

## Statistical and true symmetry of ferrierite: possible absence of straight T–O–T bridging bonds

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### *Ferrierite / Zeolite / Straight T–O–T bonds*

**Abstract.** The crystal structure of ferrierite from Monastir, Sardinia,  $(\text{Na}_{0.56}\text{K}_{1.19}\text{Mg}_{2.02}\text{Ca}_{0.52}\text{Sr}_{0.14})(\text{Al}_{6.89}\text{Si}_{29.04})\text{O}_{72} \cdot 17.86 \text{H}_2\text{O}$  was refined to an  $R$  value of 4.6%. Systematic absences were consistent with the  $Immm$  space group but the orientation of the  $\text{Mg}(\text{H}_2\text{O})_6$  octahedron indicates that the true symmetry is consistent with the subgroup  $Pnmm$ . Consequently the set of  $\bar{1}$  at  $1/4, 1/4, 1/4$ , on which the oxygen atom O5 lies in the case of  $Immm$  symmetry, disappears and the T–O5–T angle is not constrained to  $180^\circ$ . The Si/Al distribution is partially ordered, with an enrichment of Al in the tetrahedra of the six-membered ring. The  $\text{Mg}(\text{H}_2\text{O})_6$  octahedron assumes a statistical orientation around one of its axes with two configurations more frequently occupied. Another extra-framework cation site is coordinated to four framework oxygens and to four water molecules.

### Introduction

The crystal structure of the zeolite ferrierite was solved by Vaughan (1966) on a natural sample from Kamloops Lake. Gramlich-Meier et al. (1984) reexamined the structure of ferrierite on a sample from Silver Mountains, California. Both these refinements were carried out in the space group  $Immm$ . Recently a monoclinic, Mg poor, ferrierite from Altoona, Washington, was refined by Gramlich-Meier et al. (1985) in the space group  $P2_1/n$ .

The aim of this work is to clarify some unresolved questions:

a) the presence of a T–O–T angle of  $180^\circ$ . The tendency to avoid straight T–O–T angles in silicates, as energetically unfavourable, was first pointed out by Liebau (1961). Vaughan (1966) suggested that the true symmetry of ferrierite could be *Immm* or *I222* or that a random distribution of oxygen atoms around  $\bar{1}$  could produce a pseudo-centre of symmetry, but was not able to prove that this angle is not of  $180^\circ$ ;

b) the strong underestimation of the Al content deduced from Jones' relationship (1968) compared with that found by the chemical analysis, which does not give a reliable distribution of Si and Al in the tetrahedra;

c) the distribution of cations and water molecules in extra-framework sites.

## Experimental

Ferrierite from Monastir, Sardinia, (Orlandi and Sabelli, 1983) was used in the present study. On the basis of its chemical composition (see Table 1) this ferrierite can be regarded as Mg-rich and Si-poor (Wise and Tschernich, 1976).

Cell parameters (Table 1) and intensities were collected on a prismatic crystal ( $1.0 \times 0.4 \times 0.008$  mm) using a Philips PW1100 diffractometer with  $\text{MoK}\alpha$  radiation.

Intensities were corrected for absorption by a combination of the semi-empirical method proposed by North et al. (1968) with the absorption correction for the spherical shape ( $\mu = 35 \text{ cm}^{-1}$ ,  $r = 0.002$  cm). 2143 reflections were collected in the *I2/m* space group; the statistical analysis of the intensities clearly indicates orthorhombic symmetry, space group *Immm*. The number of independent reflections after averaging the symmetrically equivalent ones was 1112; of these 661 with  $I > 3 \sigma(I)$  were used in the refinement. Intensities with  $h + k + l = 2n + 1$  were subsequently collected using a Nonius CAD 4 diffractometer ( $\text{MoK}\alpha$  radiation) up to a  $2\theta$  value of  $20^\circ$ . They were non-observed, thus confirming for ferrierite from Monastir the body-centered Bravais lattice.

