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WILUITE, $Ca_{19}(Al,Mg,Fe,Ti)_{13}(B,Al,\square)_5Si_{18}O_{68}(O,OH)_{10}$, A NEW MINERAL SPECIES ISOSTRUCTURAL WITH VESUVIANITE, FROM THE SAKHA REPUBLIC, RUSSIAN FEDERATION

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Abstract

Wiluite, $Ca_{19}(Al,Mg,Fe,Ti)_{13}(B,Al,\square)_5Si_{18}O_{68}(OH,F,O)_{10}$, tetragonal, *a* 15.752(1), *c* 11.717(1) Å, *V* 2907.3(3) Å^3, space group *P4/nnc*, *Z* = 2, is a new mineral species of the vesuvianite group from the Wilui River, Sakha Republic, Russian Federation. It occurs as holosymmetric crystals with forms {100} and {101} dominant plus minor {110} and {001}, up to 3 × 3 × 5 cm, slightly elongate along [001]. No twinning was observed. Wiluite is dark green with a colorless streak, a vitreous luster, and it does not fluoresce under long- or short-wave ultraviolet light. It has a Mohs hardness of 6, is brittle with an irregular fracture, and has poor cleavage on {100}. The measured density is 3.36(3) g/cm^3, and the calculated density is 3.358 g/cm^3. In transmitted light, wiluite is colorless and nonpleochroic; it is uniaxial positive with $\omega = 1.721(2)$ and $\epsilon = 1.725(2)$. The strongest ten reflections in the X-ray powder-diffraction pattern [*d*(in Å)(I)(*hkl*)] are 2.776(100)(342), 2.617(61)(252), 2.491(61)(260), 2.592(43)(224), 1.66(26)(346), 1.640(23)(292), 2.121(20)(135), 3.52(18)(240), 1.987(15)(561), 2.929(14)(004), and 2.912(14)(233). An analysis of wiluite gave SiO_2 36.11, Al_2O_3 12.03, TiO_2 0.80, MgO 6.48, FeO 1.21, Fe_2O_3 2.28, CaO 35.54, Ce_2O_3 0.18, B_2O_3 3.06, F 0.50, H_2O 0.61, O ≡ F –0.24, sum = 99.20 wt.%. The concentration of FeO was determined by wet chemistry, and that of H_2O was determined with a LECO induction furnace; the concentration of the other elements was determined by electron-microprobe analysis. The corresponding unit formula, based on 19(Ca + Ce), is $(Ca_{18.97}Ce_{0.03})_{\Sigma 19}(Al_{6.53}Ti_{0.30}Fe_{86}Mg_{4.81}Fe_{50})_{\Sigma 13}(B_{2.63}Al_{0.53-1.84})_{\Sigma 5}Si_{17.99}O_{68}[(OH)_{2.03}O_{7.97}]_{\Sigma 10}$. Wiluite is isostructural with vesuvianite, and contains essential B [B > 2.5 *apfu* (atoms per formula unit)]; vesuvianite is uniaxial (–), wiluite is uniaxial (+). It occurs with grossular and serpentine minerals in a serpentinite. The name recalls the locality, and has been in use as a varietal name for "vesuvianite" from this locality for over 200 years.

Keywords: wiluite, new mineral species, electron-microprobe analysis, X-ray powder-diffraction data, vesuvianite, boron mineral, Yakutia, Russia.

