

Crystal structure of synthetic makatite $\text{Na}_2\text{Si}_4\text{O}_8(\text{OH})_2 \cdot 4\text{H}_2\text{O}$

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Makatite / Crystal structure

Abstract. The crystal structure of synthetic makatite, $\text{Na}_2\text{Si}_4\text{O}_8(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, [monoclinic, $a = 7.3881(5) \text{ \AA}$, $b = 18.094(3) \text{ \AA}$, $c = 9.5234(5) \text{ \AA}$, $\beta = 90.64(1)^\circ$, $P2_1/c$, $z = 4$] was solved by direct methods, (MULTAN), and Fourier syntheses and refined to $R = 0.051$ for 834 independent reflexions. The makatite structure is built up of corrugated $[\text{Si}_2\text{O}_4(\text{OH})]_n^-$ layers containing rings of six tetrahedra. The layers are connected by octahedral $[\text{Na}(\text{H}_2\text{O})_4]_n^+$ rods and sodium atoms coordinating five oxygens which form distorted trigonal bipyramids. Hydrogen atoms positions have not been determined.

Introduction

As a part of a general study of zeolites with ion exchange properties for the treatment of nuclear power station wastes we have synthesized a large number of different zeolites. Exclusion of the aluminium component from the $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ system led to the preparation of a number of hydrous layer silicates, of which some are known as minerals, e.g. magadiite ($\text{Na}_2\text{O} \cdot 14\text{SiO}_2 \cdot 9\text{H}_2\text{O}$) (McAtee, House, and Eugster, 1968), kenyaite ($\text{Na}_2\text{O} \cdot 22\text{SiO}_2 \cdot 10\text{H}_2\text{O}$) (Eugster, 1967) and makatite (Hay, 1968), and some as purely synthetic products, e.g. sodium polysilicate ($\text{Na}_2\text{O} \cdot 8\text{SiO}_2 \cdot 9\text{H}_2\text{O}$) previously reported by McCulloh (1952) and Iler (1964). Many of these layer silicates have interesting ion exchange properties and this present structure determination was undertaken in order to understand the mechanism of the ion exchange. The details of the syntheses will be published elsewhere but in general most of the preparations yielded crystals too small for single crystal X-ray work. However, in the case of makatite, the introduction

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of the complexing agent triethanolamine (Charnell, 1971) resulted in the growth of larger, more suitable crystals.

Recently Dent Glasser et al. (1980) have proposed by help of electron microscopy methods a new chain type structure for makatite with a repeat distance of 3.4 Å in the fibre direction which by our investigation is shown not to be the case.

Experimental

The cell dimensions, shown in Table 1, were refined by least squares methods from 45 single indexed lines of a powder pattern obtained in a Guinier-Hägg focusing camera with $\text{CuK}\alpha_1$ radiation. A thin platy crystal ($0.090 \times 0.052 \times 0.006 \text{ mm}^3$), selected with the Weissenberg technique, was mounted on a CAD-4 four circle diffractometer. Table 1 gives information on the data collection, reduction of the intensities and subsequent refinement. Systematic absences were $h0l: l = 2n + 1$ and $0k0: k = 2n + 1$, which is consistent with

Table 1. Experimental details

| | |
|---|--|
| Cell data | $a = 7.3881(5) \text{ \AA}$ $b = 18.094(3) \text{ \AA}$ $c = 9.5234(5) \text{ \AA}$ $\beta = 90.64(1)^\circ$ $z = 4$ Space group $P2_1/c$ $\rho_c = 2.04 \text{ g cm}^{-3}$ $\rho_m^a = 2.03 \text{ g cm}^{-3}$ |
| Radiation | $\text{CuK}\alpha$ |
| θ interval ($^\circ$) | 5–70 |
| $w-2\theta$ scan width w ($^\circ$) | $0.5 + 0.9 \tan \theta$ |
| Maximum recording time (min) | 4 |
| Measured reflexions | (5, 70 $^\circ$) all |
| μ (mm^{-1}) | 5.71 |
| Range of transmission factors | 0.73–0.97 |
| Number of reflexions measured ^b | 2386 |
| Number of reflexions with zero weight | 1552 [$I < 2\sigma_c(I)$] |
| Number of reflexions used in the final refinement, m | 834 |
| Number of parameters refined, n | 185 |
| $R = \Sigma (F_o - F_c) / \Sigma F_o $ | 0.051 |
| $R_w = [\Sigma w (F_o - F_c)^2 / \Sigma w F_o ^2]^{1/2}$ | 0.055 |
| $S = [\Sigma w (F_o - F_c)^2 / (m - n)]^{1/2}$ | 1.52 |
| g ($\times 10^{-4}$) extinction ^c | 0.22 |

