

The crystal structure of the monoclinic variety of ferrierite

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Abstract

An X-ray structure analysis has been carried out of the monoclinic variety of the zeolite ferrierite from Altoona, Washington. Crystals of this uncommon variety of ferrierite are typically diamond shaped with (100), (201) and dominant (010) faces. The crystal data are $a = 18.886(9)$, $b = 14.182(6)$, $c = 7.470(5)\text{\AA}$, $\beta = 90.0(1)^\circ$, space group $P2_1/n$, and an approximate unit cell content of $\text{Na}_3\text{KMg}_{0.5}\text{Mg}_{0.5}\text{Al}_5\text{Si}_{31}\text{O}_{72} \cdot 18\text{H}_2\text{O}$. The crystal structure was determined by direct phasing of the systematically weak b -reflections ($h + k + l = 2n + 1$) which are absent in the orthorhombic structure of ordinary ferrierite (space group $Immm$). Anisotropic refinement converged to $R = 0.079$ (1164 observed reflections). The monoclinic structure differs from that of the more abundant orthorhombic ferrierite by some changes in the conformation of the framework. This difference may be related to the Mg content.

Introduction

Ferrierite is a silica-rich zeolite mineral occurring mainly in the western United States and Canada. Localities in Japan and Europe have also been reported (Wise and Tschernich, 1976, and references cited therein; Orlandi and Sabelli, 1983). A great number of ferrierites were analyzed chemically by Wise and Tschernich who reported framework compositions ranging from $\text{Al}_5\text{Si}_{31}\text{O}_{72}$ to $\text{Al}_{8.5}\text{Si}_{27.5}\text{O}_{72}$ and wide compositional variations of the exchangeable cations. A correlation between the a lattice constant and the Si content was also observed by these authors for all ferrierites except for the specimen with "diamond shaped" crystals from Altoona.

In the present paper we report on an X-ray structure analysis of these unusual crystals of monoclinic ferrierite. The crystal structure of ordinary ferrierite, with apparent $Immm$ symmetry, was determined by Vaughan (1966) and more recently confirmed by R.G.-M. (Gramlich-Meier et al., 1985; Smith et al., in preparation). Lower symmetry has been discussed by Vaughan as a possibility, mainly because of a T–O–T angle (T = Si, Al) of 180° which is due to the site symmetry $\bar{1}$ of one of the bridging oxygen atoms, O5, in case of $Immm$ symmetry.

Experimental

Diamond shaped ferrierite crystals from Altoona, Washington were kindly supplied to us by Dr. R. W. Tschernich. Several of these crystals were examined by X-rays all indicating monoclinic symmetry. The single crystal used in the X-ray structure analysis had the diamond shape typical of the Altoona material with dominant (010) and terminating (100) and (201) faces. The crystal measured about $0.04 \times 0.015 \times 0.2 \text{ mm}^3$ in the a , b and c directions respectively. The unit cell content was taken to be $\text{Na}_3\text{KMg}_{0.5}\text{Al}_5\text{Si}_{31}\text{O}_{72} \cdot 18\text{H}_2\text{O}$ based on the composition of the anhydrous zeolite reported by Wise and Tschernich (1976) and the amount of sorbed water determined by Staples (1955).

The unit cell constants were refined on a Syntex $P2_1$ diffractometer using monochromatic $\text{MoK}\alpha$ radiation ($\lambda = 0.70926\text{\AA}$) and the setting angles of 25 reflections centered automatically. The values thus obtained were:

$$a = 18.886(9), b = 14.182(6), c = 7.470(4)\text{\AA}, \\ \beta = 90.0(1)^\circ, D(\text{calc}) = 2.16 \text{ g cm}^{-3}.$$

Precession photographs revealed monoclinic Laue symmetry and systematic absences of $0k0$ with $k = 2n + 1$ and $h0l$ with $h + l = 2n + 1$. This allowed a unique assignment of space group $P2_1/n$.

The coordinate system adopted for the monoclinic structure described in this work was that of orthorhombic ferrierite ($Immm$) in order to facilitate comparisons of parameters. Therefore, the non-standard setting of $P2_1/n$ with equivalent positions in

$$x, y, z; -x, -y, -z; 1/2 + x, 1/2 - y, 1/2 + z; \\ 1/2 - x, 1/2 + y, 1/2 - z$$

was used in the present investigation instead of the conventional $P2_1/c$.