Sommaire

Nous décrivons la wiluite, $Ca_{19}(Al,Mg,Fe,Ti)_{13}(B,Al,\square)_5Si_{18}O_{68}(OH,F,O)_{10}$, tétragonale, *a* 15.752(1), *c* 11.717(1) Å, *V* 2907.3(3) Å^3, groupe spatial *P4/nnc*, *Z* = 2, comme nouveau membre du groupe de la vésuvianite provenant de la rivière Wilui, en République de Sakha, Fédération Russe. Elle se présente en cristaux holosymétriques montrant les formes dominantes {100} et {101}, et en plus, {110} et {001}moins importantes; ils atteignent une taille maximum de 3 × 3 × 5 cm, et sont légèrement allongés sur [001]. Aucune macle n'a été décelée. La wiluite est vert foncé avec une rayure incolore et un éclat vitreux. Elle ne montre aucune fluorescence en lumière ultra-violette, soit en ondes longues ou courtes. Sa dureté est de 6; elle est cassante, et fait preuve d'une fracture irrégulière et d'un piètre clivage sur {100}. La densité mesurée est de 3.36(3), et la densité calculée, 3.358 g/cm^3. En lumière transmise, la wiluite est incolore et non pléochroïque; elle est uniaxe positive, avec $\omega = 1.721(2)$ et $\epsilon = 1.725(2)$. Les dix raies les plus intenses du spectre de diffraction X [*d*(en Å)(I)(*hkl*)] sont 2.776(100)(342), 2.617(61)(252), 2.491(61)(260), 2.592(43)(224), 1.66(26)(346), 1.640(23)(292), 2.121(20)(135), 3.52(18)(240), 1.987(15)(561), 2.929(14)(004), et 2.912(14)(233). Une analyse chimique de la wiluite a donné SiO_2 36.11, Al_2O_3 12.03, TiO_2 0.80, MgO 6.48, FeO 1.21, Fe_2O_3

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2.28, CaO 35.54, Ce_2O_3 0.18, B_2O_3 3.06, F 0.50, H_2O 0.61, O ≡ F –0.24, pour un total de 99.20% par poids. La concentration de FeO a été déterminée par voie humide, et la teneur en H_2O a été établie au moyen d'un four à induction LECO. Le niveau de concentration des autres éléments a été établi par microsonde électronique. La formule chimique qui en résulte, fondée sur 19(Ca + Ce), est $(Ca_{18.97}Ce_{0.03})_{\Sigma 19}(Al_{6.53}Ti_{0.30}Fe_{86}Mg_{4.81}Fe_{50})_{\Sigma 13}(B_{2.63}Al_{0.53}\square_{1.84})_{\Sigma 5}Si_{17.99}O_{68}[(OH)_{2.03}O_{7.97}]_{\Sigma 10}$. La wiluite est isostructurale avec la vésuvianite, et contient le bore comme constituent essentiel (>2.5 atomes de B par unité formulaire). La vésuvianite est uniaxe (–), tandis que la wiluite est uniaxe (+). On trouve la wiluite avec le grossulaire et des minéraux du groupe de la serpentine dans une serpentinite. Le nom rappelle la localité, et sert déjà depuis plus de 200 ans pour signifier la variété de "vésuvianite" provenant de cet endroit.

(Traduit par la Rédaction)

Mots-clés: wiluite, nouvelle espèce minérale, analyse à la microsonde électronique, diffraction X sur poudre, vésuvianite, minéral de bore, Yakoutie, Russie.

Introduction

It has long been known (Jannasch 1884, Widman 1890, Jannasch & Weingarten 1896) that vesuvianite can contain significant boron. Groat *et al.* (1992) showed that vesuvianite samples from several localities contain high (>1 wt.% B_2O_3) contents of boron. Groat *et al.* (1994) examined the mechanism whereby boron is incorporated into vesuvianite, and showed that boron occupies two newly identified sites in the structure. If the occupancy of one or more of these sites by boron becomes dominant, then a new mineral species is established. Vesuvianite from the Wilui River has long been known to have a high boron content, and the work of Groat *et al.* (1994) showed that vesuvianite from this locality contains sufficient boron to establish a new species. The new mineral is named wiluite, after the locality, the Wilui River, Sakha Republic (Yakutia), Russian Federation. The new mineral and mineral name have been approved by the International Mineralogical Association Commission on New Minerals and Mineral Names. Type material is deposited at the Canadian Museum of Nature, Ottawa, Ontario, Canada.

