PETARASITE, Na₂Zr₂Si₆O₁₈(Cl,OH)₂·2H₂O,  
A ZEOLITE-TYPE ZIRCONOSILICATE

SUBRATA GHOSE AND CHE'NG WAN

Department of Geological Sciences, University of Washington,  
Seattle, Washington 98195, U.S.A.

GEORGE Y. CHAO

Department of Geology, Carleton University, Ottawa, Ontario K1S 5B6

ABSTRACT

Pterarasite, Na₂Zr₂Si₆O₁₈(Cl,OH)₂·2H₂O, from Mont St-Hilaire, Quebec, is monoclinic, space group P2₁/m, with cell dimensions a 10.7956(8), b 14.4928(16), c 6.6229(6) Å, β 113.214(5)°; Z = 2. The crystal structure has been determined by direct methods and refined by least squares to a R factor of 0.051, based on 2947 observed reflections. The crystal structure of pterarasite is an open three-dimensional framework, with the composition Zr₂Si₆O₁₈, consisting of corner-sharing, six-membered silicate rings and ZrO₆ octahedra. Elliptical channels (3.5 x 5.5 Å), defined by mixed six-membered rings, consisting of pairs of SiO₄ tetrahedra linked by Zr octahedra, run parallel to the b and c axes. Other channels limited by silicate rings run parallel to c. Two sodium atoms and the water molecules are located in channels parallel to b, whereas the third sodium atom and the Cl and (OH) ions are located in channels parallel to c. The average Si–O and Zr–O bond distances are 1.615 and 2.091 Å, respectively. All three sodium atoms are heptacoordinated. The Cl and (OH) ions are solely bonded to the sodium atoms. Structure-related, the pterarasite se rattache aux zircono- (et titano-) silicates, tels la lovozerite Na₂[ZrSi₆O₁₈(OH)₄] et la kasakovite Na₆Mn[Si₆O₁₈].

Keywords: petarasite, zirconosilicate, six-membered rings, framework structure.

INTRODUCTION

Pterarasite is a new sodium zirconosilicate mineral from Mont St-Hilaire, Quebec, with the empirical chemical composition (Na₆₋₆₆Ca₀.₆₆K₀.₄₆)[(Zr₂₋₆₆Ti₁₋₆₆)Si₆O₁₈][(OH)₆₋₆₆Cl₀.₆₆]·3.₀₁H₂O (Chao et al. 1980). It occurs as irregular grains up to 10 mm across in a xenolith in nepheline syenite, in association with catapleiite, apatite and zircon. Chao et al. have determined the chemical composition and crystallographic and optical properties of pterarasite. They found it to be monoclinic, space group P2₁/m or P2₁/a, with unit-cell dimensions a 10.791(4), b 14.505(5), c 5.626(2) Å, β 113.21(3)°; Z = 2.
ment of the 2θ values (between 22 and 38°) measured for 15 reflections and their symmetry equivalents, using Mo Kα radiation (Table 1). These cell dimensions are in good agreement with those determined by Chao et al. (1980).

Collection of the Intensity Data

The X-ray intensity data were collected from the single crystal sphere by the ω-2θ method, using graphite-monochromatized Mo Kα radiation and a scintillation counter. The variable scan method was used, with the minimum scan rate being 1°/min. (50 kV, 12.5 mA). All reflections within the 2θ limit of 65° were collected in a quadrant, i.e., a total of 3734 reflections, out of which 787 were below 3σ(I), where σ(I) is the standard deviation of the intensity I, as determined from the counting statistics. The measured intensities were corrected for Lorentz, polarization and absorption factors.