Diffraction intensities were measured using a graphite monochromator and $\text{MoK}\alpha$ radiation. With a $\theta/2\theta$ scan reflections up to $\theta = 20^\circ$ were measured. A total of 994 a -reflections ($h + k + l = 2n$) was thus collected, 212 of which were less than $3\sigma(I)$ and 998 b -reflections ($h + k + l = 2n + 1$) with 616 less than $3\sigma(I)$. Lorentz and polarization corrections were applied. The oblong shape of the crystal, with expected path lengths differing by more than an order of magnitude, required an absorption correction. A linear absorption coefficient $\mu(\text{MoK}\alpha) = 9.81 \text{ cm}^{-1}$ was applied for the Gaussian integration method using the computer program ORABS (XRAY-72, Stewart et al., 1972; modified by D. Schwarzenbach, Lausanne).

Solution and refinement of the structure

The subgroup relationship between $Immm$ and $P2_1/n$ (unique axis b) does not pose the problem of different non-

Table 1. Atomic coordinates and thermal parameters (\AA^2) with estimated standard deviations in parentheses

ATOM	PP	X	Y	Z	U11 **	U22	U33	U12	U13	U23
T(11)	*	0.1548(2)	0.0058(4)	0.0004(5)	0.013(3)	0.015(3)	0.016(2)	-0.005(4)	0.001(2)	-0.001(4)
T(21)		0.0820(3)	0.2055(4)	0.0026(8)	0.007(3)	0.014(3)	0.016(4)	0.001(3)	0.000(3)	0.004(3)
T(22)		0.4143(3)	0.3056(4)	0.5054(8)	0.015(4)	0.018(3)	0.014(4)	-0.003(3)	0.003(3)	-0.000(3)
T(31)		0.2738(2)	0.0058(4)	0.2935(5)	0.021(3)	0.014(3)	0.018(3)	0.006(4)	-0.002(2)	0.004(4)
T(32)		0.2747(2)	0.0057(5)	0.7089(5)	0.021(3)	0.015(3)	0.016(3)	-0.002(4)	0.005(2)	-0.005(4)
T(41)		0.3245(2)	0.2083(3)	0.2150(7)	0.017(3)	0.012(3)	0.024(3)	-0.003(3)	-0.007(3)	-0.002(3)
T(42)		0.1756(2)	0.3031(3)	0.2983(6)	0.021(3)	0.015(3)	0.015(3)	-0.004(3)	0.006(3)	0.000(2)
T(43)		0.3176(3)	0.2124(4)	0.7996(8)	0.016(4)	0.017(3)	0.019(4)	0.001(3)	0.006(3)	0.001(3)
T(44)		0.1678(3)	0.3058(3)	0.7119(8)	0.014(3)	0.007(3)	0.021(4)	-0.001(3)	0.000(3)	0.002(3)
O(11)		-0.0017(8)	0.2088(7)	0.034(2)	0.013(6)	0.049(8)	0.05(1)	-0.003(8)	0.002(7)	0.005(8)
O(21)		0.2518(5)	0.005(1)	0.501(1)	0.037(7)	0.049(7)	0.019(6)	-0.01(1)	0.005(5)	-0.00(1)
O(31)		0.1069(6)	0.0975(9)	-0.015(2)	0.04(1)	0.025(8)	0.05(1)	0.016(8)	-0.002(9)	0.007(8)
O(32)		0.3993(7)	0.4158(8)	0.487(2)	0.04(1)	0.012(8)	0.08(1)	0.008(7)	0.017(9)	0.007(8)
O(41)		0.2029(5)	0.008(1)	0.181(1)	0.042(8)	0.067(9)	0.033(7)	0.03(1)	-0.012(6)	0.00(1)
O(42)		0.2041(5)	-0.002(1)	-0.176(1)	0.038(7)	0.064(8)	0.034(7)	-0.01(1)	0.015(6)	-0.00(1)
O(51)		0.2506(8)	0.255(1)	0.279(2)	0.042(8)	0.034(7)	0.05(1)	0.013(6)	0.015(7)	0.007(7)
O(52)		0.2396(7)	0.254(1)	-0.236(2)	0.023(8)	0.039(7)	0.064(9)	0.010(7)	-0.012(7)	-0.002(6)
O(61)		0.3403(7)	0.2306(8)	0.009(2)	0.038(9)	0.035(8)	0.03(1)	-0.019(8)	0.002(8)	-0.003(8)
