

Zektzerite: a new lithium sodium zirconium silicate related to tuhualite and the osumilite group

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Abstract

Zektzerite, $\text{LiNa}(\text{Zr,Ti,Hf})\text{Si}_6\text{O}_{15}$, is a new mineral species occurring as colorless to pink euhedral crystals in a riebeckite granite from Okanogan County, Washington. It is orthorhombic, *Cmca* or *C2ca*, with $a = 14.306(5)$, $b = 17.330(4)$, $c = 10.140(3)\text{Å}$, $Z = 8$. The strongest reflections (in A) in the X-ray powder pattern are 7.190 78 200; 4.850 100 221; 4.336 78 040; 3.480 75 241; 3.145 85 023,421; and 2.665 65 043,441. Physical properties include perfect cleavages on {100} and {010}, white streak, vitreous luster, Mohs hardness about 6, and density of 2.79 g/cm³. Optically, zektzerite is biaxial negative, almost isotropic, with $2V_x = \sim 0^\circ$. Indices are $\alpha = 1.582(3)$, $\beta = 1.584(3)$, and $\gamma = 1.584(3)$ with orientation $X = a$, $Y = b$, and $Z = c$. Dispersion is very weak, $r > v$. Zektzerite is closely related to tuhualite, $(\text{Na,K})_2\text{Fe}_2^{2+}\text{Fe}_3^{3+}\text{Si}_{12}\text{O}_{30}\cdot\text{H}_2\text{O}$, and more distantly to the osumilite group.

Introduction

It is quite uncommon in contemporary mineralogy to encounter a new mineral occurring in euhedral crystals up to 35 mm in size and sufficiently pure to enable a relatively facile characterization. Such a mineral was found by one of the authors (BC) in 1968 and was sent to the Smithsonian Institution in 1975 by Mr. Jack Zektzer, of Seattle, Washington. A detailed investigation has confirmed that it is a new species, which we have named zektzerite after Mr. Zektzer in recognition of his initiation of this effort. The new name is pronounced zex'-ter-ite. The mineral and the name were approved by the Commission on New Minerals and Mineral Names, I.M.A., prior

to publication. Holotype material is deposited in the National Museum of Natural History, Smithsonian Institution, Washington, D.C., under catalog #136030. Cotype material has been deposited in the British Museum (Natural History), London, England.

Occurrence and local geology

Zektzerite occurs in the Golden Horn batholith of Eocene age, near Washington Pass, in southwestern Okanogan County, Washington, at elevations between 4600' and 7400' (lat 48°32' N, long. 120°35' W). The intrusion has invaded Cretaceous metamorphic and igneous rocks and is now exposed through a total relief of 5300' over an area of 120 square miles

within the rugged landscape of the Northern Cascade Mountains (R. T. Stull, unpublished thesis, 1969). The batholith exists in three compositional phases. The oldest phase hosts the zektzerite and is a riebeckite granite consisting of quartz, riebeckite, and perthite. It commonly displays miarolitic and granophyric textures and is believed to have crystallized at a shallow depth at pressures between 0.5 and 1.0 kbar (Stull, 1973). Calcium and magnesium are nearly absent, and aluminum is present in quantities slightly below that of a normal granite. The lithium content, however, is somewhat higher (42 ppm) than that of a typical granite, and the riebeckite may contain up to 1290 ppm lithium.

The remaining phases in the batholith are more normal granites containing biotite, hastingsite, hornblende, plagioclase, orthoclase, and quartz. They are thought to have been derived from the alkaline granite through the incorporation of dioritic xenoliths (R. J. Stull, unpublished thesis, 1969).

Zektzerite has been found in less than fifty miarolitic cavities occurring both in situ and in talus boulders along a narrow three mile belt in the riebeckite granite. Thousands of additional pockets examined by Cannon and others (Jack Zektzer, and Russell, Robert, and John Boggs) in a fourteen square-mile area were found to contain no crystals of the new mineral. Zektzerite-bearing pockets are usually small, from 2 to 10 cm in their longest dimension, are clay-free and with walls still attached to their enclosing rock. Typical zektzerite crystals are from 4 to 15 mm in diameter and occur several to a pocket, loose or scattered upon white microcline and associated with lustrous smoky quartz crystals up to 6 cm long, well-formed riebeckite crystals up to 3 cm long, and tiny euhedral zircon crystals. Astrophyllite, elpidite, and acmite are also found as associated minerals in the miarolitic cavities. Unusual pockets may yield over a dozen zektzerite crystals ranging in size up to 2.5 cm. Two exceptional cylindrical-shaped pockets, one 21×12 cm and the other 42×9 cm, had collapsed walls showing secondary quartz growing upon the separation surfaces, and yielded about 50 zektzerite crystals, mostly under 12 mm. The pocket of the type material was relatively small (about 11×5 cm) but contained a slightly etched crystal $3.7 \times 3.5 \times 1.5$ cm, the largest one yet found.

