

The crystal structure of ferrinatriite, $\text{Na}_3(\text{H}_2\text{O})_3[\text{Fe}(\text{SO}_4)_3]$
 and its relationship to Maus's salt,
 $(\text{H}_3\text{O})_2\text{K}_2\{\text{K}_{0.5}(\text{H}_2\text{O})_{0.5}\}_6[\text{Fe}_3\text{O}(\text{H}_2\text{O})_3(\text{SO}_4)_6](\text{OH})_2$

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SUMMARY. Ferrinatriite crystallizes in space group $P\bar{3}$, with $a = 15.566(5)$, $c = 8.69(1)$ Å and $Z = 6$. The crystal structure was solved by three-dimensional Patterson and Fourier syntheses, and refined by least squares employing 2378 independent reflexions to a final R value of 0.068. The iron ions occupy special positions and are surrounded octahedrally by oxygen atoms. Fe^{3+}O_6 octahedra and SO_4 tetrahedra are linked together to form infinite chains of Fe-O-S linkages in the [0001] direction. These chains are linked to each other by $[\text{NaO}_3(\text{H}_2\text{O})_2]$ polyhedra and probably by hydrogen bonds. The topology of the arrangement is the same as that of the hypothetical $P312$ structure proposed by Moore and Araki (1974).

FERRINATRITE is a hydrated sulphate of sodium and ferric iron, found in association with several other secondary sulphates in arid environments (Palache, Berman, and Frondel, 1951). The mineral was first described by Mackintosh (1889) as ferronatriite, and he proposed the chemical formula $\text{Na}_3\text{Fe}(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$. The composition was subsequently verified by Genth and Penfield (1890), Arzruni and Frenzel (1891), and Cesbron (1965) on natural crystals, and by Scharizer (1906) on artificial material. Bandy described as ferrinatriite a mineral with chemical formula quite different from that given by Mackintosh.

On the basis of morphological studies, Gordon (1942) considered ferrinatriite to be trigonal, with an axial ratio $c/a = 0.5563$. Cesbron (1965) found: $a = 15.57(3)$, $c = 8.67(3)$ Å, $c/a = 0.557$, $Z = 6$, probable space group $P\bar{3}$.

Ferrinatriite is related to Maus's salt, which contains Na and K as alkalis. Maus's salt has been crystallized according to Van Tassel (1961), but is not stable at standard conditions and by slow dehydration gradually converts into ferrinatriite.

Experimental. We examined natural crystals from Sierra Gorda, Chile, kindly supplied by Professor Cesbron, and artificial material obtained by the decomposition of Maus's salt.

Weissenberg photographs showed both to be essentially identical, but the artificial product proved more suitable for the structural study. A small roughly spherical crystal was investigated in detail by means of Weissenberg photography. According to Cesbron no systematic absences were observed; therefore, $P\bar{3}$ or $P3$ were both possible.

Lattice parameters of artificial ferrinatriite were refined by the least-squares method, applied to twenty-seven reflexions from an X-ray powder pattern using artificial crystals. Crystal data are: $a = 15.566(5)$, $c = 8.69(1)$ Å, $\mu(\text{Mo-K}\alpha) = 19.7 \text{ cm}^{-1}$, $\mu\text{R} = 0.19$, $V = 1823.5 \text{ Å}^3$, $Z = 6$, $\rho_{\text{meas}} = 2.562 \text{ g cm}^{-3}$ (Gordon, 1942), $\rho_{\text{calc}} = 2.55 \text{ g cm}^{-3}$.

Intensities were collected on a Philips PW 1100 four circle automatic diffractometer (Istituto di Mineralogia, Perugia, Italy) using Mo-K α radiation monochromatized with a graphite crystal and employing the ω - 2θ scan technique. The scan rate was $0.05^\circ/\text{sec}$. and the scan range

was 2° . The reflections $h, k, \pm l$ were collected within a θ range of 30° ; 3572 reflections were inspected, of which 2378 with $I > \sigma(I)$ were used in the refinement.¹

The intensities were corrected for Lorentz and polarization effects. Because of the uniform crystal dimensions (cross-section 0.1 mm) and the low linear absorption coefficient, no absorption correction was applied.