^a Measured by flotation

^b One set of independent reflexions was measured

^c Zachariasen, 1968

Table 2. Final positional parameters and isotropic B -values [\AA^2]. Standard deviations in ()

| | x | y | z | B (\AA^2) |
|--------------------|------------|-----------|-----------|------------------------|
| Si(1) | 0.2822(4) | 0.2143(2) | 0.1876(4) | 0.96(9) |
| Si(2) | 0.6997(4) | 0.2182(2) | 0.1748(4) | 1.08(9) |
| Si(3) | 0.7776(4) | 0.3388(2) | 0.3891(4) | 0.83(9) |
| Si(4) | 0.2001(4) | 0.3349(2) | 0.3990(4) | 1.01(9) |
| O(1) | 0.2421(11) | 0.2241(5) | 0.0224(9) | 1.74(24) |
| O(2) | 0.2476(11) | 0.2971(4) | 0.2507(8) | 1.41(24) |
| O(3) | 0.4931(10) | 0.1951(4) | 0.2050(9) | 1.49(23) |
| O(4) | 0.7307(11) | 0.2232(5) | 0.0064(8) | 1.58(23) |
| O(5) | 0.7429(11) | 0.3001(4) | 0.2358(8) | 1.11(22) |
| O(6) | 0.9902(10) | 0.3597(4) | 0.3992(8) | 1.43(22) |
| O(7) [†] | 0.1619(11) | 0.1517(5) | 0.2585(9) | 1.78(24) |
| O(8) [†] | 0.8240(10) | 0.1546(5) | 0.2444(9) | 1.58(24) |
| O(9) [†] | 0.6662(10) | 0.4126(4) | 0.4075(8) | 1.30(23) |
| O(10) [†] | 0.3175(9) | 0.4083(4) | 0.4202(9) | 1.40(23) |
| W(1) | 0.7506(11) | 0.4108(4) | 0.0029(9) | 1.93(25) |
| W(2) | 0.2450(12) | 0.4080(5) | 0.0187(9) | 2.03(25) |
| W(3) | 0.0296(12) | 0.0123(5) | 0.2336(9) | 2.46(28) |
| W(4) | 0.4714(12) | 0.0240(5) | 0.2529(9) | 2.18(27) |
| Na(1) | 0.5000(0) | 0.5000(0) | 0.0000(0) | 2.73(23) |
| Na(2) | 0.0000(0) | 0.5000(0) | 0.0000(0) | 2.71(23) |
| Na(3) | 0.7478(8) | 0.0324(3) | 0.1285(6) | 2.72(16) |

the space group $P2_1/c$ (No. 14). A refinement of 46 accurately measured θ -values confirmed the cell parameters.

During the data collection no systematic variation was observed in three standard reflections which were checked every 2 h. I and $\sigma_c(I)$ (based on counting statistics) were corrected for Lorentz and polarization effects. The positions of the four silicon atoms were determined by direct methods, (MULTAN), and repeated difference syntheses and full matrix least squares refinements minimizing $\sum w (|F_o| - |F_c|)^2$ with weights $w^{-1} = \sigma_c^2 (|F_o|) + (0.02 |F_o|)^2$ revealed the rest of the non-H atoms. Scattering factors for neutral atoms (Doyle and Turner, 1968) were used. Anisotropic temperature factors and corrections for absorption by numerical integration and isotropic extinction gave the final $R = 0.051$ and $R_w = 0.055$. A final difference synthesis was featureless. Final positional parameters are given in Table 2 and bond lengths and angles in Tables 3 and 4¹.

¹ Additional material to this paper can be ordered referring to the no. CSD 50125, name(s) of the author(s) and citation of the paper at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG

