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Okanoganite, a new rare-earth borofluorosilicate from the Golden Horn batholith, Okanogan County, Washington

RUSSELL C. BOGGS

Department of Geological Sciences, University of California
Santa Barbara, California 93106

Abstract

Okanoganite is found in miarolitic cavities in the arfvedsonite granite phase of the Golden Horn batholith, near Washington Pass, Okanogan County, Washington. It occurs as tan to pale pink pseudotetrahedral twinned crystals up to 4 mm across. A combination of electron microprobe analyses and spectrophotometric analyses for B_2O_3 give the following formula: $(Na_{6.40}Ca_{2.40}Pb_{0.20})[(Y,Ce,Nd,La)_{31.92}Ca_{1.78}Fe_{1.61}](Si_{17.29}Ti_{0.46})B_{6.44}O_{81.00}F_{42.48}$, with an ideal formula of $(Na,Ca)_3(Y,Ce,Nd,La)_{12}Si_6B_2O_{27}F_{14}$. The crystals are pseudotetrahedral fourlings with twin plane $\{01\bar{1}4\}$, the *c* face of each individual forming the faces of the pseudotetrahedron. The mineral is rhombohedral with possible space group $R3$, $R\bar{3}$, $R32$, $R3m$, $R\bar{3}m$, $R3c$, or $R\bar{3}c$. The cell dimensions are $a = 10.72(1)$, $c = 27.05(8)$Å, Z = 3 (hexagonal cell) or $a = 10.94(3)$Å, $\alpha = 58.7(3)°$, Z = 1 (rhombohedral cell). *D*(meas) = 4.35, *D*(calc) = 4.37. The strongest lines [*d*, (I), (*hkl*)] of the X-ray powder pattern (68 given) are 4.38(41)(202); 3.11(48)(300); 2.970(100)(027); 2.939(95)(125); 2.926(50)(303); 2.676(32)(220); 1.978(35)(325,413); 1.822(32)(3.0.12); 1.784(43)(330,2.0.14). The refractive indices are $\omega = 1.753$, $\epsilon = 1.740$; the mineral shows no dichroism and is colorless in thin fragments; streak = white; H = 4. It shows no fluorescence or phosphorescence under UV radiation and does not cathodeluminesce. The name is for Okanogan County, Washington.

Introduction

The Eocene Golden Horn batholith crops out over 310 km² in the northern Cascade Mountains in Okanogan, Chelan, and Skagit Counties, Washington (Stull, 1969).

Miarolitic cavities in the batholith contain a number of rare and unusual minerals, including at least two new minerals, zektzerite, $NaLiZrSi_6O_{15}$ (Dunn *et al.*, 1977), and okanoganite, named for Okanogan County. The mineral and the name were approved by the Commission on New Minerals and Mineral Names, IMA, prior to publication; the name is pronounced oh-ka-NOG-an-ite. Type material has been deposited in the mineral collection at the University of California, Santa Barbara (specimens #UCSB 8256 and 8257). Cotype material has been deposited in the National Museum of Natural History, Smithsonian Institution, Washington, D.C. (NMNH #142512 to 142514), and in the collection of the author (specimens #T550 to T555).

Occurrence

Okanoganite occurs in miarolitic cavities, which range from 1 to 5 cm in diameter, within the peralkaline arfvedsonite granite phase of the Golden Horn batholith, which crops out as an approximately horizontal zone between 1800 and 2400 m in elevation in the southeastern part of the batholith. I first found the mineral as only a few small crystals (less than ten mg) in two cavities in September, 1976. Later additional material of better quality was found by Robert M. Boggs on specimens he collected in August, 1976, and the description is based chiefly on this material, which totals a few hundred milligrams.

Associated minerals within the cavities, which show no zonation of the minerals, are quartz, microcline (perthite), zircon, arfvedsonite, bastnaesite, zektzerite, astrophyllite, a pale green mica (probably polylithionite, based on its optics and contents of SiO_2, Al_2O_3, K_2O, and F, there being insufficient material to determine the Li_2O content), and an uniden-

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tified calcium rare-earth mineral containing fluorine. Other minerals found in the miarolitic cavities, but not associated with okanoganite, include acmite, plagioclase, elpidite, gagarinite, allanite, prehnite, epidote, fluorite, titanite, siderite, biotite, monazite, calcite, galena, anatase, fayalite, thorite, gadolinite, and several as yet unidentified minerals.

