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A NOVEL $[Si_{18}O_{45}]^{18-}$ SHEET IN THE CRYSTAL STRUCTURE OF ZERAVSHANITE, $Cs_4\ Na_2\ Zr_3\ [Si_{18}O_{45}]\ (H_2O)_2$

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ABSTRACT

The crystal structure of zeravshanite, ideally $Cs_4Na_2Zr_3(Si_{18}O_{45})(H_2O)_2$, monoclinic, *a* 26.3511(8), *b* 7.5464(3), *c* 22.9769(8) Å, β 107.237(1)°, *V* 4363.9(4) Å^3, space group *C*2/*c*, *Z* = 4, *D*(calc.) = 3.170 g.cm^{-3}, was solved by direct methods and refined to an R_1 index of 2.8% based on 4508 observed [$F_o > 4\sigma F$] unique reflections measured with Mo$K\alpha$ X-radiation on a Bruker *P*4 diffractometer equipped with a CCD detector. Electron-microprobe analysis gave the composition $(Cs_{3.80}\ Na_{0.18}\ K_{0.02})_{\Sigma 4.00}\ Na_{2.00}\ (Zr_{2.76}\ Ti_{0.19}\ Sn_{0.05}\ Fe^{3+}_{0.05})_{\Sigma 3.05}\ [Si_{18}O_{45}]\ (H_2O)_2$ based on 47 O *apfu*. In the crystal structure, there are nine tetrahedrally coordinated *Si* sites with <*Si*–O> = 1.614 Å. There are two [6]-coordinated *M* sites, mainly occupied by Zr (with minor Ti, Fe^{3+} and Sn^{4+}), with <*M*–O> = 2.067 Å. There is one [5]-coordinated *Na* site with <*Na*–O, H_2O> = 2.400 Å. There are two *A* sites primarily occupied by Cs (with minor Na and K), a [12]-coordinated *A*(1) site and an [11]-coordinated *A*(2) site with <*A*(1)–O, H_2O> = 3.369 and <*A*(2)–O> = 3.396 Å. In the crystal structure of zeravshanite, (SiO_4) tetrahedra link together to form an $[Si_{18}O_{45}]^{18-}$ sheet parallel to (101), with five- and eight-membered silicate rings. The topology of the sheet was not previously known for any silicate mineral. It can be described as a linkage of wollastonite-like $[Si_3O_9]^{6-}$ chains. The silicate sheets, (MO_6) and (NaO_n) polyhedra share common vertices to form a mixed $\{Na_2\ [Zr_3\ (Si_{18}O_{45})]\ (H_2O)_2\}^-$ framework with cages that occlude *A* atoms. The (NaO_5) square pyramids share common vertices to form $[NaO_4]$ zig-zag chains along [010]. Every square pyramid shares one edge with an *M*(2) octahedron, and *M*(2) octahedra decorate the $[NaO_4]$ chain in a *cis* fashion. One (H_2O) site that is fully occupied by (H_2O) is a ligand of *Na* and *A*(1), with one strong (1.94 Å) and one very weak birfurcated hydrogen bond (~ 3.10 Å) to oxygen atoms of the framework.

Keywords: zeravshanite, Cs–Zr silicate, crystal structure, $[Si_{18}O_{45}]$ sheet, Dara-i-Pioz, Tajikistan.

SOMMAIRE

Nous avons résolu la structure cristalline de la zéravshanite, de composition idéale $Cs_4Na_2Zr_3(Si_{18}O_{45})(H_2O)_2$, monoclinique, *a* 26.3511(8), *b* 7.5464(3), *c* 22.9769(8) Å, β 107.237(1)°, *V* 4363.9(4) Å^3, groupe spatial *C*2/*c*, *Z* = 4, *D*(calc.) = 3.170 g.cm^{-3}, par méthodes directes; nous l'avons affinée jusqu'à un résidu R_1 de 2.8% en utilisant 4508 réflexions uniques observées [$F_o > 4\sigma F$], et mesurées avec rayonnement Mo$K\alpha$ et un diffractomètre Bruker *P*4 muni d'un détecteur CCD. Une analyse à la microsonde électronique a mené à la composition $(Cs_{3.80}Na_{0.18}K_{0.02})_{\Sigma 4.00}\ Na_{2.00}\ (Zr_{2.76}Ti_{0.19}Sn_{0.05}Fe^{3+}_{0.05})_{\Sigma 3.05}\ [Si_{18}O_{45}]\ (H_2O)_2$ sur une base de 47 atomes d'oxygène par formule unitaire. Dans cette structure se trouvent neuf sites *Si* à coordinence tétraédrique, avec <*Si*–O> égal à 1.614 Å. C'est dans les deux sites *M*, à coordinence [6], que loge le Zr (avec des quantités moindres de Ti, Fe^{3+} et Sn^{4+}), avec <*M*–O> = 2.067 Å. Il y a un site *Na* à coordinence [5], avec <*Na*–O,H_2O> égal à 2.400 Å. Les deux sites *A* sont surtout remplis de Cs (avec des quantités moindres de Na et K), le site *A*(1) ayant une coordinence [12], et le site *A*(2), une coordinence [11], avec <*A*(1)–O, H_2O> égal à 3.369 et <*A*(2)–O> égal à 3.396 Å. Dans la structure de la zéravshanite, les tétraèdres (SiO_4) sont liés pour former un feuillet $[Si_{18}O_{45}]^{18-}$ contenant des anneaux à cinq et à huit membres, parallèle à (101). La topologie du feuillet n'avait pas été signalée auparavant. On peut le décrire en termes d'un agencement de chaînes de type wollastonite de stoechiométrie $[Si_3O_9]^{6-}$. Les feuillets silicatés et les polyèdres (MO_6) et (NaO_n) partagent des coins communs afin de former une trame mixte $\{Na_2\ [Zr_3\ (Si_{18}O_{45})]\ (H_2O)_2\}^-$ à cages qui contiennent les atomes *A*. Les pyramides carrées (NaO_5) partagent der coins communs pour former des chaînes $[NaO_4]$ en zig-zag le long de [010]. Chaque pyramide carrée partage une arête avec un octaèdre *M*(2), et les octaèdres *M*(2) décorent les chaînes $[NaO_4]$ en disposition *cis*. Un site (H_2O) rempli complètement de (H_2O) est un ligand de *Na* et *A*(1), avec une liaison hydrogène forte (1.94 Å) et une autre très faible et bifurquée (~3.10 Å) avec les atomes d'oxygène de la trame.

(Traduit par la Rédaction)

Mots-clés: zéravshanite, silicate Cs–Zr, structure cristalline, feuillet $[Si_{18}O_{45}]$, Dara-i-Pioz, Tajikistan.