Solution of the structure and refinement. The space group $P\bar{3}$ was initially chosen and subsequently confirmed by the success of the structure analysis. Because there are six units of $\text{Na}_3\text{Fe}(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ per cell, it is not possible to decide if heavy atoms are located in special positions. A three-dimensional Patterson map clearly showed that the Fe atoms lie on three-fold axes, and also revealed some Fe-S and Fe-O vectors. A structure-factor calculation based on peak coordinates derived from Patterson map yielded a residual R index of 0.38. A subsequent Fourier map based on phases thus derived revealed the location of nearly all the remaining non-hydrogen atoms. Full-matrix least-squares refinement was carried out on an IBM 370/158 computer using the program ORFLS (Busing, Martin, and Levy, 1962). The scattering curves were taken from Cromer and Weber (1965). After two cycles of refinement involving the scale factor, atomic coordinates, and anisotropic temperature factors with unit weights, the R-index dropped to 0.068 for 2378 reflections with $I > \sigma(I)$. At this stage a Fourier difference map was carried out but it revealed no information regarding the position of the hydrogen atoms. The final atomic coordinates and anisotropic thermal parameters with their equivalent B-values are given in Table I.

Description of the structure. The structure of ferrinatrinite is displayed in figs. 1 and 2. The first is a projection along $[0001]$ and features the atomic arrangement excluding hydrogen; the second shows chains of Fe^{3+}O_6 octahedra and SO_4 tetrahedra running along c -axis and is projected on to the (110) plane.

Tables II and III provide the list of bond lengths and bond angles with their standard deviations. There are four crystallographically independent Fe-atoms on the threefold axis in the structure, two of which, Fe(3) and Fe(4), are also on inversion centres. All four Fe^{3+} atoms exhibit quite regular octahedral coordination by oxygen atoms. Interatomic distances agree closely with those reported in the literature: $\text{Fe}(1)\text{-O} = 1.99$, $\text{Fe}(2)\text{-O} = 2.01$, $\text{Fe}(3)\text{-O} = 1.99$, $\text{Fe}(4)\text{-O} = 1.99$ Å. The narrow spread exhibited by Fe-O distances (see Table II) is explained partly by the structure, partly by the conclusion of Shannon and Prewitt (1969). In fact all non-equivalent Fe atoms possess similar environments and structure functions: each Fe octahedron is connected to six equivalent SO_4 groups at all six corners. Moreover, owing to the high symmetry involving Fe^{3+}O_6 octahedra, according to Shannon and Prewitt: 'the average cation-anion distance over all similar polyhedra in one structure is constant'. The three asymmetric SO_4 groups are approximately tetrahedral with two shorter and two longer S-O distances, with mean values of 1.46 and 1.51 Å respectively. The lengthening of S-O distances has been observed in other structures when sulphurs are also shared by Fe^{3+} atoms, but it is not a general rule.

Consequently among SO_4 tetrahedral angles only one is slightly larger than the others: $\text{O}(5)\text{-S}(1)\text{-O}(6) = 113.8(4)$, $\text{O}(7, 2)\text{-S}(2)\text{-O}(8, 2) = 113.7(4)$ and $\text{O}(11)\text{-S}(3)\text{-O}(12) = 112.7(4)$: this has also been found in goldichite (Graeber and Rosenzweig, 1971). In ferrinatrinite the SO_4 tetrahedra share two oxygen corners with Fe^{3+}O_6 octahedra, the remaining two with $\text{NaO}_5(\text{H}_2\text{O})_2$ polyhedra (five cases) and with hydrogen bonds (one case), more specifically, one group of the latter oxygens are linked to two Na^+ atoms, one to three Na^+ atoms (O(11),) and one successive H-bonds only (O(12)).

¹ $\sigma(I) = [P + 0.25(B_1 + B_2)(T_P + T_B)^2 + (0.041)^2]^{1/2}$, where P is the total peak count in time T_B , I is the intensity and equal to $[P - 0.5(T_P/T_B)(B_1 + B_2)]$.