The sequence of formation in the miarolitic cavities containing okanoganite was as follows: (earliest) arfvedsonite, microcline, quartz, astrophyllite, zektzerite, zircon, okanoganite, polylithionite, bastnaesite, and an unidentified calcium rare-earth mineral (latest).

Physical properties, habit and twinning

Okanoganite crystals are tan to pale pink and are generally about 1 mm across, with the largest crystal found being 4 mm across. They occur both as isolated fourlings perched on crystals of microcline, arfvedsonite, zircon, and zektzerite and as compactly intergrown clusters of crystals up to 8 × 4 × 4 mm.

The crystals appear to be isometric tetrahedrons, but are actually fourlings twinned on composition plane $\{01\bar{1}4\}$ with the *c* face of each individual forming the faces of the pseudotetrahedra (Figs. 1a and 1b). A few crystals have minor faces of the form $s\{10\bar{1}4\}$ beveling the edges of the crystals (Fig. 1c). A few crystals show an interpenetrating twinning with the additional composition plane $\{10\bar{1}\bar{2}\}$ (Fig. 1d). The twin law is the same in both cases, and is described by a 180° rotation about a twin axis perpendicular to $\{01\bar{1}4\}$.

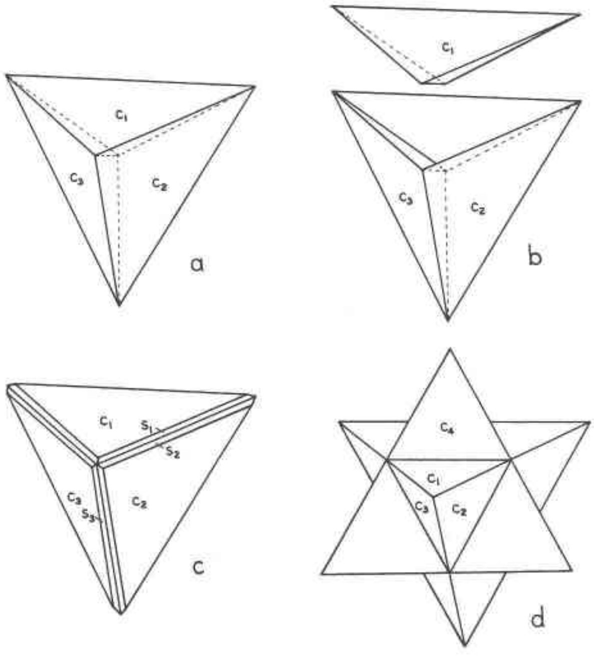

Fig. 1. Idealized drawings of crystals of okanoganite. The individuals in each fourling are differentiated by the subscripted numbers. Forms present are $c\{0001\}$ and $s\{10\bar{1}4\}$. Drawing b shows a fourling with one of the individuals separated to better show the twinning relationship.

The crystals have a hardness of 4. In a few cases the surface is altered to a softer material. In a few specimens the okanoganite has altered to an unidentified calcium rare-earth mineral containing fluorine. This mineral, which also occurs as light yellow-brown tabular crystals of crude hexagonal outline and less than 0.5 mm wide, could be a carbonate of the parisite group.

Okanoganite has a density of 4.35 (±0.04) gm/cm^3, measured with a Berman balance on a 21.3 mg crystal cluster in toluene at 21°C. Using the observed ratios of rare-earth elements and a Na:Ca ratio of 2.5:1 gives a calculated density of 4.37 gm/cm^3, in good agreement with the measured value. Okanoganite is uniaxial negative with $\omega = 1.753$ and $\epsilon = 1.740$ (each ±0.002) in white light, shows no dichroism, is colorless in thin fragments, and has a white streak. Okanoganite does not fluoresce or phosphoresce under either long or short wave UV radiation, and does not cathodeluminesce.

Applying the Gladstone–Dale relationship with the constants of Mandarino (1976) gives a value of K_c which ranges from 0.149 to 0.166, depending on which value of k for Y_2O_3 is used (0.170 or 0.195) (Mandarino, 1978), whether the Fe is considered as FeO or Fe_2O_3, and whether any or all of the Ce is CeO_2. The measured refractive indices and density give a value of 0.172 for K_p. This gives values of $(1-K_p/K_c)$ which range from 0.186 to 0.036. These values indicate poor to excellent compatibility between the density, refractive indices, and chemical composition (Mandarino, 1979).

