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SELWYNITE, $NaK(Be,Al)Zr_2(PO_4)_4 \cdot 2H_2O$, A NEW GAINESITE-LIKE MINERAL FROM WYCHEPROOF, VICTORIA, AUSTRALIA

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Abstract

Selwynite is a new alkali beryllium zirconium phosphate hydrate from a pegmatite vein in Devonian granite at Wycheproof, in northwestern Victoria, Australia. The mineral occurs as irregular infillings that consist of intergrowths of indistinct radiating crystals and as granular aggregates filling cavities up to 8 mm across in the quartz – orthoclase – albite – muscovite – schorl-bearing pegmatite. Accompanying minerals include two other Zr-bearing phosphates, kosnarite and the new species wycheproofite, as well as wardite, eosphorite, cyrilovite, leucophosphite, rockbridgeite, a kidwellite-like mineral, saleeite and montmorillonite. Selwynite is transparent deep purplish blue with a vitreous luster, but may weather to be pale lavender and translucent. The streak is pale lavender, the fracture, semiconchoidal, the cleavage, undeveloped, and the Mohs hardness, 4. The measured density is 2.94 g·cm^{-3}. Selwynite is uniaxial positive, ω 1.624, ε 1.636, and shows distinct pleochroism from medium to very pale bluish lavender. Average results of chemical analyses give Na_2O 4.77, K_2O 6.26, Rb_2O 0.20, BeO 1.43, CaO 0.98, SrO 0.16, BaO 0.16, MgO 0.15, MnO 0.99, FeO 0.49, Cs_2O 0.70, Al_2O_3 1.04, Ce_2O_3 0.03, ZrO_2 33.76, HfO_2 1.17, P_2O_5 40.90, SiO_2 0.49, F 0.37, H_2O 5.4, less O=F 0.16, total 99.29 wt.%. The simplified formula is $NaK(Be,Al)Zr_2(PO_4)_4 \cdot 2H_2O$, based on (O + F) = 18. Selwynite is tetragonal, with unit-cell parameters refined from powder data: *a* 6.570(3), *c* 17.142(6) Å, *V* 739.9(3) Å^3. For Z = 2, the calculated density for the empirical formula is 3.08 g·cm^{-3}. By analogy with gainesite the space group is $I4_1/amd$. The strongest lines in the X-ray powder-diffraction pattern [d_{obs} in Å(I_{obs})(*hkl*)] are 6.161(100)(101), 4.291(25)(004), 3.286(50)(200), 3.039(30)(105), and 2.895(20)(211). Selwynite is related to gainesite by having the larger of the two Na sites in gainesite occupied by K, and to mccrillisite (Foord *et al.* 1994), which has that site occupied by Cs. All three minerals are considered to be hydrated, with between 2 and 4 water molecules per unit cell. The mineral name honors the late A.R.C. Selwyn, founding Director of the Geological Survey of Victoria.

Keywords: selwynite, new mineral species, sodium potassium beryllium zirconium phosphate hydrate, gainesite, Wycheproof, Australia.

Sommaire

La selwynite est un phosphate sodique et potassique hydraté de béryllium et de zirconium nouvellement découvert dans un filon de pegmatite granitique recoupant un granite dévonien à Wycheproof, dans le nord-ouest de l'état de Victoria, en Australie. Le minéral remplit des interstices irréguliers en intercroissances radiaires de cristaux flous et en agrégats granulaires remplissant des cavités jusqu'à 8 mm de taille dans la pegmatite à orthose – albite – muscovite – schorl. Deux autres phosphates de Zr l'accompagnent, kosnarite et la nouvelle espèce wycheproofite, de même que wardite, éosphorite, cyrilovite, leucophosphite, rockbridgeïte, un minéral du groupe de la kidwellite, saléeïte et montmorillonite. La selwynite est transparente, bleu mauve foncé, avec éclat vitreux; elle devient de couleur lavande pâle et translucide où elle est altérée. Sa rayure est lavande pâle, et sa cassure, semi-conchoïdale; les clivages ne sont pas développés, et la dureté de Mohs est 4. La densité mesurée est 2.94. Il s'agit d'un minéral uniaxe positif, ω 1.624, ε 1.636, qui montre un pléochroïsme distinct, de lavande bleuâtre moyen à très pâle. La moyenne des résultats des analyses chimiques donne Na_2O 4.77, K_2O 6.26, Rb_2O 0.20, BeO 1.43, CaO 0.98, SrO 0.16, BaO 0.16, MgO 0.15, MnO 0.99, FeO 0.49, Cs_2O 0.70, Al_2O_3 1.04, Ce_2O_3 0.03, ZrO_2 33.76, HfO_2 1.17, P_2O_5 40.90, SiO_2 0.49, F 0.37, H_2O 5.4, moins O=F 0.16, pour un total de 99.29% (poids). La formule simplifiée est $NaK(Be,Al)Zr_2(PO_4)_4 \cdot 2H_2O$, en supposant (O + F) = 18. La selwynite est tétragonale; ses paramètres réticulaires, affinés du