The three sodium ions exhibit a sevenfold coordination comprised of five sulphate oxygens and two water molecules. Na-O bond distances are distributed over a large range with average values of 2.53 for Na(1), 2.56 for Na(2), 2.55 Å for Na(3). Longer distances, such as Na(1)-O(7, 2) = 2.87, Na(2)-O(5) = 2.90 and Na(3)-O(10) = 3.01, have been taken into account for bond-strengths computation.¹

TABLE I. Final atomic coordinates, anisotropic temperature factors, and equivalent temperature factors for ferrinatrinite

Atom	x	y	z	$\beta_{11} \times 10^3$	$\beta_{22} \times 10^3$	$\beta_{33} \times 10^3$	$\beta_{12} \times 10^3$	$\beta_{13} \times 10^3$	$\beta_{23} \times 10^3$	B(eq)*
Fe(1)	1/3	2/3	0.18650(14)	1.08 (4)	1.08 (4)	1.93(12)	0.54 (4)	0	0	0.69 (2)
Fe(2)	1/3	2/3	0.68720(14)	1.11 (4)	1.11 (4)	1.76(13)	0.56 (4)	0	0	0.70 (2)
Fe(3)	0	0	0	1.28 (6)	1.28 (6)	2.12(18)	0.64 (6)	0	0	0.80 (4)
Fe(4)	0	0	1/2	1.33 (6)	1.33 (6)	2.24(19)	0.66 (6)	0	0	0.82 (4)
S(1)	0.33668(10)	0.51279(10)	0.42828(13)	1.46 (7)	1.31 (7)	2.49(13)	0.89 (6)	0.22 (7)	0.05 (7)	0.84 (2)
S(2)	0.18098(10)	0.50891(10)	0.94452(13)	1.12 (6)	1.09 (6)	2.54(12)	0.48 (5)	0.04 (7)	0.15 (7)	0.82 (2)
S(3)	0.14288(10)	0.16484(10)	0.74514(14)	1.08 (6)	1.34 (7)	2.54(12)	0.54 (5)	0.04 (7)	-0.05 (7)	0.86 (2)
Na(1)	0.08331(21)	0.63668(23)	0.07025(31)	2.51(15)	4.05(18)	8.52(35)	1.93(14)	-0.52(18)	-0.88(20)	2.35 (6)
Na(2)	0.10843(23)	0.41626(24)	0.29914(32)	3.16(17)	3.51(18)	8.41(36)	0.81(15)	-0.07(19)	0.48(20)	2.64 (7)
Na(3)	0.21859(23)	0.25030(23)	0.40021(31)	3.07(16)	2.99(16)	8.50(35)	1.15(14)	-0.35(19)	-0.12(19)	2.39 (6)
O(1)	0.25324(31)	0.54408(31)	0.81398(42)	1.84(23)	1.42(21)	3.45(42)	0.56(18)	0.79(25)	0.43(24)	1.16 (8)
O(2)	0.37326(31)	0.58452(31)	0.56028(39)	1.83(22)	1.74(22)	2.36(39)	1.19(19)	-0.41(23)	-0.92(23)	0.95 (7)
O(3)	0.28405(32)	0.54582(31)	0.31703(42)	2.34(24)	1.77(22)	3.54(41)	1.32(20)	-0.91(25)	-0.33(24)	1.20 (8)
O(4)	0.21278(31)	0.59338(31)	0.05810(40)	1.99(22)	1.64(22)	2.93(41)	0.93(19)	0.07(24)	-0.65(24)	1.14 (8)
O(5)	0.26396(35)	0.41471(33)	0.48140(49)	2.63(26)	1.45(23)	6.90(53)	0.66(21)	0.85(29)	1.01(28)	1.22(16)
O(6)	0.42205(33)	0.51639(34)	0.35092(46)	1.96(23)	2.62(25)	5.29(47)	1.56(20)	0.51(26)	-0.24(27)	1.51 (9)
O(7)	0.51623(36)	0.60019(36)	0.88666(47)	2.66(26)	2.96(27)	5.73(50)	2.25(23)	0.68(29)	-0.19(29)	1.63 (9)
O(8)	0.57233(34)	0.75526(33)	0.02299(44)	2.40(26)	1.93(24)	3.81(44)	0.26(21)	-1.22(27)	-0.26(26)	1.60 (9)
O(9)	0.02687(30)	0.11661(30)	0.12848(41)	1.39(21)	1.77(22)	3.55(41)	0.67(18)	0.46(22)	-0.48(23)	1.16 (8)
O(10)	0.05994(31)	0.12309(30)	0.62772(40)	1.24(20)	1.55(21)	3.42(39)	0.63(17)	-0.17(23)	-0.28(23)	0.99 (8)
O(11)	0.23447(32)	0.18034(35)	0.66936(45)	1.67(22)	2.72(26)	4.74(46)	1.16(20)	0.50(26)	0.11(27)	1.50 (9)
O(12)	0.15180(35)	0.25578(34)	0.80549(50)	2.60(25)	1.94(24)	7.40(54)	1.04(21)	-0.46(30)	-1.64(29)	1.85(10)
Aq(1)	0.24914(38)	0.28210(37)	0.12922(52)	2.86(27)	2.11(27)	7.63(58)	0.75(23)	-0.29(32)	0.54(31)	2.16(11)
Aq(2)	0.64289(40)	0.59199(38)	0.19949(54)	3.33(30)	2.54(28)	8.18(61)	1.29(25)	-0.61(34)	-0.44(33)	2.26(12)
Aq(3)	0.39206(40)	0.31598(43)	0.42872(54)	3.14(30)	4.24(34)	7.70(59)	2.35(27)	0.69(34)	1.70(36)	1.89(16)