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Introduction

Zeravshanite, $Cs_4\,Na_2\,Zr_3\,(Si_{18}O_{45})\,(H_2O)_2$, is a new mineral species from the moraine of the Dara-i-Pioz glacier, the Alai mountain range, Tien-Shan mountains, northern Tajikistan (Pautov *et al.* 2004). Zeravshanite is of pegmatitic origin, and occurs in association with quartz, microcline, aegirine, polylithionite, reedmergnerite, pectolite, fluorite, stillwellite-(Ce), leucosphenite, neptunite, calcite, pyrochlore and baratovite. Zeravshanite is the third Cs-silicate mineral described from boulders in the Dara-i-Pioz moraine, after cesium-kupletskite, $(Cs,K,Na)_3\,(Mn,Fe^{2+})_7\,(Ti,Nb)_2\,(Si_8O_{24})\,(O,OH)_7$ (Yefimov *et al.* 1971), and telyushenkoite, $Cs\,Na_6\,[Be_2\,Al_3\,Si_{15}\,O_{39}\,F_2]$ (Sokolova *et al.* 2002, Agakhanov *et al.* 2003). Here, we report on the crystal chemistry of zeravshanite.

Electron-Microprobe Analysis

The chemical composition of zeravshanite (Table 1) was characterized by wavelength-dispersion electron-microprobe analysis using a JEOL JCXA–50A instrument operating at 20 kV and 20 nA. Standards were as follows: anorthite USNM137042 (Si), ilmenite USNM96189 (Ti,Fe), synthetic ZrO_2 (Zr), synthetic SnO_2 (Sn), jadeite STD (Na), microcline USNM 143966 (K), synthetic $CsTb(PO_3)_4$ (Cs) (USNM standards from the Smithsonian Institution, Washington, USA). The H_2O content was derived from the structure solution and refinement. On the basis of 47 O *apfu* (atoms per formula unit), the following chemical formula for zeravshanite was obtained: $(Cs_{3.80}\,Na_{0.18}\,K_{0.02})_{\Sigma 4.00}\,Na_2\,(Zr_{2.76}\,Ti_{0.19}\,Sn_{0.05}\,Fe^{3+}{}_{0.05})_{\Sigma 3.05}\,[Si_{18}O_{45}]\,(H_2O)_2$, ideally $Cs_4\,Na_2\,Zr_3\,[Si_{18}O_{45}]\,(H_2O)_2$.

Crystal Structure

Data collection and structure refinement

A single crystal was mounted on a Bruker *P*4 automated four-circle diffractometer equipped with graphite-filtered Mo*K*α X-radiation and a Smart 1K CCD detector. The intensities of 9428 reflections with $\bar{7} < h < 6$, $\bar{12} < k < 12$, $\bar{18} < l < 18$ were collected to 59.98° 2θ using 30 s per 0.1° frame, and an empirical absorption correction (SADABS, Sheldrick 1998) was applied. The refined unit-cell parameters (Table 2) were obtained from 3772 reflections with $I > 10\sigma I$.

On the basis of 4508 unique observed reflections, the crystal structure of zeravshanite was solved and refined with the Bruker SHELXTL Version 5.1 system of programs (Sheldrick 1997) to $R_1 = 2.8\%$ and a GoF of 0.935. Scattering curves for neutral atoms were taken from the International Tables for Crystallography (1992). *R* indices are of the form given in Table 2, and are expressed as percentages. Site occupancies for the *A*, *M* and *Na* sites were refined with the scattering curves of Cs, Zr and Na. Out of twenty-five O-atoms, three atoms, O(4), O(15) and O(21), have U_{22} values of 0.028(2), 0.033(2) and 0.035(2), compared with the average value of about 0.015 (Table 3). These three specific O atoms are bridging O-atoms, and their Si–O–Si angles are 172.5(2), 180.0 and 180.0°, respectively, compared with a <Si–O–Si> value of 147.5° (Table 4). O(4), O(15) and O(21) are special sites of the form (0, *y*, ¼), (¼, ¾, ½) and (¼, ¼, ½), respectively. An attempt to include them in the refinement as disordered general sites with partial occupancy led to the following values for <Si–O–Si (°), U_{22} (Å^2): O(4): 166.7(3), 0.029(3); O(15): 170.3(5), 0.031(4); O(21): 169.2(4), 0.014(6). With refinement of this "disordered" model,

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

SiO_2	52.76	Si	17.96
Fe_2O_3	0.18	Fe^{3+}	0.05
TiO_2	0.75	Ti	0.19
SnO_2	0.34	Sn	0.05
ZrO_2	16.64	Zr	2.76
Na_2O	3.32	Na	2.19
K_2O	0.05	K	0.02
Cs_2O	26.19	Cs	3.80
H_2O**	1.76	H*	4.00
Σ	101.99		

* based on 47 O atoms
** calculated from structure solution.

TABLE 2. MISCELLANEOUS REFINEMENT DATA FOR ZERAVSHANITE

a (Å)	26.3511(8)
b	7.5464(3)
c	22.9769(8)
β (°)	107.237(1)
V (Å^3)	4363.9(4)
Space group	*C*2/*c*
Z	4
Absorption coefficient (mm^{-1})	4.49
F(000)	3927.0
D_{calc} (g/cm^3)	3.170
Crystal size (mm)	0.200 x 0.105 x 0.084
Radiation/ filter	MoKα/graphite
2θ-range for data collection (°)	59.98
R(int) (%)	3.15
Reflections collected	13000
Independent reflections $F_o > 4\sigma\lvert F_o\rvert$	63574508
Refinement method	Full-matrix least squares on F^2, fixed weights ∝ to $1/\sigma\lvert F_o^2\rvert$
Goodness of fit on F^2	0.935
Final *R*(obs) (%) $[F_o > 4\sigma\lvert F\rvert]$	R_1 = 2.80
R indices (all data) (%)	R_1 = 4.75 wR_2 = 6.96 GoF = 0.935

the Si–O distances involving these specific O-atoms changed only within the standard deviations. Hence we have adopted the ordered model for the O(4), O(15) and O(21) sites, as the rest of the structure seems insensitive to which model is used.

At the final stages of the refinement, two H atoms of one (H_2O) group were found in the difference-Fourier map and included in the refinement with two types of constraints: (1) the distances O(donor)–H were fixed at the distances taken from the D-map; (2) the isotropic-displacement factor for a H atom was constrained to be 1.5 times larger than the displacement parameter of the O atom of the (H_2O) group.