cliché de diffraction X sur poudre, sont *a* 6.570(3), *c* 17.142(6) Å, *V* 739.9(3) Å^3. Pour Z = 2, la densité calculée pour la formule empirique est 3.08. En analogie avec la gainesite, le groupe spatial serait $I4_1/amd$. Les raies les plus intenses du cliché de diffraction X [d_{obs} en Å(I_{obs})(*hkl*)] sont 6.161(100)(101), 4.291(25)(004), 3.286(50)(200), 3.039(30)(105) et 2.895(20)(211). La selwynite est apparentée à la gainesite en ayant le plus spacieux des deux sites de Na de cette espèce occupé par le potassium, et à la mccrillisite (Foord *et al.* 1994), où ce site contient le césium. Tous les trois seraient hydratés, avec entre 2 et 4 molécules d'eau par maille élémentaire. Le minéral honore feu A.R.C. Selwyn, directeur fondateur de la commission géologique de Victoria.

(Traduit par la Rédaction)

Mots-clés: selwynite, nouvelle espèce minérale, phosphate hydraté de sodium, potassium, béryllium et zirconium, gainesite, Wycheproof, Australie.

Introduction

Three rare Zr-bearing phosphate minerals have recently been found within veins of granitic pegmatite in granite boulders at a quarry near Wycheproof (lat. 36°05′S, long. 143°14′E), a small town in northwestern Victoria, Australia. Mineral collectors discovered the veins late in 1990 and sent representative specimens to the senior author (WDB) for investigation. This mineralogical study resulted in the identification of a suite of iron phosphates, most notably well-crystallized eosphorite, and three unknown Zr-bearing phosphates, which occurred in cavities in the pegmatite (Birch 1993). Two of the unknown Zr-bearing phosphates, wycheproofite, $NaAlZr(PO_4)_2(OH)_2{\cdot}H_2O$, and selwynite, $NaK(Be,Al)Zr_2(PO_4)_4{\cdot}2H_2O$, have been approved as new species by the IMA Commission on New Minerals and Mineral Names; the third, kosnarite, $KZr_2(PO_4)_3$, was first found in granitic pegmatites in Maine in the late 1980s (Brownfield *et al.* 1993). Wycheproofite and the accompanying kosnarite have been described by Birch & Pring (1994); selwynite is the subject of this paper. The mineral's name records the contribution made to early Victorian geological exploration by Alfred Richard Cecil Selwyn (1824–1902), who was founding Director of the Geological Survey of Victoria between 1860 and 1869. Selwyn also served as Director of the Geological Survey of Canada between 1869 and 1894. The term "selwynite" was first used by Ulrich (1870) for what was thought to be a new Cr-bearing mineral from Victoria, but which was later shown to be a fine-grained green diaspore-bearing rock. The term persists amongst some lapidarists, but neither usage has any formal status. The holotype specimen of selwynite is stored in the Museum of Victoria collections, Melbourne, under catalogue number M42492.