Table 3. Selected bond distances (Å). Symmetry code: superscripts: none x, y, z ; (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $\bar{x}, \bar{y}, \bar{z}$; (iii) $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$

| Si(1) tetrahedron | | Si(3) tetrahedron | |
|----------------------------|-----------|--|-----------|
| Si(1)–O(7) ^t | 1.595(9) | Si(3)–O(9) ^t | 1.579(8) |
| Si(1)–O(3) | 1.603(8) | Si(3)–O(6) | 1.618(8) |
| Si(1)–O(1) | 1.607(9) | Si(3)–O(4 ⁱ) | 1.623(9) |
| Si(1)–O(2) | 1.636(8) | Si(3)–O(5) | 1.636(8) |
| O(1)–O(2) | 2.544(11) | O(4 ⁱ)–O(5) | 2.613(11) |
| O(1)–O(3) | 2.582(12) | O(4 ⁱ)–O(6) | 2.648(11) |
| O(1)–O(7) ^t | 2.674(12) | O(4 ⁱ)–O(9) ^t | 2.672(11) |
| O(2)–O(3) | 2.627(11) | O(5)–O(6) | 2.619(11) |
| O(2)–O(7) ^t | 2.707(11) | O(5)–O(9) ^t | 2.675(11) |
| O(3)–O(7) ^t | 2.625(11) | O(6)–O(9) ^t | 2.580(11) |
| Si(2) tetrahedron | | Si(4) tetrahedron | |
| Si(2)–O(8) ^t | 1.611(9) | Si(4)–O(10) ^t | 1.597(8) |
| Si(2)–O(3) | 1.612(8) | Si(4)–O(2) | 1.611(8) |
| Si(2)–O(5) | 1.623(8) | Si(4)–O(6) | 1.615(8) |
| Si(2)–O(4) | 1.625(9) | Si(4)–O(1 ⁱ) | 1.615(9) |
| O(3)–O(4) | 2.645(11) | O(1 ⁱ)–O(2) | 2.617(11) |
| O(3)–O(5) | 2.662(11) | O(1 ⁱ)–O(6) | 2.663(11) |
| O(3)–O(8) ^t | 2.576(11) | O(1 ⁱ)–O(10) ^t | 2.646(12) |
| O(4)–O(5) | 2.591(11) | O(2)–O(6) | 2.638(11) |
| O(4)–O(8) ^t | 2.668(11) | O(2)–O(10) ^t | 2.626(11) |
| O(5)–O(8) ^t | 2.701(11) | O(6)–O(10) ^t | 2.578(10) |
| Nonbonding Si–Si distances | | Na(1) octahedron | |
| Si(1)–Si(2) | 3.089(5) | Na(1)–W(1) | 2.456(8) |
| Si(1)–Si(4) | 3.034(5) | Na(1)–W(1 ⁱⁱⁱ) | 2.456(8) |
| Si(1)–Si(4 ⁱ) | 2.946(5) | Na(1)–W(2) | 2.522(9) |
| Si(2)–Si(3) | 3.038(5) | Na(1)–W(2 ⁱⁱ) | 2.522(9) |
| Si(2)–Si(3 ⁱ) | 2.972(5) | Na(1)–W(4) | 2.400(9) |
| Si(3)–Si(4) | 3.123(5) | Na(1)–W(4 ⁱⁱⁱ) | 2.400(9) |
| Na(2) octahedron | | Na(3) polyhedron (distorted TBP) | |
| Na(2)–W(1) | 2.450(8) | Na(3)–O(8) ^t | 2.532(10) |
| Na(2)–W(1 ⁱⁱⁱ) | 2.450(8) | Na(3)–O(9) ^t | 2.399(10) |
| Na(2)–W(2) | 2.464(9) | Na(3)–O(10 ⁱⁱⁱ) ^t | 2.343(9) |
| Na(2)–W(2 ⁱⁱ) | 2.464(9) | Na(3)–W(3) | 2.328(11) |
| Na(2)–W(3) | 2.559(9) | Na(3)–W(4) | 2.377(10) |
| Na(2)–W(3 ⁱⁱ) | 2.559(9) | | |

Table 4. Selected bond angles (°)