X-ray crystallography

A tabular single crystal was prepared by cementing one of the twinned crystals to a glass slide on one of its *c* faces and grinding away most of the other three individuals. All the crystals have slightly curved faces, resulting in multi-domained crystals which produce poor quality single-crystal photographs. The cell dimensions were determined from this crystal by means of an *hk*0 precession photograph and an *h*0*l* Weissenberg photograph. The cell dimensions from a least-squares refinement of the X-ray powder diffraction pattern (Table 1) run on a diffractometer at a scan speed of ½°/min, standardized with annealed synthetic CaF_2 ($a = 5.459$Å), using Cu*Kα* radiation ($\lambda = 1.54178$Å) are: $a = 10.72(1)$, $c = 27.05(8)$Å (hexagonal cell) or $a = 10.94(3)$Å, $\alpha = 58.7(3)°$ (rhombohedral cell).

The single-crystal photographs and the lines of the powder pattern with *d* values greater than 3.00Å showed the extinction $-h+k+l=3n$, and all lines of the powder pattern could be indexed to observe this extinction. It was not possible to confirm or deny any other extinctions due to the poor quality of the photographs. This indicates as possible space groups: $R3$, $R\bar{3}$, $R32$, $R3m$, $R\bar{3}m$, $R3c$, or $R\bar{3}c$. A Laue photograph made as an attempt to further define the space group was inconclusive due to its poor quality.

Chemical composition

Two crystal clusters were embedded in epoxy, ground and polished, and coated with approximately 200Å of carbon. Analyses were made with an ARL electron microprobe, using an accelerating voltage of 15 kV and a sample current of 10 nanoamps. The spot size was 20 μm. Standards used were rare-earth,

Table 1. X-ray powder diffraction data for okanoganite and a related unnamed rare-earth fluorosilicate from Siberia

Okanoganite				Siberian rare-earth fluoro-silicate*	
hkℓ	d_{calc}	d_{obs}	I_{obs}	d_{obs}	I_{obs}
003	9.02	9.01	4		
012	7.65	7.67	12		
104	5.47	5.48	7		
110	5.36	5.35	7		
015	4.67	4.67	13		
021	4.57	4.57	5		
202	4.39	4.35	41	4.34	20
024	3.83	3.82	4		
107	3.57	3.57	20		
205	3.52	3.51	18		
122	3.39	3.39	16	3.23	20
214	3.11	3.11	48	3.10	50
300	3.09				
009	3.00	3.01	15		
027	2.970	2.970	100	2.97	100
125	2.943	2.939	95		
303	2.926	2.926	50	2.93	80
208	2.733	2.734	15	2.73	15
220	2.679	2.676	32	2.67	50
1.0.10	2.597	2.598	20	2.60	20
131	2.562	2.564	9		
306	2.551	2.554	9		
312	2.528	2.525	7		
134	2.405	2.404	4		
0.1.11	2.377	2.377	4		
0.2.10	2.337	2.338	4		
315	2.324	2.318	4		
042	2.287	2.285	4		
404	2.195	2.193	6		
309	2.156	2.154	26	2.15	60
137	2.142	2.141	29		
232	2.103	2.101	13	2.09	20
324	2.031	2.030	24	2.03	20
1.0.13	2.030				
229	2.000	1.996	19		
235	1.981	1.978	35	1.972	50
143	1.976				
0.2.13	1.899	1.897	4	1.905	20
327	1.865	1.866	12	1.864	20
1.3.10	1.865				
3.0.12	1.822	1.822	32	1.828	60
0.0.15	1.804	1.800	7		
238	1.801				
330	1.786	1.784	43	1.785	60
2.0.14	1.784				
505	1.756	1.755	18	1.755	30
1.2.14	1.693	1.695	4		
057	1.673	1.672	16	1.674	20
425	1.668				
155	1.593	1.590	6	1.596	15
0.2.16	1.589				
3.0.15	1.558	1.558	6		
428	1.557				
339	1.535	1.535	12	1.537	25
517	1.531	1.532	13		
0.5.10	1.531				
603	1.525	1.527	10		
4.1.12	1.507	1.507	9	1.510	20
502	1.486	1.487	7	1.486	20
345	1.468	1.469	10		
523	1.466	1.466	12	1.465	25
2.3.14	1.431	1.432	4		
4.2.11	1.428	1.428	3		
526	1.411	1.409	3	1.411	20
612	1.408				
351	1.326	1.325	8		
701	1.326				
3.2.16	1.325				
532	1.321	1.318	10	1.320	20
072	1.321				
2.1.19	1.320				
0.4.17	1.313	1.313	3		
2.3.17	1.275	1.274	9	1.280	25
1.2.20	1.262	1.262	4	1.257	25
2.5.12	1.242	1.241	6	1.245	20
078	1.236	1.238	6		
538	1.236				
4.3.13	1.231	1.229	3		
6.1.11	1.228				
627	1.223	1.221	3		
173	1.220				
0.3.21	1.190	1.188	8		
541	1.189				
0.2.22	1.189				
5.1.16	1.188				
176	1.187				
3.2.19	1.184	1.184	8		
4.2.17	1.179	1.180	3		
6.1.14	1.143	1.143	9		
547	1.137	1.135	7		
805	1.136				