Determination and Refinement of the Structure

An N(Z) test of the measured X-ray intensities indicated that the centric space group $P2_1/m$ is most likely to be correct. The crystal structure has been determined by symbolic addition (Karle & Karle 1966), using the computer program MULTAN (Germain et al. 1971). In addition to the three origin-determining reflections, signs of four reflections were determined through the $Σ_1$ relationship, and five reflections were assigned symbols. The first E map indicated the positions of zirconium, two silicon and three oxygen atoms. Cycles of least-squares refinement, followed by difference-Fourier syntheses, brought out the missing silicon, oxygen and sodium atoms, the water molecules and the Cl and (OH) ions. Least-squares refinement at this stage indicated a negative temperature-factor for Na(3); subsequently, 0.20 Ca and 0.80 Na were assigned to this site, which made the temperature factor positive. The R factor at this stage was 0.080. Subsequently, the occupancy and positional parameters of Cl and the (OH) ions were refined, resulting in a lowering of the R factor to 0.069. Final refinement was carried out using anisotropic temperature factors and the block-diagonal least-squares-refinement program CRYLSQ (Stewart et al. 1972), with one block assigned to each atom. The atomic scattering factors for Na, Ca, Zr, Si, O and Cl were taken from Cromer & Mann (1968), corrected for anomalous dispersion (Cromer & Liberman 1970). The observed structure factors were weighted by the formula $1/σ^2(F_o)$, where $σ(F_o)$ is the standard deviation of the measurement of the structure factor $F_o$. The final R factor, based on all observed reflections, is 0.051. The final refinement resulted after seven cycles; even though very close to convergence, the refinement still showed oscillations in both positional and thermal parameters for Na(3), which is highly anisotropic, and, surprisingly, for Zr. Attempts to refine the structure in the space group $P2_1$ were unsuccessful. The final positional and thermal parameters are listed in Table 2. Observed and calculated structure factors (Table 3) have been deposited and may be obtained at nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Bond lengths and angles are presented in Table 4. The average standard deviations in Na–O, Zr–O and Si–O bond lengths are 0.005, 0.003 and 0.005 Å, respectively; in the O–Zr–O and O–Si–O angles, they are 0.1 and 0.2°, respectively. Because of low partial occupancy, the positional coordinates of the (OH) ions are not very reliable. Hence they have been omitted from a discussion of the crystal structure. The third water molecule shown in the empirical formula was not found; thus the ideal structural formula for petarasite is $NaZrSi_6O_{18}(Cl,OH)·2H_2O$.

Description of the Structure

The three-dimensional framework

The crystal structure of petarasite is an open three-dimensional framework with the composition [Zr$_2$Si$_6$O$_{18}$], consisting of corner-sharing, six-membered silicate rings and ZrO$_6$ octahedra. Elliptical channels (3.5 x 5.5 Å) defined by mixed six-membered rings, consisting of pairs of [SiO$_4$] tetrahedra linked by Zr octahedra, run parallel to the b and c axes (Figs. 1, 2).
Other channels limited by silicate rings run parallel to $c$. The sodium atoms, Na(1) and Na(2), and the water molecules $w(1)$ and $w(2)$ are located in channels parallel to $b$, whereas Na(3) and the Cl atoms and (OH) ions are located in channels parallel to $c$.

Conformation of the six-membered silicate ring

The [SiO$_4$] ring, of point-group symmetry $m$, deviates considerably from hexagonal symmetry. It can be considered as formed by two [SiO$_4$] groups, one pointing up and the other pointing down, bridged by two separate [SiO$_4$] groups (Fig. 3). This situation is similar to that found in lovozerite, Na$_2$ZrSi$_6$O$_{16}$ (OH)$_4$ (Ilyukhin & Belov 1960); however, in lovozerite, the ring has a chair configuration, whereas in petarasite it is nearly planar. The Si-O-Si angles within the [SiO$_4$] groups [Si(1)-O(1)-Si(1)', 148.6°; Si(3)-O(9)-Si(3)', 154.5°] are much larger than the other two between the [SiO$_4$] groups and the isolated [SiO$_4$] tetrahedra [Si(1)-O(5)-Si(2) 135.1°; Si(2)-O(7)-Si(3) 136.4°]. The maximum deviation of the silicon atoms from the least-squares plane passed through the bridging oxygen atoms [O(1), O(4), O(7) and O(9)] is 0.06 Å (Table 5).

The average Si–O bond length within the three crystallographically independent silicate tetrahedra is 1.615 Å. Each silicate tetrahedron shares two corners with adjacent silicate tetrahedra, and each of the other two corners are shared with Zr octahedra and Na polyhedra. The average Si–O bond involved in bridging two Si atoms is significantly larger (1.632 Å) than the average nonbridging ones (1.604 Å).