Atom positions and displacement parameters for zeravshanite are given in Table 3, selected interatomic distances in Table 4, assigned site-populations in Table 5, bond valences in Table 6, and details of hydrogen bonding in Table 7. Observed and calculated structure-factors are available from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

TABLE 3. FINAL ATOM POSITIONS AND DISPLACEMENT PARAMETERS (Å^2) FOR ZERAVSHANITE

	x	*y*	*z*	U_{eq}*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na	0.25296(5)	0.1907(2)	0.23718(8)	0.0375(4)	0.0170(7)	0.0481(8)	0.0449(11)	0.0226(8)	0.0057(7)	–0.0042(6)
A(1)	0.11036(1)	0.48491(3)	0.31362(1)	0.0231(1)	0.0222(1)	0.0239(1)	0.0255(1)	0.0034(1)	0.0107(1)	0.0027(1)
A(2)	0.07532(1)	0.00166(3)	0.50643(1)	0.0266(1)	0.0219(1)	0.0327(1)	0.0275(1)	0.0035(1)	0.0111(1)	0.0009(1)
M(1)	0.17912(1)	–0.00648(3)	0.32024(1)	0.0089(1)	0.0081(1)	0.0100(1)	0.0084(1)	–0.0002(1)	0.0023(1)	0.0001(1)
M(2)	0	1/2	1/2	0.0085(1)	0.0075(2)	0.0095(2)	0.0088(2)	–0.0004(1)	0.0030(1)	0(1)
Si(1)	0.04249(3)	–0.00854(9)	0.31620(4)	0.0097(2)	0.0088(3)	0.0101(3)	0.0103(4)	–0.0001(3)	0.0032(3)	0.0002(3)
Si(2)	–0.00924(3)	0.68043(9)	0.36302(4)	0.0109(2)	0.0102(4)	0.0103(3)	0.0118(4)	0.0016(3)	0.0027(3)	0.0009(3)
Si(3)	0.13751(3)	0.49717(9)	0.49844(4)	0.0101(2)	0.0084(3)	0.0111(3)	0.0107(4)	–0.0003(3)	0.0027(3)	0.0003(3)
Si(4)	0.12536(3)	0.78656(9)	0.18612(4)	0.0113(2)	0.0097(4)	0.0112(3)	0.0121(4)	–0.0011(3)	0.0022(3)	0.0002(3)
Si(5)	0.12873(3)	0.17752(9)	0.18188(4)	0.0117(2)	0.0105(4)	0.0110(3)	0.0125(4)	0.0010(3)	0.0016(3)	–0.0011(3)
Si(6)	–0.01291(3)	0.29072(9)	0.36739(4)	0.0105(2)	0.0099(4)	0.0102(3)	0.0116(4)	–0.0016(3)	0.0035(3)	–0.0006(3)
Si(7)	0.18290(3)	0.48317(9)	0.13367(4)	0.0109(2)	0.0101(3)	0.0123(3)	0.0099(4)	–0.0002(3)	0.0027(3)	–0.0004(3)
Si(8)	0.19452(3)	0.19610(9)	0.45256(4)	0.0115(2)	0.0098(4)	0.0122(3)	0.0122(5)	–0.0021(3)	0.0029(4)	0.0001(3)
Si(9)	0.19345(3)	0.80347(9)	0.45413(4)	0.0121(2)	0.0107(4)	0.0123(3)	0.0127(5)	0.0022(3)	0.0027(4)	–0.0002(3)
O(1)	0.03541(8)	0.8041(2)	0.3479(1)	0.0175(5)	0.0136(11)	0.0144(9)	0.0254(13)	0.0071(9)	0.0074(10)	–0.0016(8)
O(2)	0.00615(8)	0.4802(2)	0.3470(1)	0.0150(4)	0.0166(10)	0.0111(8)	0.0209(11)	0.0009(8)	0.0111(9)	–0.0006(7)
O(3)	0.12111(8)	0.9785(2)	0.15214(9)	0.0164(4)	0.0237(11)	0.0108(9)	0.0123(11)	0.0010(8)	0.0018(9)	–0.0014(8)
O(4)	0	0.0053(4)	1/4	0.0202(6)	0.0165(15)	0.0278(16)	0.0132(15)	0	–0.0001(12)	0
O(5)	0.02927(8)	0.1465(3)	0.3589(1)	0.0178(5)	0.0174(11)	0.0167(9)	0.0183(12)	–0.0052(9)	0.0037(10)	0.0064(8)
O(6)	0.15326(8)	0.2964(3)	0.1382(1)	0.0190(5)	0.0214(12)	0.0202(10)	0.0155(12)	0.0011(9)	0.0056(10)	–0.0085(8)
O(7)	0.16780(8)	0.1764(2)	0.2498(1)	0.0148(4)	0.0138(10)	0.0136(9)	0.0157(12)	–0.0010(8)	0.0024(9)	–0.0016(7)
O(8)	0.25862(8)	–0.0178(2)	0.31938(9)	0.0157(4)	0.0111(9)	0.0212(10)	0.0136(10)	0.0001(8)	0.0017(8)	0.0008(8)
O(9)	0.06632(8)	0.7267(3)	0.1860(1)	0.0174(5)	0.0111(11)	0.0233(10)	0.0167(12)	–0.0029(9)	0.0026(9)	–0.0043(8)
O(10)	0.16334(7)	0.7971(2)	0.2546(1)	0.0137(4)	0.0102(10)	0.0145(9)	0.0146(12)	0.0002(8)	0.0008(9)	–0.0007(7)
O(11)	0.07111(8)	0.2526(3)	0.1810(1)	0.0178(5)	0.0107(10)	0.0251(10)	0.0153(12)	0.0017(9)	0.0001(9)	0.0026(8)
O(12)	0.10194(8)	0.0107(2)	0.3144(1)	0.0174(4)	0.0113(9)	0.0209(10)	0.0213(11)	0.0016(9)	0.0068(9)	–0.0004(8)
O(13)	0.14828(8)	0.6448(3)	0.1486(1)	0.0233(5)	0.0231(12)	0.0230(11)	0.0228(13)	–0.0073(9)	0.0055(11)	0.0075(9)
O(14)	0.18302(8)	0.4936(2)	0.56416(9)	0.0147(4)	0.0125(9)	0.0210(10)	0.0103(10)	–0.0013(8)	0.0028(8)	0.0018(8)
O(15)	1/4	3/4	1/2	0.0257(8)	0.0153(17)	0.0327(17)	0.0241(20)	0.0132(15)	–0.0017(15)	–0.0008(13)
O(16)	0.14702(8)	0.6757(3)	0.4639(1)	0.0202(5)	0.0158(12)	0.0188(10)	0.0243(14)	0.0078(9)	0.0035(10)	–0.0028(8)
O(17)	0.14826(8)	0.3305(3)	0.45897(1)	0.0185(5)	0.0136(11)	0.0220(10)	0.0174(12)	–0.0074(9)	0.0011(10)	0.0055(8)
O(18)	0.17815(9)	0.0013(2)	0.4719(1)	0.0187(4)	0.0283(12)	0.0121(9)	0.0202(11)	0.0004(8)	0.0139(10)	–0.0002(8)
O(19)	0.19696(8)	0.1933(2)	0.38368(9)	0.0145(4)	0.0161(11)	0.0150(9)	0.0127(12)	–0.0009(8)	0.0047(9)	–0.0006(7)
O(20)	0.19362(8)	0.8007(2)	0.3848(1)	0.0172(5)	0.0211(12)	0.0147(9)	0.0159(12)	–0.0001(8)	0.0056(10)	–0.0006(8)
O(21)	1/4	1/4	1/2	0.0242(8)	0.0117(16)	0.0345(17)	0.0218(20)	–0.0099(14)	–0.0021(15)	0.0001(12)
O(22)	0.07918(8)	0.4893(2)	0.5036(1)	0.01845(4)	0.0105(9)	0.0251(11)	0.0211(11)	–0.0013(9)	0.0069(9)	–0.0004(8)
O(23)	–0.01509(8)	0.2945(2)	0.4360(1)	0.0152(4)	0.0189(11)	0.0142(9)	0.0129(12)	0.0001(8)	0.0051(10)	–0.0015(8)
O(24)	–0.01099(8)	0.6938(2)	0.4317(1)	0.0161(5)	0.0212(12)	0.0145(9)	0.0129(12)	0.0008(8)	0.0054(10)	0.0015(8)
O(25)*	0.2501(2)	–0.0217(5)	0.1590(2)	0.0885(15)	0.0595(26)	0.1340(38)	0.0700(31)	–0.0354(27)	0.0162(22)	0.0410(24)
H(1)	0.237(3)	–0.069(5)	0.182(2)		0.10615					
H(2)	0.261(2)	–0.110(6)	0.132(2)		0.10615					

