-sharing via OH anions to form chains parallel to **b**.

TABLE 6. Bond-valence analysis for lakebogaite

	Ca/Na1*	Na2	Fe1	Fe/Al2*	U1	U2	P1	P2	P3	P4	Total
O1				0.58			1.34				1.91
O2					0.68		1.30				1.98
O3			0.49				1.21				1.70
O4	0.18					0.63	1.17				1.99
O5		0.17			0.61			1.38			2.16
O6				0.58				1.33			1.91
O7			0.47					1.26			1.73
O8						0.70		1.20			1.90
O9	0.16	0.07			0.45				1.35		2.03
O10			0.55						1.34		1.89
O11	0.17			0.49					1.20		1.86
O12					0.38	0.52			1.12		2.02
O13			0.51							1.42	1.93
O14		0.17		0.48						1.35	2.00
O15					0.52	0.41				1.21	2.14
O16	0.27	0.06				0.52				1.07	1.92
O17					1.80						1.80
O18					1.63						1.63
O19						1.65					1.65
O20						1.56					1.56
OH1			0.59	0.56							1.15
OH2			0.56	0.54							1.10
OW1	0.26										0.26
OW2	0.25	0.19									0.44
OW3	0.22	0.14									0.36
OW4	0.18	0.11									0.28
OW5											0.00
OW6											0.00
OW7											0.00
Total	1.69	0.90	3.17	3.22	6.06	5.99	5.02	5.17	5.01	5.05	

* The occupancies of the mixed sites have been taken into account for calculation of the respective BVS values: (Ca/Na1 = 0.85Ca + 0.15Na, Fe/Al2 = 0.90Fe + 0.10Al).

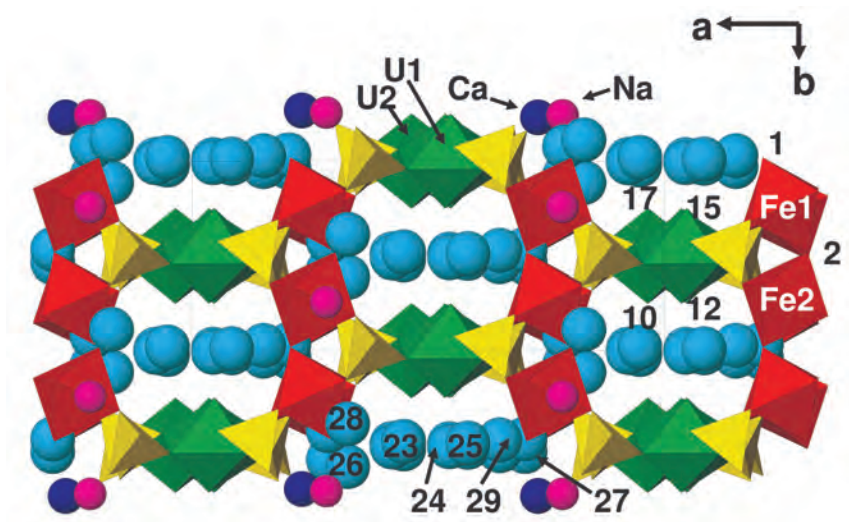


FIGURE 3. Polyhedral representation of the structure of lakebogaite, viewed along [001]. The water molecules are labeled, as are the apical anions of the UO_7 and $\text{FeO}_4(\text{OH})_2$ polyhedra.

The Na^+ and Ca^{2+} cations occupy eight-sided channels along [010], formed via the connection of two UO_7 , two $\text{Fe}^{3+}\text{O}_4(\text{OH})_2$, and four PO_4 polyhedra. The four water molecules centered at OW1 to OW4 are also located in these channels and coordinate to the Na^+ and Ca^{2+} cations. The remaining water molecules, OW5 to OW7, occupy large ten-sided channels that are directed along [001] and intersect the [010] channels. The [001] channels are illustrated in Figure 3. The water molecules OW5 to OW7 do not coordinate to any cations and are presumably held in place by hydrogen bonding.