* Heated at 600°C, Proshchenko et al., 1966

Ca, Al silicate glasses for the rare-earth elements (Drake and Weill, 1972), albite for Na and Si, wollastonite for Ca, hematite for Fe, synthetic $PbSO_4$ for Pb, rutile for Ti, and fluorite for F. Interelement effects were corrected with a modified version of the computer program EMPADR 7 (Rucklidge and Gasparrini, 1969).

An ion microprobe scan indicated the presence of a significant amount of B, as well as minor amounts (less than 100 ppm) of Li, Al, K, Zr, Th, and U. It also showed the absence of any significant amount of any other elements, including H and Eu.

The B_2O_3 content was determined spectrophotometrically with carminic acid on two samples of 8.5 and 13.5 mg, using a slight modification of the technique of Ross *et al.* (1956) on a Beckman DU spectrophotometer.

A summary of the analyses is presented in Table 2. The crystals show no regular compositional zoning and only a slight random variation of a few percent from point to point within the crystals. The low total is probably due to errors arising from using rare-earth standards which contain less of a given rare-earth oxide than okanoganite (about 4 wt. percent in the standard *vs.* up to 20 wt. percent in okanoganite). The empirical formula is $(Na_{6.40}Ca_{2.40}Pb_{0.20})[(Y, Ce, Nd, La)_{31.92}Ca_{1.78}Fe_{1.61}](Si_{17.29}Ti_{0.46})B_{6.44}O_{81.00}F_{42.48}$, which approximates to an ideal formula of $(Na,Ca)_3(Y,Ce,Nd,La)_{12}Si_6B_2O_{27}F_{14}$ with Z = 3 for the hexagonal cell or Z = 1 for the rhombohedral cell.

Table 2. Composition of okanoganite and a related unnamed rare-earth fluorosilicate from Siberia

	Okanoganite	Siberian rare-earth fluoro-silicate*
Na_2O	2.74	2.11
CaO	3.24	5.60
PbO	0.63	—
MnO	—	2.15
MgO	—	0.20
FeO	1.60	—
Fe_2O_3	—	3.69
ΣREE_2O_3	64.75	60.67
B_2O_3	3.1	—
Al_2O_3	—	1.27
P_2O_5	—	2.83
TiO_2	0.50	0.14
ThO_2	—	0.93
SiO_2	14.35	14.00
H_2O	—	2.00
F	11.15	7.85
	102.06	103.44
-O≡F	4.69	3.30
Total	97.37	100.14
Y_2O_3	20.46	14.01
La_2O_3	5.88	6.25
Ce_2O_3	15.42	13.71
Pr_2O_3	1.83	2.37
Nd_2O_3	7.70	9.22
Sm_2O_3	1.64	3.03
Gd_2O_3	5.28	4.19
Tb_2O_3	0.44	0.42
Dy_2O_3	2.08	3.52
Ho_2O_3	0.96	0.85
Er_2O_3	1.26	1.70
Tm_2O_3	0.20	0.06
Yb_2O_3	0.79	} 1.34
Lu_2O_3	0.81	
ΣREE_2O_3	64.75	60.67

* Proshchenko et al., 1966

Similar minerals

A number of other rare-earth silicates containing boron and/or fluorine are known. Many of these are poorly described and most of them are metamict. The following is a brief comparison of each with okanoganite.