The Zr octahedron

The Zr octahedron is nearly regular; the Zr–O distances vary from 2.082 to 2.103 Å, and the O–Zr–O angles from 84.4 to 95.9°. The average Zr–O distance, 2.091 Å, is significantly larger than that (2.074 Å) found in zektzerite, NaLiZrSi$_4$O$_{12}$, where Zr octahedra share edges with LiO$_4$ tetrahedra (Ghose & Wan 1978).

The sodium polyhedra

All three sodium atoms are seven-coordinated. The Na(1)O$_6$(H$_2$O)Cl and Na(2)O$_6$(H$_2$O)Cl polyhedra are distorted monocapped octahedra, whereas the Na(3)O$_7$Cl polyhedron is a distorted hexagonal pyramid (Fig. 4). For a proper shielding of the charge of the Na(3) ion, a second Cl atom may be considered part of the Na(3) coordinations [Na(3)–Cl 3.520 Å];
Figure 1. Petarasite, $\text{Na}_2\text{Zr}_2\text{Si}_6\text{O}_{18}(\text{Cl},\text{OH})\cdot2\text{H}_2\text{O}$: partial projection of the structure down the $c$ axis, showing the corner-sharing, six-membered silicate rings and $\text{ZrO}_6$ octahedra. Note the elliptical channels parallel to the $c$ axis, which accommodate $\text{Na}(3)$ and Cl atoms.

Figure 2. Petarasite: partial projection of the structure down the $b$ axis showing elliptical channels parallel to $b$, which house the sodium atoms $\text{Na}(1)$ and $\text{Na}(2)$ and the water molecules. The six-membered silicate rings and the rest of the structure can be reconstructed by passing mirror planes through vertices of silicate tetrahedra pointing up (or down).
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The Na(3) polyhedron is a distorted hexagonal bipyramid. Other than this long distance, the other Na–Cl distances average 2.982 Å, which is considerably larger than the Na–Cl distance in sodium chloride (2.820 Å). Interestingly, the Cl atom is bonded to six sodium atoms in a distorted octahedral coordination, as in NaCl. The average Na–(H2O) distance, 2.356 Å, is considerably shorter than the average Na–O distance, 2.673 Å.

The water molecules and the proposed hydrogen bonding

The water molecules w(1) and w(2) are located on mirror planes within channels parallel to b. The hydrogen atoms associated with the water molecules can occur either on the mirror plane or across it, the former possibility being more likely on account of the near neighbor environments. The oxygen atom O(1) located on the mirror plane is the acceptor of one H bond from w(1) [O(1)–w(1) 2.775 Å]. The other H bond appears to be bifurcated, with the two O(4) oxygen atoms across the mirror plane being the acceptors [O(1)–O(4) 2.840 Å]. The water molecule w(3) has a similar arrangement; O(9) on the mirror plane is one acceptor [O(9)–w(3) 2.906 Å] and the two O(7) atoms across the mirror plane are acceptors of the other bifurcated H bond [O(7)–w(2) 2.936 Å].

Related Structures

Although the presence of six-membered silicate rings is well known from minerals such as beryl, cordierite and dioptase, petarasite belongs structurally to the group of sodium zircono- (or titanato-) silicates such as lovozerite Na2ZrSi6O18(OH)6 (Ilyukhin & Belov 1960) and kazakovite Na4Mn[Ti(Si2O7)6] (Voronkov et al. 1979) [cf., the synthetic phase, Na8Cd8[Si6O18] (Simonov et al. 1967)]. All these phases are characterized by an open corner-sharing zircono- (or titanato-) silicate framework with open channels that house the sodium atoms and, as in petarasite, water molecules and chlorine atoms as well. In all cases, the diameter of the open channel is defined by mixed six-membered rings of alternating [SiO4] groups and Zr (or Ti) octahedra. Another zeolite-type zirconosilicate from Mont St-Hilaire is lemoynite, (Na,K)2CaZr2Si6O18•5–6H2O, with large channels parallel to [100], [101] and [001], where the Na, K and Ca atoms and the water molecules are located (LePage & Perrault 1976).
The [ZrSi$_6$O$_{18}$] framework in lemoynite contains silicate layers that consist of six-membered silicate rings.

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Fig. 4. Petarasite: coordination of the sodium atoms showing thermal vibration ellipsoids. The unusually anisotropic "thermal" vibration of Na(3), which is partly replaced by Ca, might be due to positional disorder.


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