O(62)		0.1482(7)	0.2899(8)	0.504(2)	0.055(9)	0.032(8)	0.013(9)	-0.004(7)	0.003(8)	-0.006(7)
O(71)		0.1175(6)	0.2535(9)	0.176(2)	0.05(1)	0.055(9)	0.029(8)	-0.013(8)	-0.006(8)	0.001(7)
O(72)		0.3898(6)	0.2520(8)	0.326(2)	0.054(9)	0.033(8)	0.030(8)	-0.008(7)	-0.009(7)	-0.012(7)
O(73)		0.3774(7)	0.2634(9)	-0.318(2)	0.05(1)	0.043(9)	0.033(9)	0.003(9)	0.010(8)	0.009(8)
O(74)		0.1023(7)	0.2619(8)	-0.177(2)	0.049(9)	0.023(8)	0.034(9)	-0.011(7)	0.005(8)	0.010(7)
O(81)		0.3237(7)	0.0969(9)	0.245(2)	0.06(1)	0.018(8)	0.05(1)	-0.008(8)	0.011(9)	0.005(8)
O(82)		0.1790(6)	0.4132(8)	0.248(2)	0.03(1)	0.016(8)	0.05(1)	0.006(7)	0.012(9)	0.005(8)
O(83)		0.3183(6)	0.0997(9)	-0.238(2)	0.03(1)	0.024(8)	0.05(1)	0.003(7)	-0.001(8)	0.020(8)
O(84)		0.1707(6)	0.4161(8)	-0.245(2)	0.040(9)	0.009(8)	0.05(1)	-0.012(7)	-0.007(8)	0.003(7)
I	1.35	0.4990(6)	0.2731(7)	-0.012(2)	0.012(5)	0.18(1)	0.045(7)	0.01(1)	-0.000(4)	0.02(1)
II	0.50	0.402(1)	0.441(2)	0.002(4)	0.02(2)	0.08(2)	0.07(2)	-0.01(2)	0.01(2)	-0.00(2)
II'	0.50	0.096(2)	0.071(2)	0.505(4)	0.11(3)	0.10(2)	0.05(2)	-0.05(2)	-0.00(2)	0.00(2)
III	0.50	0.5	0.5	0	0.03(3)	0.5(1)	0.19(6)	-0.13(7)	-0.01(4)	0.0(1)
IV	0.50	-0.000(1)	-0.007(2)	-0.267(4)	0.03(2)	0.25(4)	0.09(2)	-0.01(3)	0.00(2)	0.10(4)
V	0.50	0.487(3)	0.113(7)	0.04(2)	0.03(3)	0.8(1)	0.6(2)	0.09(6)	-0.12(6)	-0.2(2)
VI	0.50	0.451(2)	0.049(5)	-0.031(8)	0.15(5)	0.4(1)	0.35(7)	0.22(6)	-0.13(5)	-0.20(7)
VII	0.25	0.490(3)	0.072(4)	-0.22(1)	0.08(4)	0.05(4)	0.19(7)	0.01(3)	-0.00(4)	0.06(5)
VIII	0.25	0.500(3)	0.048(6)	0.25(1)	0.17(5)	0.3(1)	0.23(9)	-0.02(5)	0.00(5)	-0.24(8)
IX	0.25	0.500(4)	0.053(4)	0.40(1)	0.14(5)	0.09(5)	0.3(1)	-0.04(4)	0.13(8)	-0.13(5)

* Population parameters are given for the non-framework atoms I-IX only and are referred to neutral oxygen. Estimated standard deviations are 0.05.

** Form of the anisotropic temperature factor:
 $\text{EXP}[-2(\text{PI}^{**2})\{(\text{U11}^{**}(\text{H}^{**2}))(\text{astar}^{**2}) + \dots + 2\text{U23}^{**}\text{K}^{**}\text{L}^{**}\text{BSTAR}^{**}\text{CSTAR}^{**}\text{COSASTAR}^{**}\}]$

equivalent settings (cf. Ito, 1973; Billiet, 1981). The glide planes at $y = 1/4$ and $3/4$ and the screw axes at $x = 1/4$ and $3/4$, $z = 1/4$ and $3/4$ conserved during the symmetry reduction require a center of symmetry at the origin. However, the center $\bar{1}$ at $1/4, 1/4, 1/4$, at the position of oxygen O5 of the *Immm* ferrierite, is not retained in the monoclinic space group. The T-O-T bond angle at O5 is thus no longer confined to 180° in the monoclinic structure. The use of Sigma-2 phase relationships for the phasing of systematically weak reflections like the *b*-reflections in this example was first proposed by Hauptman and Karle (1953,