Physical Properties

Wiluite occurs as isolated holosymmetric crystals up to 3 × 3 (5 cm (‖ *a*, *b*, *c*, respectively). The dominant forms are {100} and {101}, with minor {110} and {001}; no twinning was observed. Wiluite is dark green with a colorless streak and a vitreous luster; it does not fluoresce under longwave or shortwave ultraviolet light. It is brittle with a poor cleavage on {100}, and as an irregular fracture and a Mohs hardness of 6. The density was measured with a Berman balance using toluene at 29°C; the measured density is 3.36(3) g/cm^3, and the calculated density is 3.358 g/cm^3.

Optical Properties

In transmitted light, wiluite is colorless and nonpleochroic. Although morphologically tetragonal, wiluite shows "anomalous" optical properties in cross-polarized light (Groat *et al.* 1993). There is strong optical sector zoning; {001} sectors shows a cross-hatched pattern, possibly due to twinning, and the {110} and {100} sectors show fine striations. The {001} sector has a low birefringence and is slightly biaxial, with $0 < 2V < 10°$; the {100} sectors have higher birefringence, and $2V$ varies within the range $10 < 2V < 25°$. The ω and ε indices of refraction of the {001} sector in monochromatic light (590 nm) are 1.721(2) and 1.725(2), respectively. The compatibility index is 0.008: superior. Boron-free and boron-poor vesuvianites are uniaxial (or slightly biaxial) negative. The composition (*i.e.*, B content) at which the optic sign changes is not known, but the optic sign is a simple indicator of high-B vesuvianite and wiluite.

Chemical Composition

Crystals were analyzed chemically with a JEOL 733 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV and a specimen current of 25 nA. Data on standards were collected to 0.25% precision or for 25 seconds, whichever was less. Data on each element were collected to 0.5% precision or for 50 seconds. The beam size was 10 or 20 μm, and counting times on peak and background, 20 and 10 s, respectively. The following standards were used: diopside (Si), almandine (Al,Mg,Fe), titanite (Ti), tephroite (Mn), gehlenite (Ca), elbaite (B), glass S–254 (Ce) and fluororiebeckite (F). The FeO content was determined by titration. The H_2O content was determined with a LECO induction furnace. Data were reduced using conventional ZAF techniques. The mean of twenty-five determinations is given in Table 1; the crystals are chemically homogeneous. The chemical formula was calculated on the basis of 19 *X* cations (= Ca + Ce), as recommended by Groat *et al.* (1992); the resulting formula is given in Table 1. A simplified formula may be written as $Ca_{19}\ (Al,Mg,Fe,Ti)_{13}\ (B,Al,\square)_5\ Si_{18}\ O_{68}\ (O,OH)_{10}$.

The Limiting B Content of Wiluite

As shown by Groat *et al.* (1994, 1996), B occupies the *T*(1) [0.055, 0.055, 1/4] and *T*(2) [1/4 1/4 1/4] sites in

TABLE 1. CHEMICAL COMPOSITION* (wt.%) AND UNIT FORMULA (*apfu*) FOR WILUITE

SiO_2	36.11	Si	17.99
Al_2O_3	12.03		
TiO_2	0.8	B	2.63
MgO	6.48	Al	0.53
FeO	1.21	□	1.84
Fe_2O_3	2.28	Σ	5
CaO	35.54		
Ce_2O_3	0.18	Al	6.53
B_2O_3	3.06	Ti	0.3
F	0.5	Fe^{3+}	0.86
H_2O	0.61	Fe^{2+}	0.5
O ≡ F	–0.24	Mg	4.81
Total	99.2	Σ	13
		Ca	18.97
		Ce	0.03
		Σ	19
		O	68
		OH	2.03
		O	7.97
		Σ	10

* Na, Cl not detected

the vesuvianite-type structure. In the structural formula of wiluite, there are four $T(1)$ sites and one $T(2)$ site, summing to a total of 5 T sites per formula unit. Ideally, only one of these sites needs to be more than half-occupied by B to give rise to a new mineral species; thus there are four potential end-members involving the T sites: $T(1) = T(2) = \square$; $T(1) = \square$, $T(2)$ = B; $T(1)$ = B, $T(2) = \square$; $T(1) = T(2)$ = B. However, some of the resulting species can only be identified *via* crystal-structure refinement to derive B occupancies of the $T(1)$ and $T(2)$ sites. This is obviously not practical. Here, we define wiluite as containing >2.5 B *apfu*, such that the $T(1)$ and $T(2)$ sites have an aggregate occupancy of greater than 0.5.