Zektzerite-barren pockets within the riebeckite granite may be more than 26 cm in diameter and contain, in addition to the minerals already mentioned, chlorite, sericite, calcite, fluorite, and rarely allanite, stilbite, bastnaesite, and loellingite. Hydro-

thermal alteration in all phases of the batholith has left many pockets within the affected zones stripped of all minerals but quartz and feldspar. Magnetite, fluorite, and siderite, usually altered to hydrous iron oxides, have been subsequently deposited in some pockets.

Morphology, optical and physical properties

Zektzerite occurs as euhedral crystals up to $37 \text{ mm} \times 35 \text{ mm} \times 15 \text{ mm}$, and some are lightly coated with an iron oxide film. The crystals are orthorhombic, pseudo-hexagonal, and the morphology suggests the class $2/m \ 2/m \ 2/m$. The dominant forms are $\{100\}$, $\{010\}$, and $\{011\}$, and most of the crystals are tabular on $\{100\}$. There is a pearly luster on $\{100\}$, and $\{011\}$ is lightly striated parallel to a . A sketch of an idealized crystal of zektzerite is shown in Figure 1, and a sketch of zektzerite on riebeckite in Figure 2.

Zektzerite crystals are colorless to pink, have a white streak, and may exhibit color zoning. Many crystals show translucent interiors which are pink, colorless, or cream-colored, and which are surrounded by a whitish chatoyant zone 1–2 mm thick on prism and pinacoid faces. There are cleavages parallel to $\{100\}$ and $\{010\}$, both perfect and easily

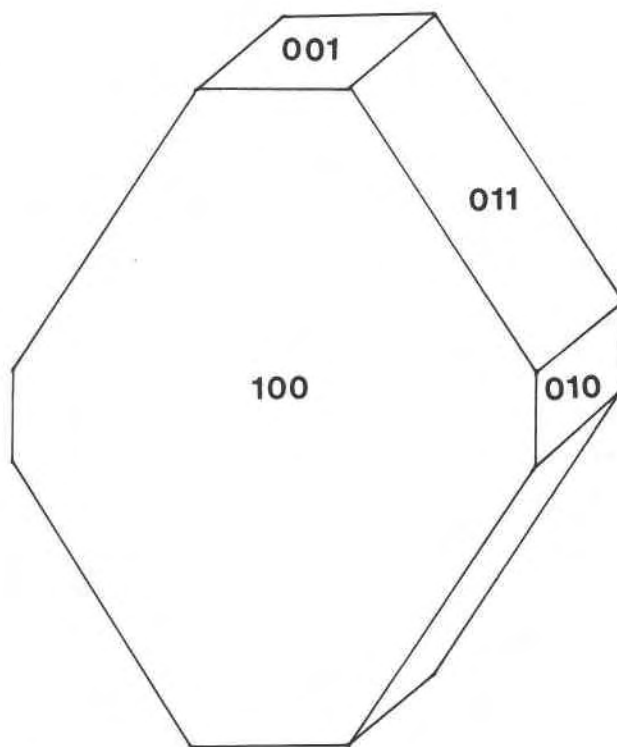


Fig. 1. Idealized drawing of a typical zektzerite crystal. (drawing by Bart Cannon)