1959). Studies of the Sayre equation (cf. Giacobozzo, 1980) indicate that this method can be expected to work if the phases of the *a*-reflections are known. Because of the strong similarity of the pattern of the *a*-reflections and that of orthorhombic ferrierite a refinement in *Immm* using the *a*-reflections was first performed. Anisotropic thermal parameters were introduced in the final cycles. This *a*-refinement converged at a conventional *R*-value of 0.11 and provided a framework model which compared well with Vaughan's results.

The phases of the *a*-reflections of this model were kept

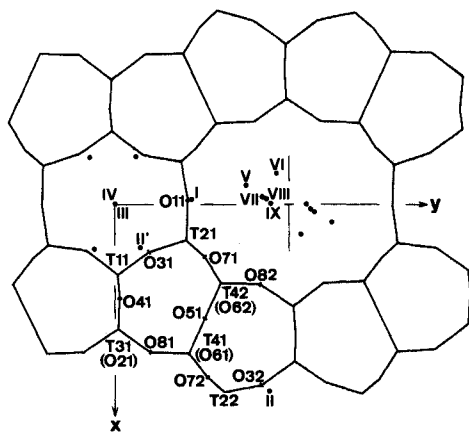


Fig. 1. Atom labelling in the asymmetric unit of monoclinic ferrierite. Non-framework atoms are denoted by Roman numerals. Positions V-IX refer to the less well defined sites in the large channels of the zeolite.

fixed for the phasing of the *b*-reflections. A slightly modified version of MULTAN-78 (Main et al., 1978) was used. The ABSFOM and RESID criteria of the program system clearly indicated a unique result. A partial Fourier map based on

Table 2. Selected interatomic distances (Å)

T(11)-O(31) 1.59(1) ⁺	T(21)-O(11) 1.60(1)	T(22)-O(11) 1.61(1)
-O(32) 1.64(1)	-O(31) 1.61(1)	-O(32) 1.59(1)
-O(41) 1.63(1)	-O(71) 1.61(2)	-O(72) 1.61(1)
-O(42) 1.62(1)	-O(74) 1.61(1)	-O(73) 1.60(1)
Average 1.62	Average 1.61	Average 1.60
T(31)-O(21) 1.61(1)	T(32)-O(21) 1.61(1)	T(41)-O(51) 1.62(2)
-O(41) 1.58(1)	-O(42) 1.59(1)	-O(61) 1.60(1)
-O(81) 1.64(1)	-O(83) 1.61(1)	-O(72) 1.61(1)
-O(82) 1.62(1)	-O(84) 1.66(1)	-O(81) 1.60(1)
Average 1.61	Average 1.62	Average 1.61
T(42)-O(51) 1.58(2)	T(43)-O(52) 1.61(1)	T(44)-O(52) 1.59(2)
-O(62) 1.63(1)	-O(61) 1.64(1)	-O(62) 1.61(2)
-O(71) 1.59(2)	-O(73) 1.60(1)	-O(74) 1.61(1)
-O(82) 1.61(1)	-O(83) 1.62(1)	-O(84) 1.60(2)
Average 1.60	Average 1.62	Average 1.60
I -O(61) 3.06(2)	II -O(21) 3.05(3)	II' -O(21) 3.09(4)
-O(62) 2.96(2)	-II' 1.84(5)	-III 2.06(4)
-II 3.00(3)	-III 2.03(3)	-IV 2.69(6)
-II' 2.87(4)	-IV 2.70(5)	-IV* 2.72(6)
-V 2.3(2)	-IV* 2.65(5)	III -IV 1.75(5)
IV -O(32) 2.98(5)	V -VI 1.3(2)	VI -O(83) 3.02(8)
-O(32)* 3.03(5)	-VI* 2.6(2)	-VI* 2.4(1)
	-VII 1.9(2)	-VII 1.6(1)
	-VII* 3.0(2)	-VII* 2.8(1)
VII -VIIII 1.7(2)	-VIII 1.9(3)	-VIII 2.3(2)
-IX 2.2(2)	-VIII 2.8(2)	-VIII* 2.3(2)
-IX* 2.9(2)		
	VIII -IX 1.1(2)	
	-IX* 3.0(2)	

⁺ Estimated standard deviations are given in parentheses and refer to the last decimal place.