| Si(1) tetrahedron | | Si(3) tetrahedron | |
|---|-----------------|---|----------|
| O(1)–Si(1)–O(2) | 103.4(5) | O(4 ⁱ)–Si(3)–O(5) | 106.6(4) |
| O(1)–Si(1)–O(3) | 107.1(5) | O(4 ⁱ)–Si(3)–O(6) | 109.6(4) |
| O(1)–Si(1)–O(7) ⁱ | 113.3(5) | O(4 ⁱ)–Si(3)–O(9) ⁱ | 113.1(5) |
| O(2)–Si(1)–O(3) | 108.4(4) | O(5)–Si(3)–O(6) | 107.2(4) |
| O(2)–Si(1)–O(7) ⁱ | 113.9(5) | O(5)–Si(3)–O(9) ⁱ | 112.6(4) |
| O(3)–Si(1)–O(7) ⁱ | 110.4(5) | O(6)–Si(3)–O(9) ⁱ | 107.6(4) |
| Si(2) tetrahedron | | Si(4) tetrahedron | |
| O(3)–Si(2)–O(4) | 109.6(5) | O(1 ⁱ)–Si(4)–O(2) | 108.4(5) |
| O(3)–Si(2)–O(5) | 110.8(4) | O(1 ⁱ)–Si(4)–O(6) | 111.1(5) |
| O(3)–Si(2)–O(8) ⁱ | 106.2(5) | O(1 ⁱ)–Si(4)–O(10) ⁱ | 111.0(5) |
| O(4)–Si(2)–O(5) | 105.9(5) | O(2)–Si(4)–O(6) | 109.7(4) |
| O(4)–Si(2)–O(8) ⁱ | 111.1(5) | O(2)–Si(4)–O(10) ⁱ | 109.9(5) |
| O(5)–Si(2)–O(8) ⁱ | 113.3(4) | O(6)–Si(4)–O(10) ⁱ | 106.8(4) |
| Si(1)–O(3)–Si(2) | 147.9(6) | | |
| Si(1)–O(2)–Si(4) | 138.3(5) | | |
| Si(1)–O(1)–Si(4 ⁱ) | 132.2(6) | Range: 132.2(6)–150.1(6) | |
| Si(2)–O(5)–Si(3) | 137.6(5) | | |
| Si(2)–O(4)–Si(3 ⁱ) | 132.4(6) | | |
| Si(3)–O(6)–Si(4) | 150.1(6) | | |
| Na octahedra | | Range of angles | |
| W–Na(1)–W | 82.6(3)–97.4(3) | | |
| W–Na(2)–W | 83.9(3)–96.1(3) | | |
| Na(3) polyhedron (distorted TBP) | | | |
| Equatorial angles | | Axial angles | |
| O(9 ⁱ)–Na(3)–W(3) | 131.0(4) | O(8) ⁱ –Na(3)–O(10 ⁱⁱⁱ) ⁱ | 165.4(4) |
| O(9 ⁱ) ⁱ –Na(3)–W(4) | 104.8(4) | | |
| W(3)–Na(3)–W(4) | 123.0(4) | | |

Description of the structure

The silicate layer (Fig. 1) can be described as being built up of unbranched *vierer* single chains $(\text{Si}_4\text{O}_{12})_n$ (Liebau, 1972). Such chains are found for instance in copper sodium silicate, $\text{Cu}_3\text{Na}_2(\text{Si}_4\text{O}_{12})$, (Kawamura and Kawahara, 1976) and in Batisite, $\text{Na}_2\text{BaTi}_2\text{O}_2(\text{SiO}_3)_4$, (Nikitin and Belov, 1962). In the makatite structure these chains are parallel to the *a*-axis and all the free corners in a single chain point in the same direction, either up or down. The layers are formed by a *c*-glide connection of the chains which results in a very puckered silicate sheet shown in Figure 2.

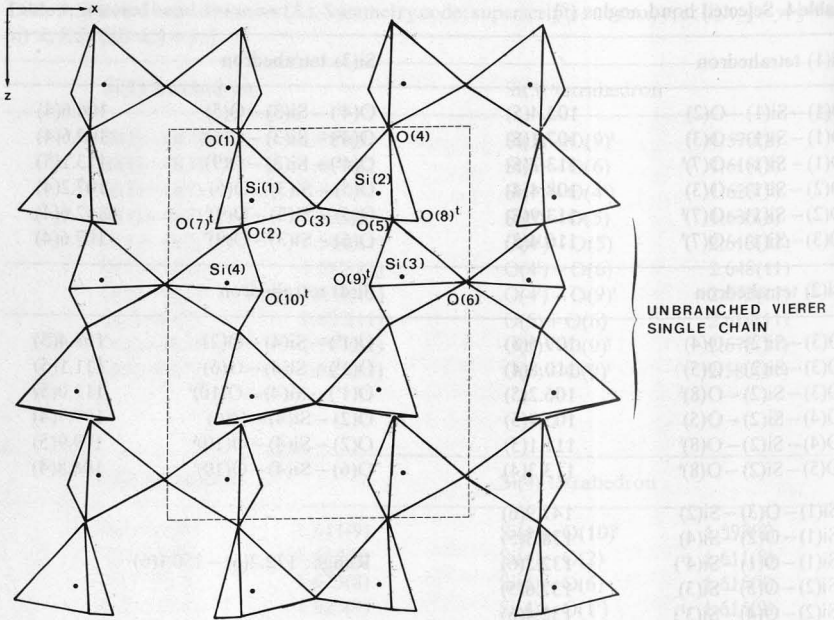


Fig. 1. One $[\text{Si}_2\text{O}_4(\text{OH})]_n^-$ layer projected \parallel to $[010]$