The corresponding end-member formula for wiluite is as follows:

$$Ca_{19}\,[Al_5Mg_8]\,B_5\,(Si_{18}O_{68})\,O_{10}.$$

X-Ray Diffraction

The powder-diffraction pattern (Table 2) for a bulk sample was recorded on a Siemens D5000 diffractometer operating at 40 kV and 30 mA, using BaF_2 as an internal standard. Cell dimensions were refined using 30 reflections ($CuK\alpha_1$ radiation), and are given in Table 2.

Single-crystal precession photographs ($MoK\alpha$ X-radiation) indicate tetragonal symmetry. Very careful examination of extinction conditions and Laue symmetry on precession photographs and by single-crystal diffractometry showed the crystal to have *4/mmm* Laue symmetry; furthermore, the extinction conditions are compatible with *P4/nnc* space-group symmetry. Details of the refined crystal-structure are given by Groat *et al.* (1994), and the polarized infrared spectrum is given by Groat *et al.* (1995).

Occurrence and Associated Minerals

Wiluite occurs associated with grossular in a matrix of fine-grained serpentine minerals, carbonate, limonitized pyrite, chlorite and "achtarandite", a tetrahedral pseudomorph of an unknown precursor mineral from the Wilui River region, Yakutia, Russia (Grew 1996), tentatively identified as wadalite (Galuskina *et al.* 1998). The association suggests that the primary mineral assemblage was that of a skarn that was subse-

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR WILUITE

I_{est}	d_{meas} (Å)	d_{calc} (Å)	*h*	*k*	*l*
5	5.86	5.86	0	0	2
5	4.7	4.7	0	2	2
5	4.04	4.04	2	2	2
4	3.94	3.94	0	4	0
18	3.52	3.52	2	4	0
5	3.27	3.27	0	4	2
8	3.02	3.02	2	4	2
14	2.929	2.929	0	0	4
14	2.912	2.912	2	3	3
100	2.776	2.775	3	4	2
8	2.701	2.701	3	5	0
61	2.617	2.617	2	5	2
43	2.592	2.592	2	2	4
11	2.524	2.525	1	3	4
61	2.491	2.491	2	6	0
7	2.451	2.452	0	5	3
7	2.35	2.35	0	4	4
9	2.325	2.325	1	4	4
6	2.3	2.3	3	3	4
8	2.228	2.228	1	7	0
13	2.147	2.147	4	6	1
20	2.121	2.12	1	3	5
8	2.1	2.1	2	6	3
10	2.069	2.068	3	7	0
6	2.046	2.047	4	6	2
6	2.037	2.037	3	7	1
9	2.012	2.012	3	6	3
15	1.987	1.988	5	6	1
12	1.773	1.773	1	7	4
26	1.66	1.66	3	4	6
23	1.64	1.64	2	9	2
13	1.634	1.634	0	8	4
8	1.624	1.624	2	5	6
6	1.591	1.591	7	7	0
8	1.568	1.568	6	6	4
7	1.559	1.559	1	6	6

Refined unit-cell based on 30 reflections: *a* 15.7521(7), *c* 11.7169(9) Å.

quently serpentinized, altering all of the skarn minerals except wiluite and grossular. The mineral is widely distributed in both institutional and private mineral collections worldwide.

Other Localities

Groat *et al.* (1992, 1994, 1995) reported chemical compositions for several samples of B-bearing "vesuvianite". In fact, the following additional localities contain wiluite: Templeton Township, Ottawa County, Quebec (Groat *et al.* 1994), and Bill Waley mine, Tulare County, California (Groat *et al.* 1996). Several other localities reported by Groat *et al.* (1992, 1994) have B-bearing vesuvianite.

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