* B(eq) is the equivalent isotropic thermal vibration parameter.

The $\text{NaO}_5(\text{H}_2\text{O})_2$ polyhedra are linked by their corners to SO_4 tetrahedra and to Fe^{3+}O_6 octahedra, and by their edges to each other via two water molecules. In addition Aq(1), Aq(2), and Aq(3) function as proton donors.

Applying Moore's and Araki's (1974) symbolism, the stoichiometry $MT_3\psi_{12}$ of ferrinatrinite involving Fe^{3+} atoms octahedrally coordinated by oxygens (M) and S^{6+} tetrahedrally coordinated by oxygens (T) has the following topological property: if we assume half of tetrahedral oxygens are bonded to one M and one T , $MT_3\psi_{12}$ is an indefinitely extending chain of octahedra and tetrahedra.

The topology of ferrinatrinite was predicted by Moore and Araki for the hypothetical $P312$ structure with stoichiometry $M_2[\text{TO}_4]_3$. Ferrinatrinite belongs to the third type of minimal

¹ See the Appendix, to appear in the Miniprint section of this volume (p. M6).

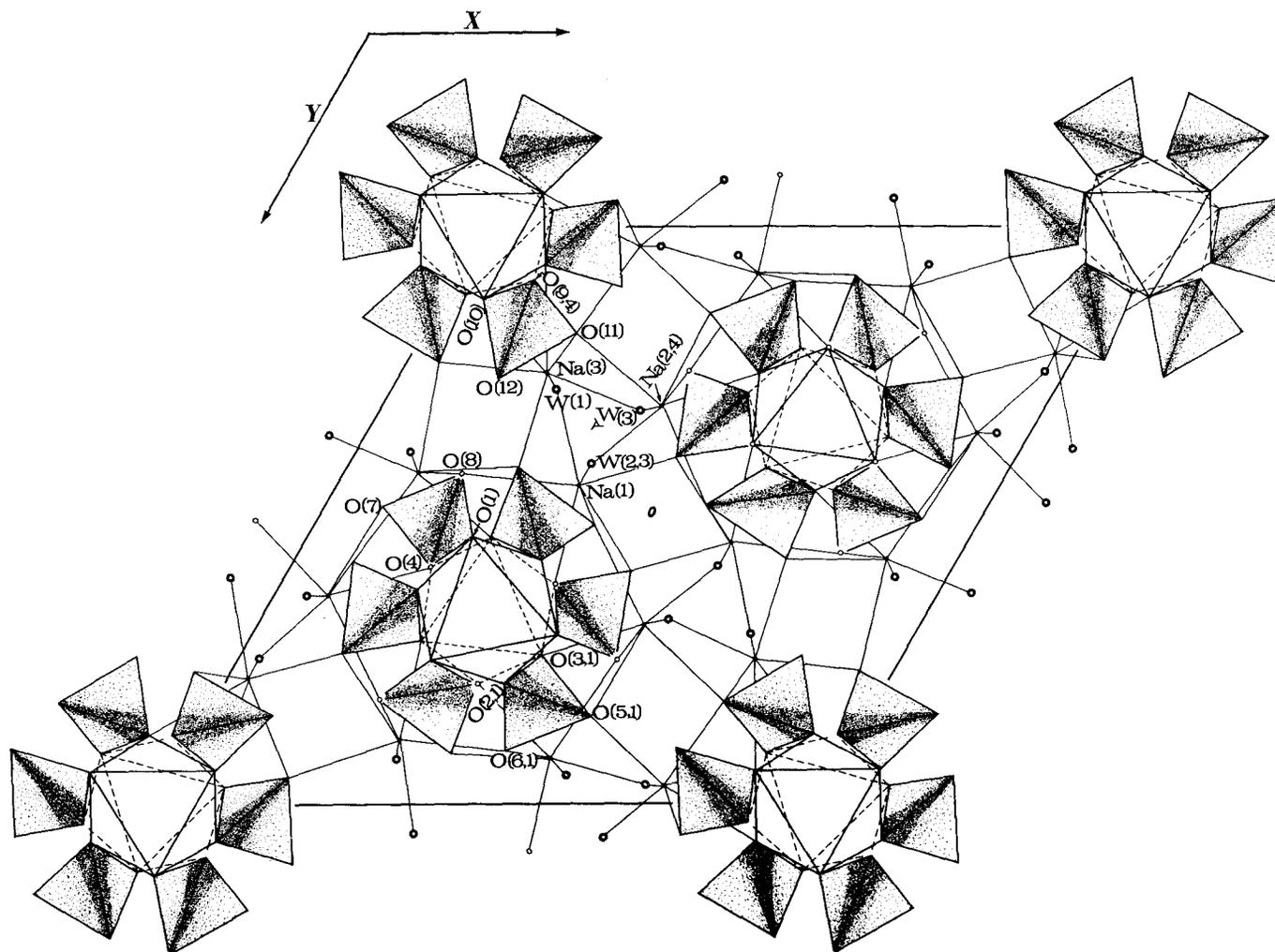


FIG. 1. Projection of the structure of ferrinatriite down $[0001]$. λ and O indicate pseudo-triad screw and pseudo-diad axes respectively.

Erratum: For W read Aq

loops illustrated by Moore and Araki, which is an infinite chain of corner-linked trigonal bipyramids with Fe as apices and S as meridional vertex. These chains may be derived from the two trigonal bipyramids of Fe–O–S linkages present in coquimbite and paracoquimbite (Giacovazzo, Menchetti, and Scordari, 1970; Fang and Robinson, 1970; Robinson and Fang, 1971).

Moore and Araki found their postulated structure of rhombohedral $\text{Fe}_2[\text{SO}_4]_3$, to be the 'imploded' version of the structures just mentioned; the topology of this structure is identical to that one of coquimbite and paracoquimbite, but is different from that of ferrinatrinite, which is a polarization of topological configuration related to rhombohedral $\text{Fe}_2[\text{SO}_4]_3$, coquimbite, and paracoquimbite.