* (H_2O)

Coordination of the cations

There are nine tetrahedrally coordinated *Si* sites with a grand <*Si*–O> distance of 1.614 Å. The *Si*–O distances range from 1.638 (maximal, to a bridging O-atom) to 1.577 Å (minimal, to an apical O-atom) (Table 4). There are two octahedrally coordinated *M* sites, occupied primarily by Zr: *M*(1) (1.82 Zr + 0.14 Ti^{4+} + 0.04 Fe^{3+}) and *M*(2) (0.91 Zr + 0.04 Sn^{4+} + 0.05 Ti^{4+}) with <*M*(1)–O> = 2.056 and <*M*(2)–O> = 2.086 Å. The *M*(1) octahedron has site-symmetry 1, and the *M*(2) octahedron has site-symmetry $\bar{1}$, and the *M*(1) and *M*(2) octahedra occur in the ratio 2:1. There is one [5]-coordinated site occupied by Na with <*Na*–O,H_2O> = 2.400 Å. Four O-atoms and an (H_2O) group form a distorted square pyramid around the *Na* site. There are two *A* sites, [12]- and [11]-coordinated, respectively, and occupied primarily by Cs with minor Na and K (Table 5) with <*A*–O> = 3.369 and 3.396 Å, respectively. The *A*(1) site is coordinated by eleven O-atoms and an (H_2O) group; the *A*(2) site is coordinated solely by O atoms. The refined and calculated site-scattering values and the observed and calculated <*A*–ϕ> and <*M*–ϕ> distances (ϕ: unspecified anion) indicate the site populations given in Table 5.

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR ZERAVSHANITE

Si(1)–O(1)	1.627(2)	*Si*(2)–O(1)	1.618(2)	*Si*(3)–O(14)		1.627(2)
Si(1)–O(4)	1.603(1)	*Si*(2)–O(2)	1.635(2)	*Si*(3)–O(16)		1.621(2)
Si(1)–O(5)	1.630(2)	*Si*(2)–O(9)	1.628(2)	*Si*(3)–O(17)		1.624(2)
Si(1)–O(12)	1.586(2)	*Si*(2)–O(24)	1.595(2)	*Si*(3)–O(22)		1.577(2)
<*Si*(1)–O>	1.612	<*Si*(2)–O>	1.619	<*Si*(3)–O>		1.612
Si(4)–O(3)	1.633(2)	*Si*(5)–O(3)	1.638(2)	*Si*(6)–O(2)		1.630(2)
Si(4)–O(9)	1.619(2)	*Si*(5)–O(6)	1.617(2)	*Si*(6)–O(5)		1.608(2)
Si(4)–O(10)	1.597(2)	*Si*(5)–O(7)	1.594(2)	*Si*(6)–O(11)		1.630(2)
Si(4)–O(13)	1.600(2)	*Si*(5)–O(11)	1.615(2)	*Si*(6)–O(23)		1.595(2)
<*Si*(4)–O>	1.612	<*Si*(5)–O>	1.616	<*Si*(6)–O>		1.616
Si(7)–O(6)	1.630(2)	*Si*(8)–O(17)	1.626(2)	*Si*(9)–O(15)		1.601(1)
Si(7)–O(8)	1.598(2)	*Si*(8)–O(18)	1.631(2)	*Si*(9)–O(16)		1.625(2)
Si(7)–O(13)	1.620(2)	*Si*(8)–O(19)	1.603(2)	*Si*(9)–O(18)		1.630(2)
Si(7)–O(14)	1.608(2)	*Si*(8)–O(21)	1.596(1)	*Si*(9)–O(20)		1.595(2)
<*Si*(7)–O>	1.614	<*Si*(8)–O>	1.614	<*Si*(9)–O>		1.613
Na–O(7)	2.349(2)	*M*(1)–O(7)	2.081(2)	*M*(2)–O(22)	x2	2.065(2)
Na–O(8)d	2.429(2)	*M*(1)–O(8)	2.103(2)	*M*(2)–O(23)	x2	2.092(2)
Na–O(8)d	2.527(2)	*M*(1)–O(10)	2.067(2)	*M*(2)–O(24)	x2	2.102(2)
Na–O(10)	2.302(2)	*M*(1)–O(12)	2.002(2)	<*M*(2)–O>		2.086
Na–O(25)	2.392(4)	*M*(1)–O(19)	2.053(2)			
<*Na*–O>	2.400	*M*(1)–O(20)	2.031(2)			
		< *M*(1)–O>	2.056			
Si(1)–O(1)–*Si*(2)	141.7(1)					
Si(2)–O(2)–*Si*(6)	128.9(1)	*A*(1)–O(1)	3.353(2)	*A*(2)–O(1)		3.785(2)
Si(4)–O(3)–*Si*(5)	129.2(1)	*A*(1)–O(2)	3.062(2)	*A*(2)–O(3)		3.208(2)
Si(1)–O(4)–*Si*(1)e	172.5(2)	*A*(1)–O(7)	3.344(2)	*A*(2)–O(5)		3.423(2)
Si(1)–O(5)–*Si*(6)	146.9(2)	*A*(1)–O(9)	3.355(2)	*A*(2)–O(16)		3.416(2)
Si(5)–O(6)–*Si*(7)	143.8(2)	*A*(1)–O(10)	3.234(2)	*A*(2)–O(17)		3.505(2)
Si(2)–O(9)–*Si*(4)	138.7(2)	*A*(1)–O(11)	3.401(2)	*A*(2)–O(18)		3.040(2)
Si(5)–O(11)–*Si*(6)	139.6(2)	*A*(1)–O(12)	3.586(2)	*A*(2)–O(22)		3.682(2)
Si(4)–O(13)–*Si*(7)	160.6(2)	*A*(1)–O(16)	3.599(2)	*A*(2)–O(23)		3.300(2)
Si(3)–O(14)–*Si*(7)	134.6(1)	*A*(1)–O(17)	3.396(2)	*A*(2)–O(23)a		3.241(2)
Si(9)–O(15)–*Si*(9)f	180.00	*A*(1)–O(19)	3.235(2)	*A*(2)–O(24)b		3.347(2)
Si(3)–O(16)–*Si*(9)	142.4(1)	*A*(1)–O(20)	3.322(2)	*A*(2)–O(24)c		3.407(2)
Si(3)–O(17)–*Si*(8)	142.5(1)	*A*(1)–O(25)	3.543(4)	<*A*(2)–O>		3.396
Si(8)–O(18)–*Si*(9)	130.7(2)	<*A*(1)–O>	3.369			
Si(8)–O(21)–*Si*(8)g	180.00					
<*Si*–O–*Si*>	147.47					