Unnamed rare-earth fluorosilicate, from Siberia, USSR

This mineral is the most closely related to okanoganite. Its cell dimensions, *a* = 10.68(4), *c* = 26.9(1)Å, are similar. The powder diffraction pattern (Table 1) differs only in not showing many of the lower-intensity lines observed from okanoganite. The chemical composition is also similar (Table 2), but differs mainly in containing phosphorus and aluminum instead of boron (Proshchenko *et al.*, 1966). It may be either the phosphorus and aluminum analog of okanoganite or the same species if boron, aluminum, and phosphorus do not occupy a separate site in the structure but only substitute for silicon.

Melanocerite, caryocerite, and tritomite

These three minerals are similar to each other and are considered either as identical or separate species by different authors. They differ from okanoganite by being enriched in the Ce-group lanthanides and having lower REE_2O_3 contents, ranging from 43.5 to 56.3 weight percent. All are metamict and recrystallize on heating in air to a mixture of an apatite phase and a CeO_2 phase. In one case a melanocerite was shown to have a few weak lines of an apatite phase before heating (Portnov *et al.*, 1968).

Spencite [=tritomite-(Y)]

This species differs from okanoganite in having a lower REE_2O_3 content, ranging from 28.0 to 50.7 weight percent, a higher SiO_2 content of from 16.8 to 26.4 weight percent, and a lower F content of from 0.0 to 1.1 weight percent. Spencite is metamict and recrystallizes on heating in air to a mixture of an apatite phase and a CeO_2 phase, but may have originally crystallized with a hellandite structure (Hogarth *et al.*, 1973) or a datolite structure (Frondel, 1961).

Yftisite

This mineral differs from okanoganite in having a lower REE_2O_3 content of 50.7 weight percent and is orthorhombic. The partial chemical analysis, which totals 87.31 percent, does not show the presence or absence of B_2O_3 (Pletneva *et al.*, 1971).

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References

Drake, M. J. and D. F. Weill (1972) New rare-earth element standards for electron microprobe analysis. *Chem. Geol., 10,* 179–181.

Dunn, P. J., R. C. Rouse, B. Cannon and J. A. Nelen (1977) Zektzerite: a new lithium sodium zirconium silicate related to tuhualite and the osumilite group. *Am. Mineral., 62,* 416–420.

Frondel, C. (1961) Two yttrium minerals: spencite and rowlandite. *Can. Mineral., 6,* 576–581.

Hogarth, D. D., H. R. Steacy, E. I. Semenov, E. G. Proshchenko, M. E. Kazakova and Z. T. Kataeva (1973) New occurrences and data for spencite. *Can. Mineral., 12,* 66–71.

Mandarino, J. A. (1976) The Gladstone–Dale relationship—Part I. Derivation of new constants. *Can. Mineral., 14,* 498–502.

——— (1978) The Gladstone–Dale relationship. Part II. Trends among constants. *Can. Mineral., 16,* 169–174.

——— (1979) The Gladstone–Dale relationship. Part III. Some general applications. *Can. Mineral., 17,* 71–76.

Pletneva, N. I., A. P. Denisov and N. A. Elina (1971) A new variety in the group of rare-earth fluosilicates. *Materialy po Mineralogii Kol'skogo Poluostrova, 8,* 176–179. (in Russian) (not seen; extracted from *Mineral. Abstr.*, 74-1453, 1974 and *Am. Mineral., 62,* 396, 1977).

Portnov, A. M., G. A. Sidorenko, V. T. Dubinchuk, N. N. Kuznetsova and T. A. Ziborova (1969) Melanocerite from the north Baikal Region. *Dokl. Akad. Nauk SSSR, 185,* No. 4, 901–904. [transl. *Doklady of the Academy of Sciences U.S.S.R., Earth Sciences Section, 185,* 107–109 (1969)].

Proshchenko, E. G., N. G. Batalieva and A. V. Bykova (1966) A rare-earth fluosilicate from a Siberian pegmatite. *Zapiski Vsesoyuznyi Mineralogicheskogo Obshchestva,* 95, 339–345. (in Russian); *Mineral. Abstr.*, 18–125, 1967.

Ross, W. J., A. S. Meyer Jr. and W. C. White (1956) Determination of boron in fluoride salts. *U.S. Natl. Tech. Inf. Serv., ORNL-2135.*

Rucklidge, J. and E. L. Gasparrini (1969) *EMPADR VII, a Computer Program for processing Electron Microprobe Analytical Data.* Department of Geology, University of Toronto, Ontario.

Stull, R. J. (1969) *The Geochemistry of the Southeastern Portion of the Golden Horn Batholith, Northern Cascades, Washington.* Ph.D. Thesis, University of Washington, Seattle, Washington.

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