**Table 1.** Crystallographic and chemical data for the Monastir ferrierite.

$a = 19.231(2) \text{ \AA}$	Space group <i>Pnmm</i>
$b = 14.145(2) \text{ \AA}$	$Z = 1$
$c = 7.499(1) \text{ \AA}$	Chemical composition:
$V = 2039.9 \text{ \AA}^3$	$(\text{Na}_{0.56}\text{K}_{1.19}\text{Mg}_{2.02}\text{Ca}_{0.52}\text{Sr}_{0.14}\text{Ba}_{0.02})(\text{Al}_{6.89}\text{Si}_{29.04})\text{O}_{72}$ $\cdot 17.86\text{H}_2\text{O}$

Number of electrons in extra-framework sites from — chemical analysis = 213  
— structure refinement = 240

Final  $R = 4.6\%$

Final  $R_w = 5.2\%$

### Structure refinement

The structure refinement was carried out in the space group *Immm*. Atomic scattering factors for neutral atoms were used in the refinement. Extinction and anomalous-scattering corrections were not applied. Starting coordinates, for the framework atoms, were from Vaughan (1966). The extra-framework sites were located from three-dimensional electron density syntheses. At the end of the anisotropic refinement the *R* and *R<sub>w</sub>* values were 4.6% and 5.2% respectively.

The number of electrons found in the extra-framework sites by X-ray structure refinement was 240, a high value when compared with the 213 electrons from the chemical analysis (see Table 1). A similar result was obtained by Gramlich-Meier et al. (1984) for ferrierite from Silver Mountains where structure refinement and chemical analysis give 244 e<sup>-</sup> and 213 e<sup>-</sup> respectively. An overestimation of the extra-framework ions was found by Alberti et al. (1986) also for the structure of Elba mordenite.

Positional and thermal parameters are reported in Table 2, interatomic distances and angles in Tables 3 and 4<sup>1</sup>.

### Discussion

The structure refinement of ferrierite in the centrosymmetric space group *Immm* constrains O5 on  $\bar{1}$  so that the T4–O5–T4 angle must be 180°. There is however evidence that the true symmetry of ferrierite is lower than *Immm*. In the true orthorhombic ferrierites so far refined, Mg is coordinated to six water molecules, in an almost regular octahedral configuration, at the center of a cage which can be called “ferrierite cage”. Mg lies on a site with symmetry *mmm*, two of the six water molecules are along the *z* axis in a site symmetry *mm* and the last four are in the *xy* plane. This Mg(H<sub>2</sub>O)<sub>6</sub> octahedron however has two possible configurations (see Fig. 1) which occur 50% of the times and differ by a rotation of about 45° around the *z* axis. The orientation of each of these two configurations disobeys the symmetry *mmm*, in particular the (100) and (010) mirror planes disappear so that the true symmetry lowers to the subgroup *Pnmm*. Therefore, the point symmetry of ferrierite remains *mmm* but the set of  $\bar{1}$  at 1/4, 1/4, 1/4, on which O5 is placed in the *Immm* space group, disappears. Consequently the straight T4–O5–T4 angle can be only apparent because of fractional statistical occupation of multiple sites of the symmetry element.

The thermal parameters of O5 support this hypothesis as:

- this atom has one of the highest *B<sub>eq</sub>* among oxygens (see Table 2);
- it is strongly anisotropic (its principal root-mean-square (r.m.s.) displacements are 0.16, 0.24, 0.26 Å), with the smallest r.m.s. displace-

<sup>1</sup> The list of structure factors may be obtained from the authors upon request.

**Table 2.** Atomic coordinates, occupancy factors (%), anisotropic thermal parameters ( $U_{ij}$ ) and equivalent isotropic temperature factors ( $B_{eq}$ ,  $\text{\AA}^2$ ) for ferrierite [ $B_{eq} = \frac{8}{3} \pi^2 (U_{11} + U_{22} + U_{33})$ ].