Thermal data have been published by Mackintosh (1889), Scharizer (1906), and Cesbron (1964). Ferrinatrinite, contrary to Maus's salt from which it is derived, is a mineral stable at standard temperature and pressure. A DTA curve by the last author shows only one endothermic peak involving the water loss, which agrees with the result of the TGA curve: the curves stress the fact that ferrinatrinite completely dehydrates in the range between 115 and 170 °C. These results are confirmed by the crystal structure, since Aq(1), Aq(2), and Aq(3) are coordinated to two Na^+ ions and each donates two hydrogen bonds. Loss of water, therefore, leads to a continuous destruction of the crystal structure.

The crystal structure accounts for some physical properties of ferrinatrinite. The elongated habit on [0001] can be explained by uninterrupted chains of strong bonds in the same direction. The PBC's, Periodic Bonds Chains of Hartman and Perdok (1955), contain columns of Fe^{3+}O_6 octahedra and SO_4 tetrahedra, in which are all the strong bonds. In fact the bonds between these chains are formed by Na–O and probably by hydrogen bonds, which are much weaker than Fe–O and S–O bonds.

With similar arguments the $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ cleavages observed by Bandy (1938) and Gordon (1942) are explained by considering the types of the linkages in these planes, which consist of relatively weak Na–O and probably hydrogen bonds between the octahedra-and-tetrahedra chains. However, the same kind of weak bonds are present in the $(12\bar{3}0)$ plane; this also accounts for a possible $\{12\bar{3}0\}$ cleavage.

Relationships between ferrinatrinite and Maus's salt. From a chemical viewpoint artificial ferrinatrinite can be obtained by slow dehydration of Maus's salt with K partially substituted by Na at standard conditions. Recently the crystal structure of two related compounds have been solved: Maus's salt with only K as alkali ions (Giacovazzo, Scordari, and Menchetti, 1975) and metavoltine $\text{K}_2\text{Na}_6\text{Fe}^{2+}(\text{SO}_4)_{12}\text{O}_2 \cdot 18\text{H}_2\text{O}$ (simplified formula) (Giacovazzo *et al.*, 1976). We may compare the crystal structure of Maus's salt and that of ferrinatrinite in order to find the structural relationships between these salts. The cells are both hexagonal with a $P6_3/m$ and $P\bar{3}$ symmetry respectively. In fig. 3 the two-dimensional lattices with their symmetry elements are shown for Maus's salt (broken lines) and for ferrinatrinite (unbroken lines). From this figure one can see that the network of ferrinatrinite is built up from the corresponding two-dimensional lattice translations of Maus's salt and the network has an area three times greater than that of Maus's salt. The calculated length of the hexagonal network edge of ferrinatrinite based on the length of the Maus's salt edge (9.72 Å) is 16.82 Å, close to the experimental value (15.57 Å). The difference between calculated and measured values is explicable on the basis of the rearrangement involving the new structure and on the basis of the presence of Na^+ ions in ferrinatrinite instead of K^+ ions present in Maus's salt. As regards the symmetry, some observations may be useful. In the unit cell of ferrinatrinite, there are some pseudo-symmetry elements inherited from the symmetry cell of Maus's salt. As fig. 1 shows, in agreement with the old positions related to $\bar{6}$ and 2_1 (see fig. 3) there are pseudo-screw triads and pseudo-rotation