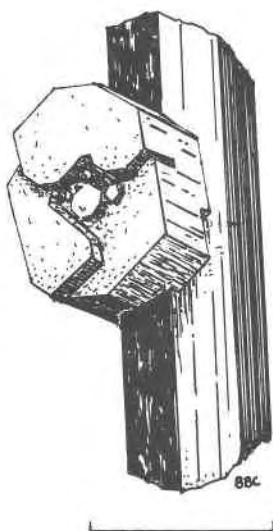


Fig. 2. Sketch of zektzerite on riebeckite. Scale-bar is 1 cm. (sketch by Bart Cannon)

produced. The luster on cleavage surfaces and fracture surfaces is vitreous. The Mohs hardness is about six. The density, measured on a Berman balance in toluene at 23°C, and employing a temperature correction, is 2.79 g/cm³, in excellent agreement with the calculated value of 2.80 g/cm³. Although most of the material is much too fractured and cloudy for gem applications, some clear sections, fully transparent and colorless, might be cut as gemstones. Zektzerite fluoresces a light yellow color in short-wave ultraviolet radiation. There is no response to long-wave ultraviolet radiation, and no phosphorescence in either wavelength.

Zektzerite is almost isotropic, birefringence being 0.002. The mineral is biaxial negative with $2V_x = \sim 0^\circ$. The refractive indices for sodium light are $\alpha = 1.582$, $\beta = 1.584$, and $\gamma = 1.584$, all ± 0.003 , the optical orientation being $X = a$, $Y = b$, and $Z = c$. The dispersion of the optic axes is very weak, $r > v$.

Chemical composition

The idealized formula of zektzerite is $\text{LiNaZrSi}_6\text{O}_{15}$ ($Z = 8$), with minor titanium and hafnium substituting for zirconium. The mineral was chemically analyzed with an ARL-SEM-Q electron microprobe using an operating voltage of 15kV and a sample current of 0.15 microamps. The intensities were corrected by computer using Bence-Albee factors. Sodium, zirconium, hafnium, and silicon were determined using the following standards: andesine (An_{40}) for sodium, hafnium-bearing zircon for zirconium and hafnium, and quartz for silicon. Lithium was determined by flame photometry. A spectrographic

analysis indicated the absence of other elements except in trace amounts. Water, as determined by the Penfield method, on 300 mg., is absent. The results of the analysis of zektzerite are presented in Table 1. From the analysis, the calculated formula is $\text{Li}_{1.00}\text{Na}_{1.02}(\text{Zr}_{0.94}\text{Ti}_{0.05}\text{Hf}_{0.01})\text{Si}_{6.06}\text{O}_{15.15}$, which agrees very well with the ideal $\text{LiNaZrSi}_6\text{O}_{15}$.

X-ray crystallography

Precession photographs of zektzerite indicated that the mineral is orthorhombic, space group $C2ca$ or $Cmca$, with approximate unit-cell parameters $a = 14.3$, $b = 17.4$, and $c = 10.2\text{A}$. These translations were then verified by means of overexposed cone-axis or rotation photographs around each axis. Using powder-diffractometer data gathered with monochromatized $\text{CuK}\alpha$ radiation and quartz ($a = 4.9133$, $c = 5.4049\text{A}$) as an internal standard, a least-squares refinement of the above parameters yielded the values $a = 14.306 \text{ esd } 0.005$, $b = 17.330 \text{ esd } 0.004$, and $c = 10.140 \text{ esd } 0.003\text{A}$. The unit-cell volume is $2514.0 \text{ esd } 0.9\text{A}^3$, and the axial ratio $a:b:c$ is $0.82550:1:0.58511$. A powder pattern complete to $50^\circ 2\theta$ and obtained with a diffractometer and internal standard as indicated above is given in Table 2. Indexing of the reflections was accomplished with the assistance of the single-crystal photographs.

Relationships to other minerals

Tuhualite, $4[(\text{Na},\text{K})_2\text{Fe}_2^{2+}\text{Fe}_2^{3+}\text{Si}_{12}\text{O}_{30} \cdot \text{H}_2\text{O}]$, is orthorhombic, $Cmca$, with $a = 14.31$, $b = 17.28$, and $c = 10.11\text{A}$ (Merlino, 1969). The near identity to the unit cell and space group of zektzerite is obvious, and if the water in tuhualite is ignored, the atomic proportions in the two minerals are also the same. Such

Table 1. Chemical analysis of zektzerite

	$\text{LiNaZrSi}_6\text{O}_{15}$ Theoretical	Zektzerite Analysis	Atomic Proportions	Number of Atoms on the Basis of 15 Oxygens
Li_2O	2.82	2.8*	1.00	0.99
Na_2O	5.85	5.9	1.02	1.01
ZrO_2	25.26	21.84		
HfO_2	----	0.50	1.01	1.00
TiO_2	----	0.75		
SiO_2	68.07	68.24	6.06	6.00
Total	100.00	100.0		