Atom	$x/a$	$y/b$	$z/c$	Occu- pancy	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$B_{eq}$
T1	0.1550(3)	0	0	100 <sup>a</sup>	0.024(3)	0.014(2)	0.013(2)	0	0	0	1.3
T2	0.0838(2)	0.2023(2)	0	100 <sup>a</sup>	0.020(2)	0.013(1)	0.009(1)	0	0	-0.002(2)	1.1
T3	0.2715(2)	0	0.2922(5)	100 <sup>a</sup>	0.030(2)	0.019(2)	0.013(2)	0	-0.001(2)	0	1.6
T4	0.3231(1)	0.2026(1)	0.2069(3)	100 <sup>a</sup>	0.023(1)	0.017(1)	0.005(1)	-0.001(1)	-0.001(1)	0.000(1)	1.2
O1	0	0.2158(9)	0	100	0.022(8)	0.037(8)	0.039(8)	0	0	0	2.6
O2	0.2495(8)	0	1/2	100	0.068(11)	0.034(8)	0.008(7)	0	0	0	2.9
O3	0.1029(5)	0.0892(6)	0	100	0.044(8)	0.030(5)	0.078(8)	0	0	0.010(5)	4.0
O4	0.2019(5)	0	0.1777(13)	100	0.045(7)	0.098(8)	0.037(7)	0	-0.021(6)	0	4.8
O5	1/4	1/4	1/4	100	0.046(7)	0.051(6)	0.055(7)	-0.004(6)	0.001(7)	0.021(5)	4.0
O6	0.1564(6)	0.2813(6)	1/2	100	0.063(8)	0.058(7)	0.000(4)	0	0	-0.015(6)	3.2
O7	0.1151(3)	0.2505(5)	0.1822(9)	100	0.042(5)	0.071(5)	0.025(4)	-0.028(4)	-0.011(4)	-0.009(4)	3.0
O8	0.3209(3)	0.0912(4)	0.2470(9)	100	0.062(5)	0.024(3)	0.051(4)	-0.013(3)	0.012(5)	-0.00(4)	3.5
Mg	0	0	1/2	100 <sup>b</sup>	0.035(7)	0.053(6)	0.019(5)	0	0	0	2.8
K	0.4254(8)	0	0	41(1) <sup>c</sup>	0.060(10)	0.057(9)	0.102(12)	0	0	0	5.8
W1	0	0	0.2351(17)	100 <sup>d</sup>	0.039(10)	0.071(9)	0.020(7)	0	0	0	3.4
W2	0.0982(12)	0.0668(20)	1/2	50 <sup>d</sup>	0.040(18)	0.131(27)	0.022(13)	0	0	-0.031(16)	5.1
W3	0.0458(18)	0.1329(21)	1/2	50 <sup>d</sup>	0.210(42)	0.137(31)	0.050(16)	0	0	-0.141(27)	10.5
W4	0	0.4212(36)	0.2071(77)	50 <sup>d</sup>	0.180(32)	0.320(67)	0.469(77)	-0.275(53)	0	0	25.5
W5	0	0.6468(28)	0.3670(55)	50 <sup>d</sup>	0.030(13)	0.309(39)	0.291(44)	0.201(29)	0	0	16.6
W6	0.538(20)	1/2	0.2564(74)	39(2) <sup>d</sup>	0.036(25)	0.067(23)	0.117(43)	0	-0.019(42)	0	5.8

<sup>a</sup> The occupancy refers to a scattering curve of Si 80% and Al 20%.

<sup>b</sup> The occupancy refers to the scattering curve of Mg.

<sup>c</sup> The occupancy refers to the scattering curve of K.

<sup>d</sup> The occupancy refers to the scattering curve of oxygen.

**Table 5.** Percent of Al in the tetrahedral sites calculated according to Alberti and Gottardi method (1986) and Jones' relationship (1968) for Monastir (this work), Kamloops Lake (Vaughan, 1966), Silver Mountain (Gramlich-Meier et al., 1984) and Altoona (Gramlich-Meier et al., 1985) ferrierites.

	Monastir		Kamloops Lake		Silver Mountains		Altoona*	
	A.G.	Jones	A.G.	Jones	A.G.	Jones	A.G.	Jones
T1	12	4	9	3	21	14	15	11
T2	31	21	23	15	26	17	4	1
T3	12	10	0	0	9	7	9	7
T4	4	0	0	0	1	0	5	3
Average	12.7	7.4	6.1	3.6	10.6	6.7	7.2	4.1
From chemical analysis	19.2		16.1		19.3		14.3	

\* The percent of Al for the tetrahedra not equivalent in space group  $P2_1/n$  but equivalent in space group  $Immm$  have been averaged.

of O5 (0.26 Å). It is therefore indistinguishable from ordinary thermal motion.