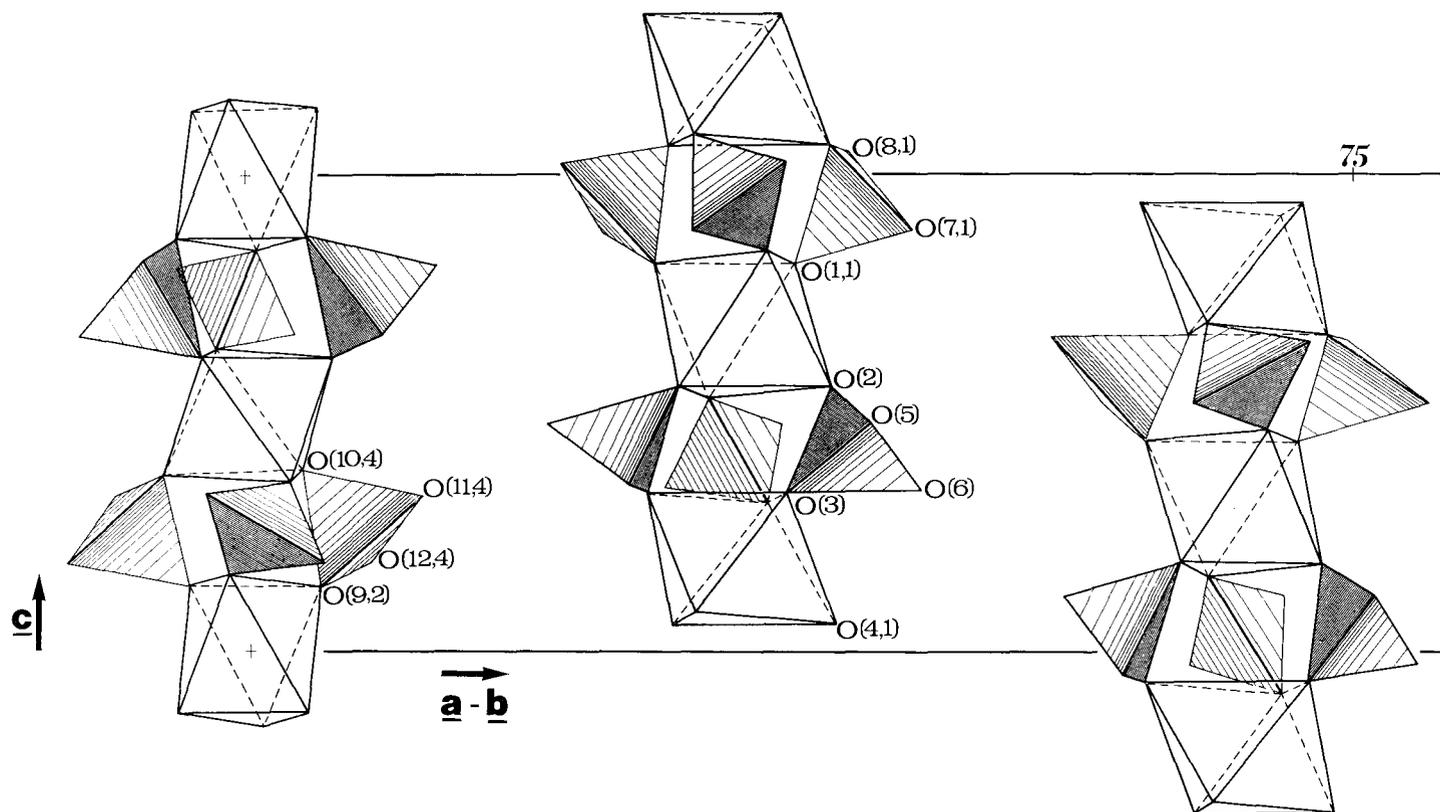


FIG. 2. Octahedral and tetrahedral chains in ferrinatriite projected on the (110) plane. To avoid overlap, some oxygen atoms are slightly shifted from the refined positions.

diad axes. As regards the rearrangement of Fe^{3+}O_6 octahedra and SO_4 tetrahedra, we can note that in Maus's salt there are clusters of composition $[\text{Fe}_3\text{O}(\text{H}_2\text{O})_3(\text{SO}_4)_6]$ represented in fig. 4 (left side). Three Fe^{3+}O_6 octahedra sharing an oxygen atom, lying on a \bar{b} axis, are connected by their corners sharing six SO_4 tetrahedra. These clusters, as fig. 5 shows, are