*By flame photometry

Table 2. X-ray diffraction data for zektzerite

I_{obs}	d_{obs}	d_{calc}	hkl
5	8.664	8.665	020
78	7.190	7.153	200
3	6.598	6.587	021
15	5.522	5.516	220
100	4.850	4.846	221
3	4.606	4.607	112
47	4.374	4.376	022
78	4.336	4.333	040
47	4.137	4.136	202
2	3.974	3.984	041
14	3.679	3.682	132
34	3.576	3.576	400
75	3.480	3.481	241
19	3.305	3.306	420
20	3.231	3.232	113
45	3.196	3.197	151
85	3.145	3.149	023
11	2.991	2.992	421
38	2.924	2.923	242
17	2.887	2.888	402
8	2.806	2.806	060
12	2.769	2.769	152
3	2.727	2.723	422
8	2.705	2.702	313
14	2.678	2.678	351
63	2.665	2.665	260
1	2.593	2.661	043
4	2.540	2.661	441
10	2.511	2.589	261
4	2.426	2.535	004
3	2.393	2.510	062
8	2.370	2.423	442
11	2.250	2.389	204
21	2.196	2.372	171
11	2.159	2.368	262
8	2.140	2.247	460
2	2.097	2.196	063
3	2.091	2.158	353, 602
2	2.070	2.137	443
4	2.056	2.099	263
8	2.049	2.094	622
4	2.033	2.089	640
4	2.014	2.068	404
3	1.995	2.054	462
2	1.934	2.046	641
7	1.905	2.031	281
3	1.890	2.016	372
7	1.878	2.012	424
5	1.874	1.992	082
5	1.852	1.931	642
19	1.842	1.905	064
		1.903	225
		1.893	731
		1.886	514
		1.880	354
		1.875	191
		1.853	480
		1.842	373
		1.841	264

relationships strongly imply a close structural relationship between zektzerite and tuhualite. According to Merlino (1969), tuhualite is a novel type of chain silicate, containing double chains of silicate tetrahedra with a period of six ("Sechser-Doppelkette") linked by vertex-sharing to chains of iron coordination polyhedra. The latter chains consist of alternating, edge-sharing Fe^{3+}O_6 octahedra and Fe^{2+}O_4 tetrahedra. This anomalous ordering of the smaller, higher-valence cation in the larger octahedral site is explained as being necessary for local charge balance in the structure. Such a situation is unnecessary in zektzerite, however, since the higher-valence cation (Zr^{4+}) is well-suited to octahedral coordination by oxygen and the lower valence cation (Li^+) is likewise appropriate in tetrahedral coordination.

Sogdianite, $2[(\text{K}, \text{Na})_2(\text{Zr}, \text{Ti}, \text{Fe})_2(\text{Li}, \text{Al})_3\text{Si}_{12}\text{O}_{30}]$, bears a close compositional similarity to zektzerite but is hexagonal, $P6/mcc$, with $a = 10.083$ and $c = 14.24\text{A}$ (Bakakin *et al.*, 1974). A crystallographic relationship between the two minerals becomes apparent when it is noted that the orthohexagonal unit cell of sogdianite has parameters $a = 10.083\sqrt{3} = 17.464$, $b = 10.083$, and $c = 14.24\text{A}$. This cell is dimensionally nearly identical to that of zektzerite. The same relationship exists between osumilite,



and tuhualite, and is a reflection of similarities in their crystal structures (Merlino, 1969). Presumably, these shared features are also common to sogdianite and zektzerite.

Lastly, mention should be made of a curious similarity between zektzerite and the synthetic compound $\text{Ni}_4\text{Nb}_2\text{O}_9$. (Bertaut *et al.*, 1961). Like zektzerite, it is orthorhombic (but of unknown space group) with $a = 10.144$, $b = 17.468$, and $c = 14.318\text{A}$. Chemically, it is so different from zektzerite that the near identity of their unit-cell parameters is probably fortuitous. However, in the absence of crystal structure determinations for either compound, some kind of structural relationship cannot be entirely ruled out.

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