The apical and equatorial U-O distances (Table 5) are typical for the uranyl ion in pentagonal bipyramidal coordination (Burns et al. 1997). The Ca^{2+} cation is coordinated to eight O atoms and

water molecules in a relatively narrow bond-distance range of 2.43 to 2.62 Å. The Na^+ cation is coordinated to only five O atoms and water molecules within a similar bond-distance range, and has three considerably longer bonds to O9, O16, and O6 (2.81, 2.86, and 3.12 Å).

Calculated bond-valence sums (Brown and Altermatt 1985; Burns et al. 1997) for lakebogaite (Table 6) confirm that the iron is trivalent, that the site designated Na2 is monovalent while the site designated Ca/Na1 is predominantly divalent, consistent with the refined site occupancy ($\text{Ca}_{0.85}\text{Na}_{0.15}$). The bond-valence sums (BVS) also confirm that the bridging anions in the [010] chains of corner-linked octahedra, OH1 and OH2, are both hy-

droxyl ions (BVS values of 1.15 and 1.10 valence units, v.u.). The improved bond-valence parameters of Burns et al. (1997) were used for U^{6+} . These gave BVS values of 6.06 and 5.99 v.u. for U1 and U2, respectively. However, the uranyl group anions, O17 to O20 (see Fig. 3) have low BVS values in the range 1.56 to 1.80 v.u. Such low values are typical of uranyl anions when the Burns et al. (1997) BVS parameters are used (e.g., Kolitsch and Giester 2001). In anhydrous uranyl compounds, the uranyl anions are often also coordinated to large cations such as Ba and Cs, that bring the valence sums closer to 2 (Krivovichev and Burns 2002; Wallwork et al. 2006). In the case of lakebogaite, the only components that are less than 3 Å from the uranyl anions are the water molecules OW5, OW6, and OW7. It is possible that one or more of these may in fact be hydronium ions, H_3O^+ , or a mixture of H_2O and minor Na, or a partially occupied Na site. Such an assignment could also explain the shortfall of one positive charge in the formula of lakebogaite.

A feature of the lakebogaite structure is the seemingly incomplete occupation of the U1 site, 0.888(4). For comparison the refined occupancy of U2 was 0.994(5). A possible explanation is that uranium is partially replaced by aluminum in the U1 site. Such a situation occurs in synthetic zirconolite (Grey et al. 2003), where a hexagonal bipyramidal site usually occupied by large cations such as Ca^{2+} can be partially occupied by small cations such as Ti^{4+} and Al^{3+} . The small cation is displaced from the center of the site toward the equatorial oxygen atoms to take up either four or five coordination. In lakebogaite, the electron microprobe analyses gave 0.30 Al^{3+} per formula unit, whereas the structure refinement accounted for only 0.1 atoms of aluminum substituting at the Fe2 site. An inspection of the difference Fourier map showed peaks displaced by ~ 0.7 Å from U1 that had two short distances (1.7 to 1.8 Å) and three longer distances (2.0 to 2.3 Å) to O anions, comparable to the ranges found for five-coordinated cations in synthetic zirconolite (Grey et al. 2003). Inclusion of aluminum at these sites and refinement of the site occupancies gave a small decrease in the R factor. The possible disordering of the aluminum over several such sites, at low site occupancies, prevented a more definitive confirmation of the hypothesis. It is

also not possible to ascertain whether the mentioned peaks may represent artifacts due to an imperfect absorption correction or other systematic errors.