Occurrence

The quarry in which the selwynite occurred is on the eastern side of a low granite knoll known locally as Mount Wycheproof, about 0.5 km east of the town. The knoll consists of a pale grey, medium-grained, muscovite-bearing, S-type granite of Devonian age. It projects through the flat-lying Tertiary sediments of the Murray Basin, which cover much of northwestern Victoria. The pegmatite veins were found in boulders, close to being *in situ*, at the base of the southeastern face of the quarry; these boulders have now been entirely removed by mineral collecting activities. Quartz, orthoclase, albite, muscovite and schorl form the veins, which are between 4 and 12 cm thick. The veins contain miarolitic and interstitial cavities up to several cm across. These may be lined with crystals of eosphorite or filled with other phosphate minerals, including wardite, cyrilovite, rockbridgeite, leucophosphite, a kidwellite-like mineral and saleeite, as well as the Zr-bearing species. Some cavities appear to have formed by dissolution of primary phosphates, including fluorapatite, and are now occupied by skeletal or powdery aggregates consisting of quartz, muscovite, eosphorite and cyrilovite.

Selwynite has been found in only three cavities. On the type specimen, it forms the infilling of an interstitial cavity 8 mm across in feldspars and quartz. Eosphorite and cream-colored montmorillonite accompany the selwynite.

Appearance, Physical and Optical Properties

Selwynite forms irregular infillings that consist of intergrowths of indistinct radiating crystals. No single crystals or crystal faces have been observed. Its most striking feature is the deep purplish blue color, although in one cavity, weathering has reduced the selwynite to a granular pale lavender translucent aggregate mixed with limonite and clay. Unweathered selwynite is transparent, with a vitreous luster, pale lavender streak, semiconchoidal fracture and no distinct cleavage. It is nonfluorescent in short-wave and long-wave ultraviolet light. The estimated Mohs hardness is 4, and the measured density, obtained by suspension in a mixture of methylene iodide and acetone, is 2.94 g·cm^{-3}.

Optical determinations show selwynite to be uniaxial positive, ω 1.624(2), ε 1.636(2), measured in blue-filtered white light. Pleochroism is distinct, with *O* medium bluish lavender, and *E* very pale bluish lavender.

Chemical Composition

Concentrations of the major elements in selwynite were determined using a Cameca SX–50 electron microprobe operating at 15 kV, a specimen current of about 0.2 μA, and beam size of 10 μm. The following standards were used: jadeite (Na), synthetic $KTaO_3$ (K), wollastonite (Ca, Si), corundum (Al), periclase (Mg), hematite (Fe), pure Mn metal (Mn), monazite (Hf, Ce), fluorapatite (F), strontianite (Sr), benitoite (Ba), synthetic pollucite (Cs) and kosnarite from the type locality in Maine (Zr, P). The microprobe data were corrected using the PAP program. The amount of water was determined using a Perkin–Elmer CHN analyzer. The concentrations of Rb and Be were determined by inductively coupled plasma – mass spectrometry (ICP–MS); Li was not detected.

The analytical data and empirical formula for selwynite are shown in Table 1. Elements have been grouped mainly on the basis of the structural formula proposed for gainesite (Moore *et al.* 1983), although it should be noted that the Be site in selwynite is slightly deficient in total cations. The simplified formula for selwynite is $NaK(Be,Al)Zr_2(PO_4)_4 \cdot 2H_2O$. No Zn was detected; as noted for mccrillisite (Foord *et al.* 1994), the small amount of Mn appears to be responsible for the intense bluish purple color.

X-Ray Crystallography

X-ray powder diffraction data for selwynite were recorded using a Guinier–Hägg camera 100 mm in diameter, with Cu*K*α radiation. The data (Table 2) were indexed by analogy with those of gainesite and conform to a tetragonal unit-cell with the following parameters, refined from the powder data: *a* 6.570(3), *c* 17.142(6) Å, *V* 739.9(3) Å^3 and *c/a* 2.6091. For *Z* = 2, the calculated density is 3.08 g·cm^{-3}. The space group $I4_1/amd$ was assigned to selwynite by analogy with gainesite. For the calculated density (3.08 g·cm^{-3}), the Gladstone–Dale compatibility index for selwynite is excellent; using the measured density (2.94 g·cm^{-3}) the compatibility index is fair. A determination of the crystal structure of selwynite is in progress; results will be reported separately.