The layer consists entirely of rings of six tetrahedra and through each ring there is an almost perfect mirror plane parallel to the yz -plane. However, this is inconsistent with the space group and indicates pseudoorthorhombic symmetry which is broken only by one sodium position Na(3). This perhaps explains why it was difficult to find the right symmetry for natural makatite (Sheppard et al., 1970). The layers are connected by two different types of sodium-oxygen polyhedra as shown in Figure 2. Na(1) and Na(2) are coordinated to six water oxygens and form edge sharing octahedral rods parallel to the a -axis; these rods are probably connected to the layers by hydrogen bonds. Na(3) is coordinated in a distorted trigonal bipyramid to two water oxygens, which share corners with the octahedral rods, and to three oxygens in the silicate layers, thus connecting the layers in the b -direction.

Ion exchange studies

Some preliminary ion exchange experiments with Rb^+ , Cs^+ , Ag^+ , Tl^+ , Sr^{2+} , Ba^{2+} have been performed for exchange times which ranged from 1 to 3 days. The exchange was complete for Ag^+ , Tl^+ and Rb^+ , smaller for Sr^{2+} and

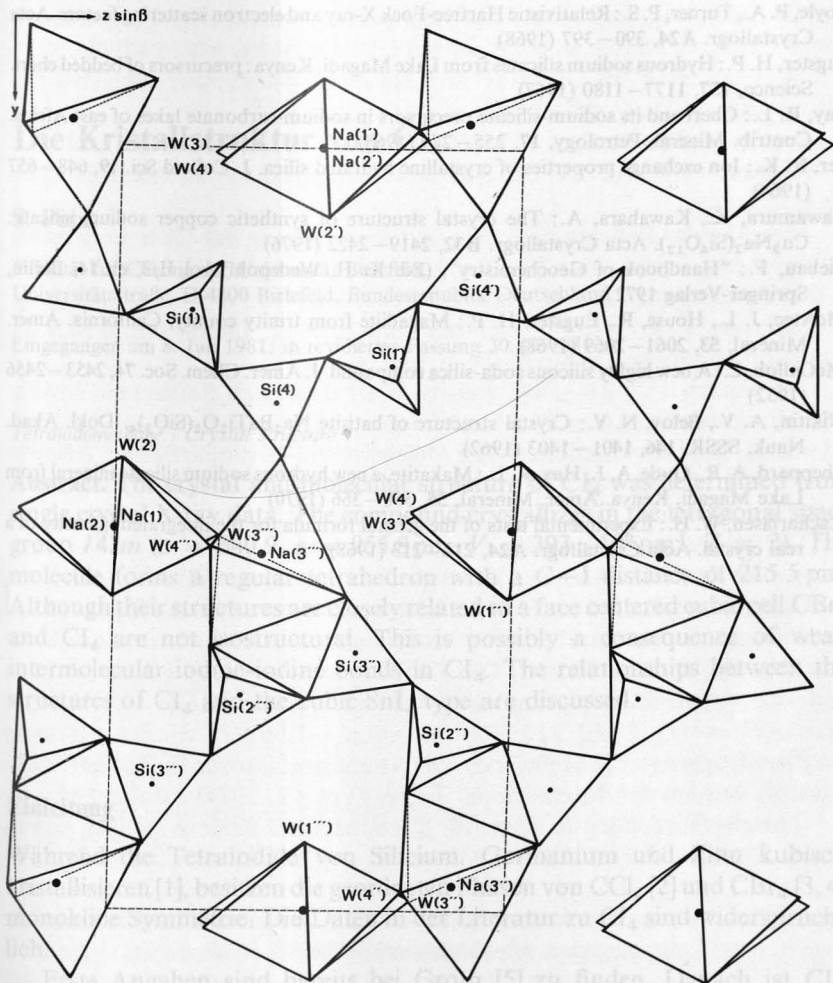


Fig. 2. Projection of the makatite structure with half the unit cell along a

Ba^{2+} and very small for Cs^+ . Guinier powder diffractograms showed various distortions of the structure, smallest for Ag^+ and largest for Tl^+ and Rb^+ . A more detailed report of the ion exchange work will follow.

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