In all three refined orthorhombic ferrierites the Mg content in the unit cell is strictly 2.0 atoms, which is also the population of the Mg site. In monoclinic ferrierite from Altoona the Mg content is only 0.5 atoms per unit cell. As Na or K ions are too large for an octahedral and fully solvated coordination in the "ferrierite cage", the ion distribution in this cage changes and also the (001) mirror plane disappears. Therefore the  $Pnmm$  symmetry of orthorhombic ferrierite is reduced to the  $P12_1/n1$  subgroup, which is the symmetry of Altoona ferrierite. Therefore the  $Mg(H_2O)_6$  octahedron seems, for steric reasons, to be responsible for the  $mmm$  symmetry of the "ferrierite cage" and consequently for the orthorhombic symmetry of the normal ferrierites.

In Monastir ferrierite the chemical analysis gives an Al content of 19.2% (Table 1), whereas, according to Jones' relationship (1968), the Al content should be only 7.4%. High discrepancies have been found also for the other ferrierites as is shown in Table 5. Recently Alberti and Gottardi (1985) showed that in framework silicates the Al content is always underestimated when there is a disordered Si/Al distribution, and proposed a method to calculate this underestimation (Alberti and Gottardi, 1986).

In Table 5 the values of calculated numbers of Al are reported based on Jones' relationship and Alberti and Gottardi's method. The better agreement between the Al content given by the chemical analysis and that obtained with this last method is evident even if the discrepancies remain considerable.

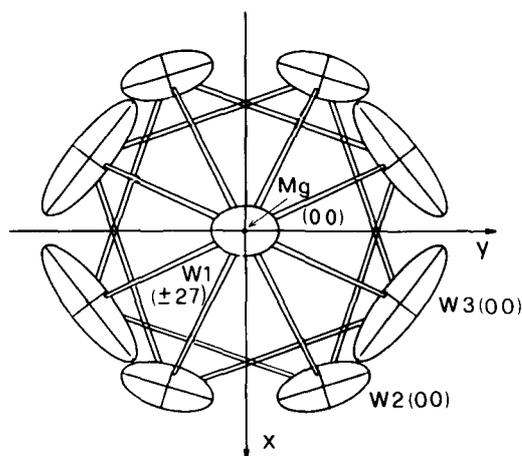


Fig. 1. Projection of the  $\text{Mg}(\text{H}_2\text{O})_6$  octahedron, in its two orientations, on the (001) plane. The thermal ellipsoids enclose 50% probability.

T2 and in minor amount T1, the tetrahedra of the six-membered ring of tetrahedra, are the richest in Al, at least for the orthorhombic ferrierites. This result is in agreement with the results of Fripiat et al. (1985) who showed the preference of Al for the tetrahedra of the six-membered ring through ab initio molecular orbital calculations. The discrepancies between the Al content given by chemical analysis and by X-ray refinements, however, leave some doubts on the accuracy of this Si/Al distribution.

As said before, Mg is octahedrally coordinated to six water molecules in two possible configurations. The thermal ellipsoids of the two water molecules in the  $xy$  plane are strongly anisotropic with the largest r.m.s. displacement in the  $xy$  plane and about orthogonal to the Mg...W vector (see Fig. 1). It seems that these water molecules do not really occupy two positions only but that they are delocalized on a circle in the  $xy$  plane, with the sites found in the refinement occupied more frequently than the others.

Among the other extra-framework sites, site K has been assumed to be a cation site because of its relatively low temperature factor and its coordination. This site is coordinated to four O8 framework oxygens on one side and to four water molecules on the other (occupancies and short distances do not allow coordination of more than four of the W4, W5 or W6 molecules). About 15 of the 70  $e^-$  of the extra-framework cations were not located. Site K was considered to be "most likely" occupied by Na or K also by Gramlich-Meier et al. (1984).

W4 and W5 sites have an unusually high temperature factor (see Table 2) but are strongly anisotropic (their r.m.s. displacements are 0.33, 0.42, 0.82 Å and 0.17, 0.31, 0.71 Å respectively) with the highest r.m.s.

displacement parallel to the axis  $x$ . Static disorder (according to the true space group  $Pnmm$ ) rather than effective thermal motion is probably responsible for this effect.

Finally it must be pointed out that strong similarities have been found in the structure refinement of Monastir ferrierite and Elba mordenite (Alberti et al., 1986). In both cases the true symmetry is a subgroup of the apparent symmetry, many extra-framework sites have very high temperature factors, not all the cation sites can be localized, and the number of electrons found in the structure refinement is considerably higher than that found by chemical analysis.

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