a: –x, –y, –z+1; b: x, y–1, z; c: –x, –y+1, –z+1; d: –x+1/2, y+1/2, –z+1/2; e: –x, y, –z+1/2; f: –x+1/2, –y+3/2, –z+1; g: –x+1/2, –y+1/2, –z+1.

Structure Topology

A new type of silicate sheet: $[Si_{18}O_{45}]^{18-}$

In the crystal structure of zeravshanite, (SiO_4) tetrahedra link together to form a sheet of the form $[Si_{18}O_{45}]^{18-}$ (Fig. 1a). In the sheet, five- and eight-membered rings of (SiO_4) tetrahedra occur in a ratio of 2:1. Each eight-membered ring is connected to six five-membered rings, and each five-membered ring is linked to three eight-membered rings. Within the sheet, alternating eight-membered and five-membered rings form ribbons along the [010] direction. Ribbons of five-membered and eight-membered rings alternate along the [101] direction. The topology of the $[Si_{18}O_{45}]$ sheet is related to the zigzag $(5^2.8)_2(5.8^2)_1$ net (Smith & Bennett 1984, Hawthorne & Smith 1988). Figure 2a shows a net representation of the $[Si_{18}O_{45}]$ sheet, and Figure 2b shows the corresponding ideal $(5^2.8)_2(5.8^2)_1$ net. A principal feature of both nets is the presence of infinite chains of edge-sharing pentagons along [010]. The ideal net (Fig. 2b) has a repeat of two five-membered and two eight-membered chains. The repeat of the net corresponding to the $[Si_{18}O_{45}]$ sheet is three times longer owing to distortion of the tetrahedra. An $[Si_3O_9]^{6-}$ wollastonite chain can be regarded as an important building block of the sheet (Fig. 1b). In the sheet, these chains extend along [010]. Along [10$\bar{1}$], three chains have tetrahedra with their apical vertices pointing up, and the next three chains have tetrahedra with their apices pointing down. This arrangement of tetrahedra within the sheet is related to the arrangement of inversion centers in the plane of the sheet.

In the crystal structure of zeravshanite, silicate sheets, ($M\phi_6$) octahedra and ($Na\phi_5$) polyhedra link together to form a mixed framework (Fig. 3). The *A* atoms are located in large cages of the framework. Figure 4 shows the connectivity of the ($M\phi_6$) and ($Na\phi_5$) polyhedra and the (SiO_4) tetrahedra. Each isolated $[M(2)O_6]$ octahedron shares three vertices with one silicate sheet and three other *trans* vertices with an adjacent silicate sheet (Figs. 4a, b, 5a). Distorted ($Na\phi_5$) square pyramids share common vertices to form zig-zag chains along [010] (Fig. 4b). The chain of ($Na\phi_5$) pyramids is decorated by $M(1)$ octahedra: each $[M(1)\phi_6]$ octahedron shares two edges with two ($Na\phi_5$) pyramids. The cages containing the *A* atoms extend along [201], giving rise to channels bounded by eight-membered rings of (SiO_4) tetrahedra (Figs. 5a, b).

Hydrogen bonding

There are two (H_2O) groups per formula unit of zeravshanite, occupying one general site in the struc-

TABLE 5. REFINED SITE-SCATTERING VALUES (*epfu*) AND ASSIGNED SITE-POPULATIONS (*apfu*) FOR ZERAVSHANITE

	Refined site-scattering	Assigned site populations	Calculated site-scattering values	$\langle X-\phi\rangle_{calc}$*	$\langle X-\phi\rangle_{obs.}$
A(1)	54.10(8)	1.91 Cs + 0.09 Na	53.02	3.238	3.371
A(2)	53.84(8)	1.89 Cs + 0.09 Na + 0.02 K	52.66	3.207	3.396
M(1)	39.33(7)	1.82 Zr + 0.14 Ti^{4+} + 0.04 Fe^{3+}	38.46	2.090	2.057
M(2)	40.39(4)	0.91 Zr + 0.04 Sn^{4+} + 0.05 Ti^{4+}	39.50	2.093	2.087

*Calculated by summing constituent ionic radii; values from Shannon (1976)
ϕ = unspecified anion

ture. The (H_2O) group is bonded to Na and to an *A*(1) atom (Table 6, Fig. 6). There is a short hydrogen bond of 1.94 Å from H(1) to O(19), which is a common vertex for the *Si*(8) tetrahedron and the *M*(1) octahedron. There is a weak bifurcated hydrogen bond from H(2) to O(19) and O(3), the latter bridging between *Si*(4) and *Si*(5), with H…O distances of 3.17 and 2.95 Å, respectively. Details of the hydrogen bonding are given in Table 7 and Figure 6.