TABLE II. *Interatomic distances, with standard deviations in parentheses*

Fe(1)	—O(3)x3	1.996(5) Å	Na(2)	—O(3)	2.454(7)	S(1)	—O(2)	1.501(5)
	—O(4)x3	1.984(5)		—O(5)	2.903(8)		—O(3)	1.513(6)
Fe(2)	—O(1)x3	2.008(5)		—O(6,2)	2.666(7)		—O(5)	1.447(7)
	—O(2)x3	2.007(5)		—O(8,2)	2.633(7)		—O(6)	1.468(6)
Fe(3)	—O(9)x6	1.990(5)		—O(11,5)	2.533(7)	S(2)	—O(1)	1.495(5)
Fe(4)	—O(10)x6	1.995(5)		—Aq*(2,2)	2.336(8)		—O*(4)	1.513(5)
				—Aq(3,5)	2.406(8)		—O(7,2)	1.449(6)
Na(1)	—O(4)	2.423(7)	Na(3)	—O(5)	2.398(8)		—O*(8,2)	1.450(5)
	—O(6,2)	2.637(7)		—O(10)	3.006(7)	S(3)	—O(9,5)	1.503(5)
	—O*(7,2)	2.866(7)		—O(10,4)	2.538(7)		—O(10)	1.512(5)
	—O*(7,5)	2.355(7)		—O(11)	2.641(7)		—O(11)	1.479(6)
	—O(8,1)	2.704(7)		—Aq(1)	2.404(8)		—O(12)	1.446(7)
	—Aq(1,2)	2.332(8)		—Aq(3)	2.375(8)			
	—Aq*(2,5)	2.409(8)		—O(11,5)	2.521(7)			

TABLE III. *O—S—O and O—Fe—O angles, with standard deviations in parentheses*

O(3)—Fe(1)—O(4)	88.2(2)°	O(10)—Fe(4)—O(10,1)	92.0(2)°	O(1)—S(2)—O*(8,2)	109.5(3)°
O(3)—Fe(1)—O(3,1)	90.5(2)			O*(4)—S(2)—O(7,2)	107.6(3)
O(3)—Fe(1)—O(4,1)	89.5(2)	O(2)—S(1)—O(3)	107.7(3)	O*(4)—S(2)—O*(8,2)	108.1(3)
O(3)—Fe(1)—O(4,2)	179.1(3)	O(2)—S(1)—O(5)	110.3(3)	O(7,2)—S(2)—O*(8,2)	113.7(4)
O(4)—Fe(1)—O(4,1)	91.4(2)	O(2)—S(1)—O(6)	108.9(3)	O(10)—S(3)—O(11)	108.4(3)
O(1)—Fe(2)—O(2)	86.5(2)	O(3)—S(1)—O(5)	106.8(3)	O(10)—S(3)—O(12)	108.2(3)
O(1)—Fe(2)—O(1,1)	92.7(2)	O(3)—S(1)—O(6)	109.2(3)	O(10)—S(3)—O(9,4)	108.5(3)
O(1)—Fe(2)—O(2,1)	178.9(3)	O(5)—S(1)—O(6)	113.8(4)	O(11)—S(3)—O(12)	112.7(4)
O(1)—Fe(2)—O(2,2)	88.1(2)	O(1)—S(2)—O*(4)	108.5(3)	O(11)—S(3)—O(9,4)	108.4(3)
O(2)—Fe(2)—O(2,1)	92.6(2)	O(1)—S(2)—O(7,2)	109.3(3)	O(12)—S(3)—O(9,4)	110.6(3)
O(9)—Fe(3)—O(9,1)	91.6(2)				

Erratum: col. 2, line 2, for 90.5(2) read 90.9(2).

situated at the origin of the cell at mean z of $1/4, 3/4$. The process of dehydration involving the water loss of the three Fe-octahedra leads to a consequent resettlement of the Maus's salt clusters in structural units of ferrinatrinite with composition $[\text{Fe}_3^{3+}(\text{SO}_4)_6]$, see fig. 4. The latter, lying on threefold axes, are connected to each other by three additional SO_4 tetrahedra to build up infinite chains of tetrahedra and octahedra. The relationship between Maus's salt

and ferrinatrinite as regards the c parameters is outlined in fig. 6. From these, we can deduce the stacking sequence of octahedra and tetrahedra in Maus's salt and in ferrinatrinite along $[0001]$, as well as the relationships between the c parameters of two salts: c_M (Maus's salt) = 18.96 Å and c_F (ferrinatrinite) = 8.69 Å, the latter about half the former.

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