TABLE 1. CHEMICAL COMPOSITION OF SELWYNITE

wt%	1		2	
Na_2O	4.77	Na	1.00	
K_2O	6.26	K	0.92	1.03
Rb_2O	0.20	Na	0.06	
BeO	1.43	Cs	0.03	
CaO	0.98	Rb	0.02	
SrO	0.16	Be	0.40	0.86
BaO	0.16	Al	0.14	
MgO	0.15	Ca	0.12	
MnO	0.99	Mn	0.10	
FeO	0.49	Fe	0.05	
Cs_2O	0.70	Mg	0.03	
Al_2O_3	1.04	Sr	0.01	
Ce_2O_3	0.03	Ba	0.01	
ZrO_2	33.76	Zr	1.89	1.93
HfO_2	1.17	Hf	0.04	
P_2O_5	40.90	P	3.98	4.04
SiO_2	0.49	Si	0.06	
F	0.37	O	15.80	
H_2O	5.4	F	0.13	
-O=F	0.16	H_2O	2.07	
Total	99.29			

1. Average result of 9 microprobe analyses; H_2O by CHN; Rb, Be by ICP
2. Empirical formula based on 18(O+F)

TABLE 2. X-RAY-DIFFRACTION DATA FOR SELWYNITE

I/Io	d_{obs}(Å)	d_{calc}(Å)	hkl
100	6.161	6.135	101
25	4.291	4.286	004
50	3.286	3.285	200
30	3.039	3.039	105
20	2.895	2.896	211
5	2.609	2.607	204
5	2.431	2.431	116
2	2.230	2.322	220
5	2.169	2.172	301
2	2.143	2.143	008
2	2.055	2.045	303
2	2.020	2.019	312
5	1.847	1.847	305
5	1.828	1.829	109
2	1.813	1.812	321
2	1.715	1.714	0010

a 6.570(3)Å, c 17.142(6)Å, *V* 739.9(3)Å^3

Relationship to Gainesite and McCrillisite

Selwynite is the K-analogue of gainesite and of mccrillisite. Although gainesite was originally described by Moore *et al.* (1983) as being anhydrous, it is now considered, on the basis of new chemical data (this study and Foord *et al.* 1994), that all three members of the "gainesite group" are hydrated, containing between 2 and 4 molecules of water per unit cell (between 1 and 2 water molecules per formula unit). The location and nature of these water molecules in the three structures are currently being investigated. Apart from differences in constituents within the Be site, the main distinction among the three minerals is the substitution of K and Cs for Na in the larger of the two distinct alkali ion sites. The progressive increase in unit-cell parameters, indices of refraction and density as the occupancy of the alkali sites change from NaNa (gainesite) to NaK (selwynite) and to NaCs (mccrillisite) has already been noted by Foord *et al.* (1994). These data are summarized in Table 3.

TABLE 3. COMPARISON OF UNIT-CELL PARAMETERS, INDICES OF REFRACTION AND DENSITY FOR GAINESITE, SELWYNITE AND MCCRILLISITE

	gainesite (NaNa)	selwynite (NaK)	mccrillisite (NaCs)
aÅ	6.567	6.570	6.573
c	17.119	17.142	17.28
$V(A^3)$	738.25	739.9	746.6
ω	1.618	1.624	1.634
ϵ	1.630	1.636	1.645
optic sign	(+)	(+)	(+)
D_{meas} (gcm^3)	2.94	2.94	3.125
D_{calc}	2.89	3.08	3.30

PARAGENESIS

The three Zr-bearing phosphates found in the granitic pegmatite veins at Wycheproof seem to have crystallized, with wardite and eosphorite, under reducing conditions during late-stage cooling of the Wycheproof granite. There is no evidence for leaching of zircon to provide the Zr, so it seems likely that small quantities of late-stage fluids enriched in Zr, P, Na and K were responsible for the crystallization of these minerals. Kosnarite, which is anhydrous, may have crystallized at slightly higher temperatures; it occurs partly enclosed by wycheproofite (Birch *et al.* 1994). Selwynite has not been found directly associated with wycheproofite or kosnarite, but instead occurs with wardite and eosphorite. This finding suggests that the ratio of Na:K in the initial fluids may have determined whether selwynite or kosnarite – wycheproofite crystallized in any one cavity.

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