Related Si–O Sheets

There are two types of Si–O sheets of five- and eight-membered rings previously known in silicate minerals. They are of the form $[Si_6O_{15}]^{6-}$ and occur in the crystal structures of nekoite, $Ca_3[Si_6O_{15}](H_2O)_7$, space group *P*1, *a* 7.588, *b* 9.793, *c* 7.339 Å, α 111.77, β 103.50, γ 86.53°, *Z* = 1 (Alberti & Galli 1980), and okenite, $Ca_{10}[Si_6O_{16}][Si_6O_{15}]_2(H_2O)_{18}$, space group $P\bar{1}$, *a* 9.69, *b* 7.28, *c* 22.02 Å, α 92.7, β 100.1, γ 110.9°, *Z* = 1 (Merlino 1983). The crystal structure of okenite is of special interest as it contains two types of Si–O motif: an $[Si_6O_{15}]^{6-}$ sheet and an $[Si_6O_{16}]^{8-}$ chain, which is a combination of four and six-membered rings. The topologies of the $[Si_{18}O_{45}]^{18-}$ sheet in zeravshanite (Fig. 1a) and $[Si_6O_{15}]^{6-}$ sheets in nekoite (Fig. 7a) and okenite (Fig. 7b) are identical. However, corresponding tetrahedra in each sheet point in different directions and hence these three sheets are geometrical isomers. The sheets may also be described in terms of aggregations of silicate chains. In zeravshanite, the $[Si_{18}O_{45}]^{18-}$ sheet is built of $[Si_3O_9]^{6-}$ wollastonite chains in which all tetrahedra point the same way (Fig. 1a). In nekoite and okenite, the sheet is built of two types of chains. One chain is a wollastonite chain as in zeravshanite (Figs. 7c, d). The other chain is a wollastonite-like chain in which two tetrahedra point down and one tetrahedron points up (Figs. 7c, d). Note that the t_1 repeats of the sheets in nekoite and okenite are four times smaller than the t_1 repeat in zeravshanite.

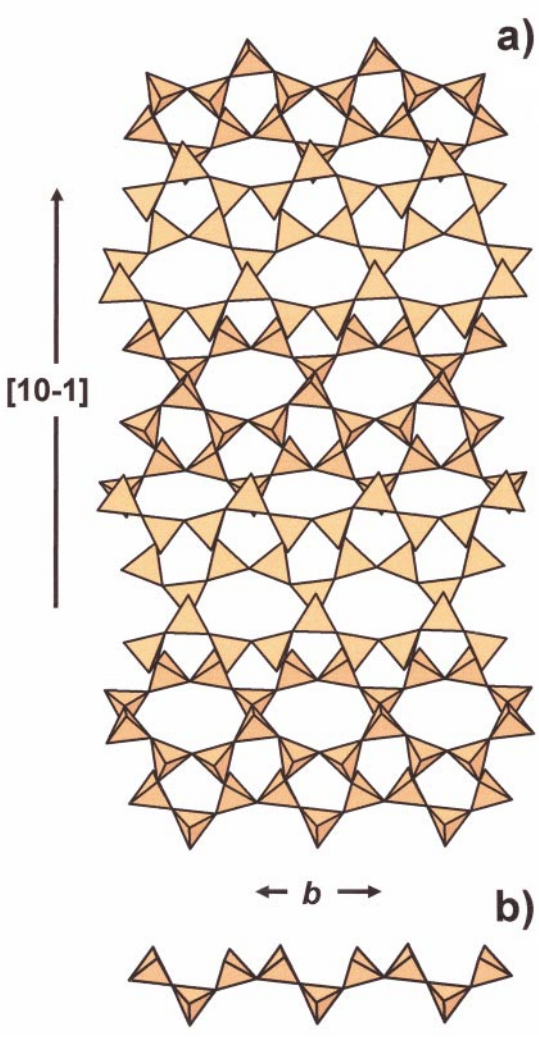

FIG. 1. A new type of Si–O sheet $[Si_{18}O_{45}]^{18-}$ with five- and eight-membered Si–O rings: (a) general view; (b) a fragment of the sheet, a wollastonite-like $[Si_3O_9]^{6-}$ chain. (SiO_4) tetrahedra are orange.

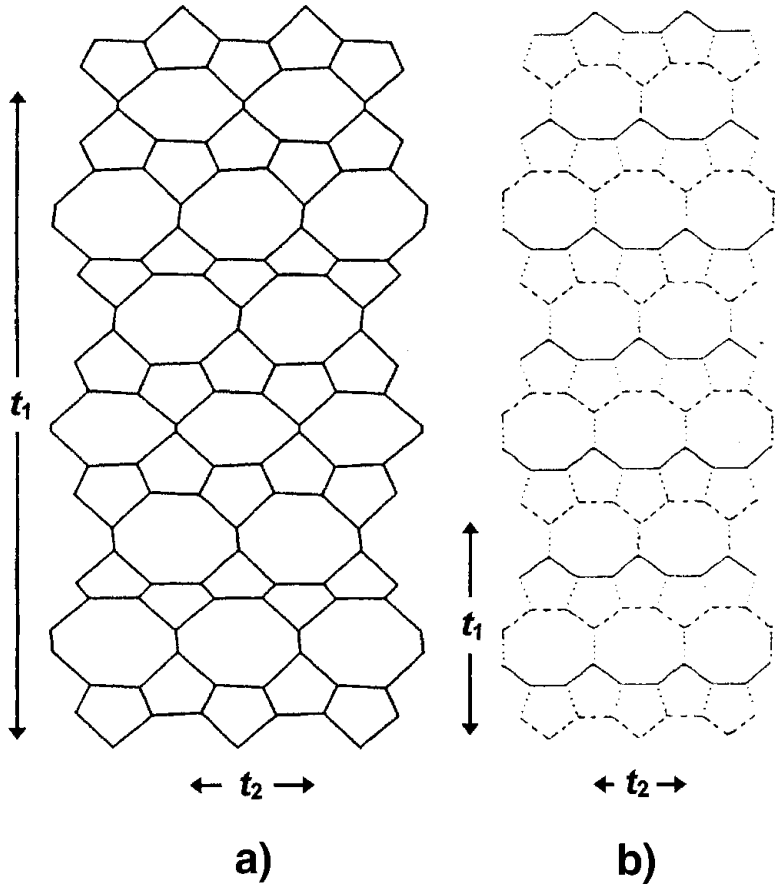

FIG. 2. Representation of the Si–O sheet $[Si_{18}O_{45}]^{18-}$ as a net: (a) the distorted $(5^2.8)_2(5.8^2)_1$ net describing the $[Si_{18}O_{45}]^{18-}$ sheet; (b) the ideal $(5^2.8)_2(5.8^2)_1$ net derived from number 98c net of Smith & Bennett (1984) by insertion of horizontal (solid and dashed lines) and zig-zag (dotted lines) edges (after Hawthorne & Smith 1988); t_1 and t_2 are the repeat translations.