It is interesting to note that the uranyl mineral ulrichite, $Ca_2Cu_2(UO_2)_2(PO_4)_4 \cdot 8H_2O$ (Birch et al. 1988), also from the Lake Boga quarry, has the same ratio of large cations:octahedral cations:uranyl ions:tetrahedral cations as in lakebogaite, yet has a completely different structure containing isolated UO_7 groups (Kolitsch and Giester 2001). Lakebogaite has structural features in common with the uranyl phosphate, parsonsite, $Pb_2[(UO_2)(PO_4)_2](H_2O)_n$ (Burns 2000; Locock et al. 2005) and the uranyl arsenate, hallimondite, $Pb_2[(UO_2)(AsO_4)_2](H_2O)_n$, with $0 \leq n \leq 0.5$ in each case (Locock et al. 2005). The structures of parsonsite and hallimondite contain pairs of edge-shared UO_7 pentagonal bipyramids and have the same arrangement of phosphate tetrahedra that share corners and edges with the uranyl polyhedra. However, the way in which these clusters are interlinked to form chains differs. In lakebogaite, the clusters are linked via common corner-connected tetrahedra to form chains parallel to *c* as shown in Figure 2, whereas in parsonsite and hallimondite the tetrahedra that interlink the $(UO_2)_2O_8$ dimers share a corner with one dimer and an edge with the other, thus giving a different chain orientation.

X-ray powder diffraction data

The X-ray powder diffraction pattern (Table 7) for lakebogaite was obtained using a 57.3 mm Gandolfi camera with $CuK\alpha$. Unit-cell parameters refined from the powder data are $a = 19.58(9)$, $b = 7.09(2)$, $c = 18.68(7)$ Å, $\beta = 115.8(4)^\circ$, $V = 2336(2)$ Å³.

Paragenesis

The Lake Boga Granite contains up to 65 ppm uranium, with most contained within primary accessory uraninite and monazite (up to 8 wt% U) (Mills et al. 2008). Late-stage hydrothermal fluorapatite crystals also contain uranium, as thin U-enriched zones parallel to crystal growth patterns, and as sporadic uraninite inclusions. Weathering of uraninite and fluorapatite within the upper few meters of the granite resulted in groundwater becoming locally enriched in U, P, and Ca. The presence of patches of magmatic chalcopyrite in the same zone had the effects of lowering pH and providing Cu and Fe for groundwater (Acero et al. 2007). Lakebogaite and the other, more common uranyl phosphates in the Lake Boga Granite have crystallized from these groundwaters. Because U is rapidly fixed in uranyl phosphates (Murakami et al. 1997; Jerden and Sinha 2003), it is likely that crystallization has taken place only short distances from the sites of oxidation. Attempts at U–Th dating of the uranyl phosphates from the Lake Boga quarry have yielded apparent ages from 115 to >550 ka (Maas et al. 2006), although these need to be assessed against variable crystal growth mechanisms and possible loss/gain of U during repeated groundwater residence. The pristine appearance of the uranyl phosphate crystals does not suggest these factors have been major influences on the apparent ages. It is likely therefore that lakebogaite and the other uranyl phosphates have acted to sequester uranium released during weathering of the granite over time scales of several hundred thousand years. This aspect of the uranium geochemistry and geochronology of the Lake Boga Granite is under further study.

TABLE 7. X-ray powder diffraction data for lakebogaite

d_{meas}	d_{calc}	I/I_0	I/I_c	hkl
6.60	6.586	10	10	1 1 0
5.15	5.098	1	1.4	2 0 2
4.65	4.670	1	0.6	2 0 4
4.07	4.052	2	0.7	4 0 4
3.80	3.779	2	1	3 1 4
3.56	3.548	2	0.8	0 2 0
	3.533		1.4	3 1 2
3.31	3.314	2	0.4	1 1 4
	3.293		1.7	2 2 0
3.16	3.197	4 <i>b</i>	2	5 1 4
	3.139		1.6	6 0 4
2.797	2.809	2	1.1	0 0 6
2.659	2.669	1	0.9	4 2 4
	2.646		1.0	5 1 2
2.423	2.441	1 <i>b</i>	0.5	4 2 2
	2.412		0.4	8 0 2
2.002	2.012	2 <i>bb</i>	0.3	8 2 4
	2.010		0.3	4 0 6
	2.007		0.1	9 1 6
	1.995		0.2	8 2 2
	1.984		0.5	2 2 6

Note: *b* = broad, *bb* = very broad.

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