SUMMARY

This is the first occurrence of an $[Si_{18}O_{45}]^{18-}$ sheet in a structure of a mineral. The topology of the sheet can be described as a linkage of wollastonite-like $[Si_3O_9]^{6-}$ chains that produces five-membered and eight-membered rings. The topology of the $[Si_{18}O_{45}]^{18-}$ sheet is related to the zigzag $(5^2.8)_2(5.8^2)_1$ plane net.

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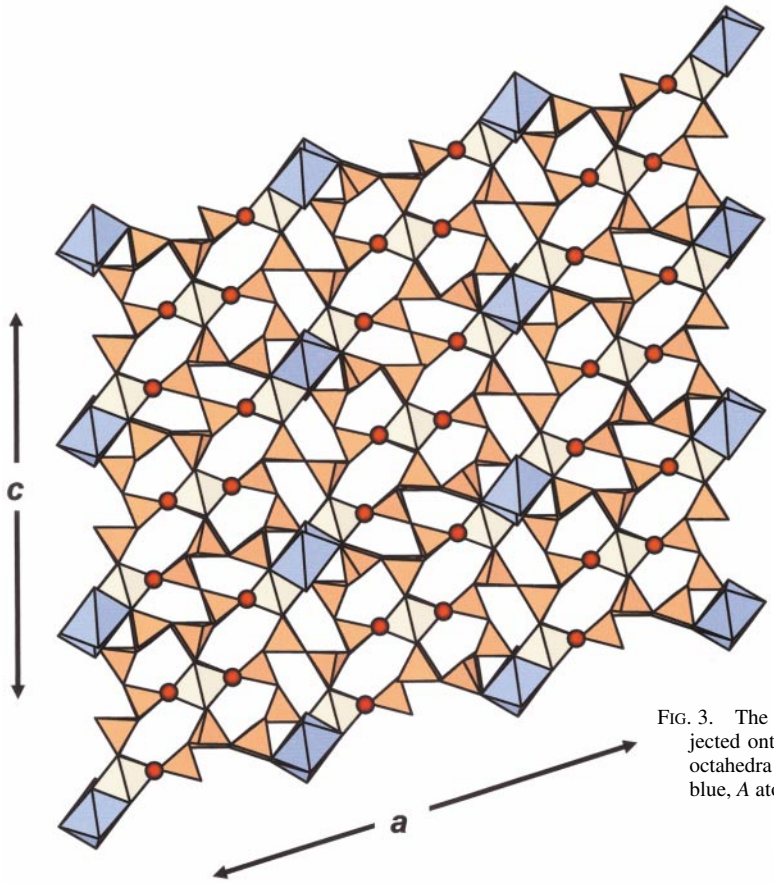

FIG. 3. The crystal structure of zeravshanite projected onto (010). Si tetrahedra are orange, *M* octahedra are yellowish green, *Na* polyhedra are blue, *A* atoms are shown as red circles.

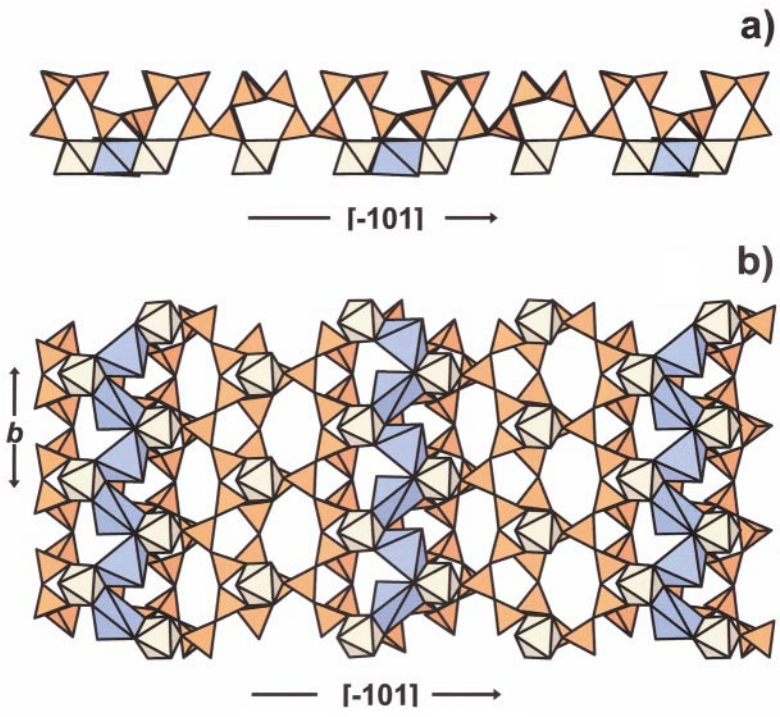

FIG. 4. Linkage of (SiO_4) tetrahedra and *M* and Na polyhedra: (a) $[Si_{18}O_{45}]^{18-}$ sheet with adjacent *M* and Na polyhedra viewed down [010]; (b) zig-zag chains of Na polyhedra decorated by *M*(1) octahedra extend along the *b* axis. Legend as in Figure 3.

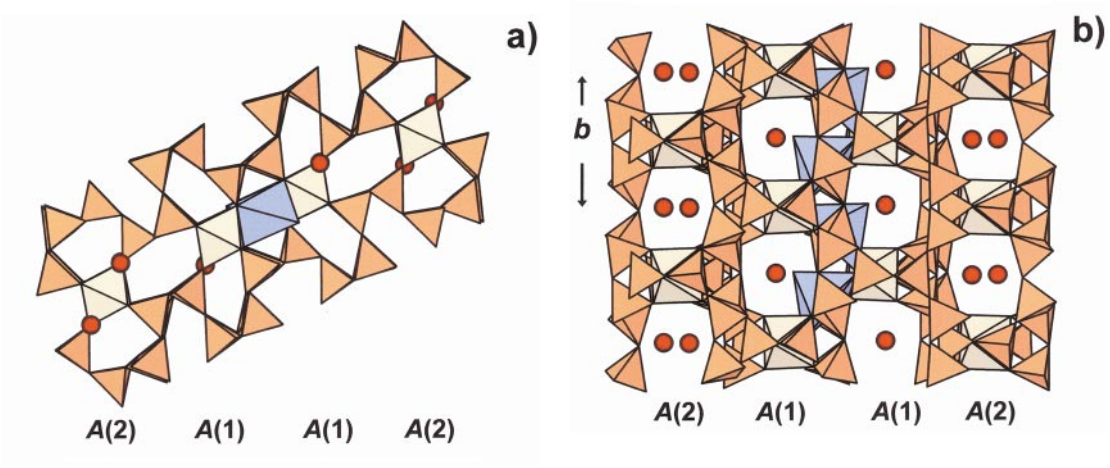

FIG. 5. A fragment of the crystal structure of zeravshanite showing location of the *A* sites: (a) viewed down [010]; (b) viewed down [201]. Legend as in Figure 3.

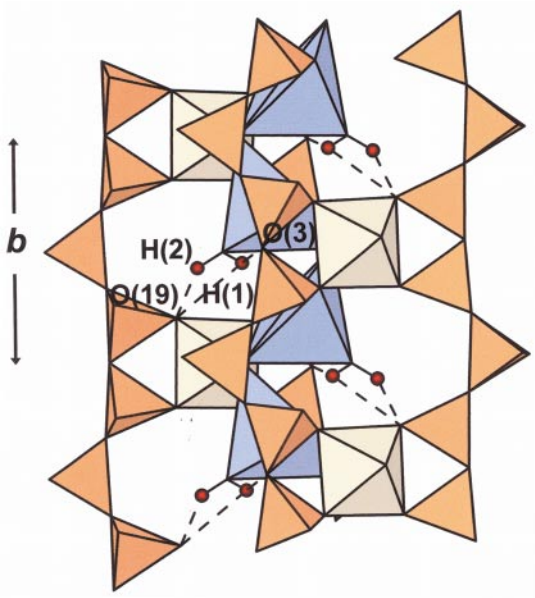

FIG. 6. Hydrogen bonding in the crystal structure of zeravshanite. Atoms H(1) and H(2) of the (H_2O) group are shown as red circles, hydrogen bonds are shown as dashed lines.

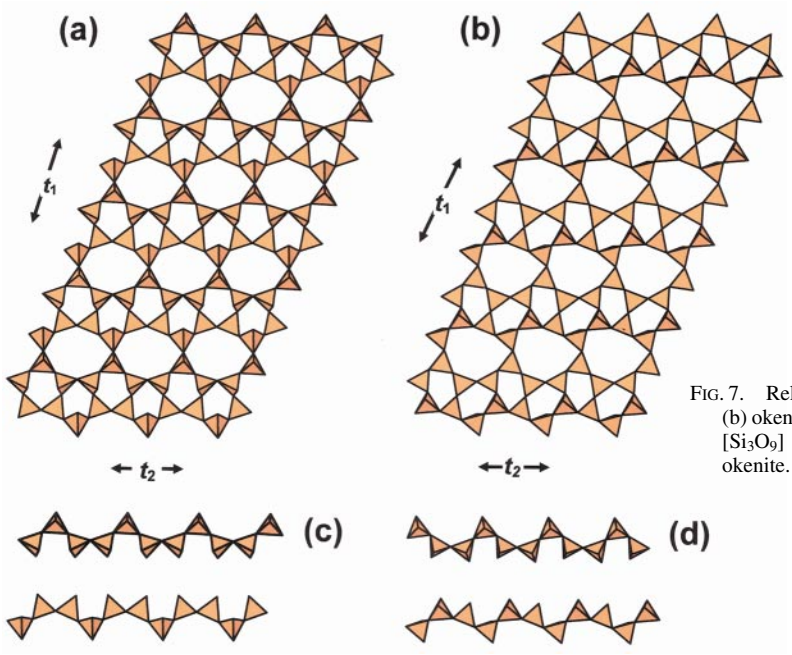

FIG. 7. Related Si–O sheets in (a) nekoite, and (b) okenite. Two types of chains of the form $[Si_3O_9]$ are shown for (c) nekoite, and (d) okenite.

TABLE 6. BOND-VALENCE* (*vu*) TABLE FOR ZERAVSHANITE

	Na	*A*(1)	*A*(2)	*M*(1)	*M*(2)	*Si*(1)	*Si*(2)	*Si*(3)	*Si*(4)	*Si*(5)	*Si*(6)	*Si*(7)	*Si*(8)	*Si*(9)	H(1)	H(2)	Σ
O(1)		0.091	0.04			0.987	1.013										2.131
O(2)		0.163					0.966				0.979						2.108
O(3)			0.12						0.971	0.961					0.01		2.062
O(4)						1.052$^{\times 2}\downarrow$											2.104
O(5)			0.078			0.995					1.038						2.111
O(6)										1.013		0.979					1.992
O(7)	0.226	0.092		0.659						1.078							2.055
O(8)	0.196 0.165			0.619								1.069					2.049
O(9)		0.09					0.984		1.008								2.082
O(10)	0.247	0.115		0.682					1.016								2.06
O(11)		0.082								1.019	0.979						2.08
O(12)		0.059		0.828		1.101											1.988
O(13)									1.057			1.008					2.068
O(14)								0.989				1.038					2.027
O(15)														1.057$^{\times 2}\rightarrow$			2.114
O(16)		0.055	0.079					1.003						0.995			2.132
O(17)		0.083	0.067					0.995					0.989				2.134
O(18)			0.171										0.974	0.982			2.127
O(19)		0.121		0.716									1.049		0.01	0.10	1.996
O(20)		0.096		0.76										1.075			1.931
O(21)													1.072$^{\times 2}\rightarrow$				2.144
O(22)			0.049		0.700$^{\times 2}\downarrow$			1.128									1.877
O(23)			0.112 0.100		0.647$^{\times 2}\downarrow$						1.075						1.934
O(24)			0.090 0.080		0.631$^{\times 2}\downarrow$		1.078										1.879
O(25)	0.197	0.061													0.98	0.90	2.138
Σ	1.031	1.108 [12] 0.933 [9]	0.986 [11]	4.264	3.956	4.135	4.041	4.115	4.052	4.071	4.071	4.094	4.084	4.109	1.00	1.00	

* bond-valence parameters from Brown (1981)

TABLE 7. HYDROGEN BONDING IN THE CRYSTAL STRUCTURE OF ZERAVSHANITE

D–H...A	D–A (Å)	D–H (Å)	H–A (Å)	∠D – H.. A (°)
O(25)-H(1)–O(3)	3.355(5)	0.79(1)	2.95(1)	114.5(1.9)
O(25)–H(1)–O(19)	2.887(4)		3.17(1)	62.3(1.8)
O(25)–H(2)–O(19)		1.01(1)	1.94(1)	154.0(1.9)
∠H(1)–O(25)–H(2) (°)	112.0(1.9)			

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