* Symmetry related atoms.

Table 3. Selected bond angles (in degrees)

O-T-O angles		
Central atom T(11)	Central atom T(21)	Central atom T(22)
O(31)-O(32) 106.7*	O(11)-O(31) 109.2	O(11)-O(32) 108.0
O(31)-O(41) 111.0	O(11)-O(71) 106.3	O(11)-O(72) 109.5
O(31)-O(42) 109.2	O(11)-O(74) 110.1	O(11)-O(73) 105.7
O(32)-O(41) 108.6	O(31)-O(71) 110.2	O(32)-O(72) 110.0
O(32)-O(42) 110.5	O(31)-O(74) 109.7	O(32)-O(73) 111.0
O(41)-O(42) 110.8	O(71)-O(74) 111.3	O(72)-O(73) 112.4
Central atom T(31)	Central atom T(32)	Central atom T(41)
O(21)-O(41) 105.6	O(21)-O(42) 107.2	O(51)-O(61) 111.5
O(21)-O(81) 111.5	O(21)-O(83) 112.2	O(51)-O(72) 110.4
O(21)-O(82) 109.0	O(21)-O(84) 108.7	O(51)-O(81) 110.8
O(41)-O(81) 110.5	O(42)-O(83) 110.7	O(61)-O(72) 106.2
O(41)-O(82) 112.5	O(42)-O(84) 112.2	O(61)-O(81) 109.4
O(81)-O(82) 106.3	O(83)-O(84) 106.0	O(72)-O(81) 108.5
Central atom T(42)	Central atom T(43)	Central atom T(44)
O(51)-O(62) 108.5	O(52)-O(61) 109.8	O(52)-O(62) 111.4
O(51)-O(71) 112.1	O(52)-O(73) 112.9	O(52)-O(74) 110.4
O(51)-O(82) 111.4	O(52)-O(83) 109.8	O(52)-O(84) 112.0
O(62)-O(71) 105.7	O(61)-O(73) 105.6	O(62)-O(74) 105.4
O(62)-O(82) 110.1	O(61)-O(83) 108.5	O(62)-O(84) 109.8
O(71)-O(82) 108.9	O(73)-O(83) 110.0	O(74)-O(84) 107.6
T-O-T angles		
T(21)-O(11)-T(22) 161.3*	T(42)-O(62)-T(44) 145.0	
T(31)-O(21)-T(32) 149.4	T(21)-O(71)-T(42) 159.2	
T(11)-O(31)-T(21) 160.3	T(22)-O(72)-T(41) 146.4	
T(11)-O(32)-T(22) 150.5	T(22)-O(73)-T(43) 157.5	
T(11)-O(41)-T(31) 156.0	T(21)-O(74)-T(44) 143.4	
T(11)-O(42)-T(32) 156.6	T(31)-O(81)-T(41) 144.8	
T(41)-O(51)-T(42) 167.8	T(31)-O(82)-T(42) 148.8	
T(43)-O(52)-T(44) 171.9	T(32)-O(83)-T(43) 148.3	
T(41)-O(61)-T(43) 146.9	T(32)-O(84)-T(44) 143.5	

* Estimated standard deviations of 0.8 and 1.0 degrees for the O-T-O and T-O-T angles respectively.

the phased *b*-reflections only was then computed. The resulting *b*-map was used to determine the small shift vectors and a starting model of reduced symmetry was thus obtained.

Atomic scattering factors for neutral Si- and O-atoms (*International Tables for X-ray Crystallography*, 1962) were applied throughout the refinement and all non-framework atoms were assigned scattering factors of oxygen. The subsequent refinement using the XRAY-72 program system (Stewart et al., 1972) included both *a*- and *b*-reflections. Difference Fourier maps served to locate non-framework atoms which were labelled with Roman numerals. Non-framework positions with population parameters below 0.25 were discarded in the refinement. Least squares weights $w = 1/\sigma(I)$ were used in the final cycles.¹

The final parameters are listed in Table 1 and atom positions are shown in projection along [001] in Figure 1. Interatomic distances and bond angles are presented in Tables 2 and 3. Final *R*-values for all observed reflections

¹ To receive a copy of the observed and calculated structure factors, order Document AM-85-268 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D. C. 20009. Please remit \$5.00 in advance for the microfiche.

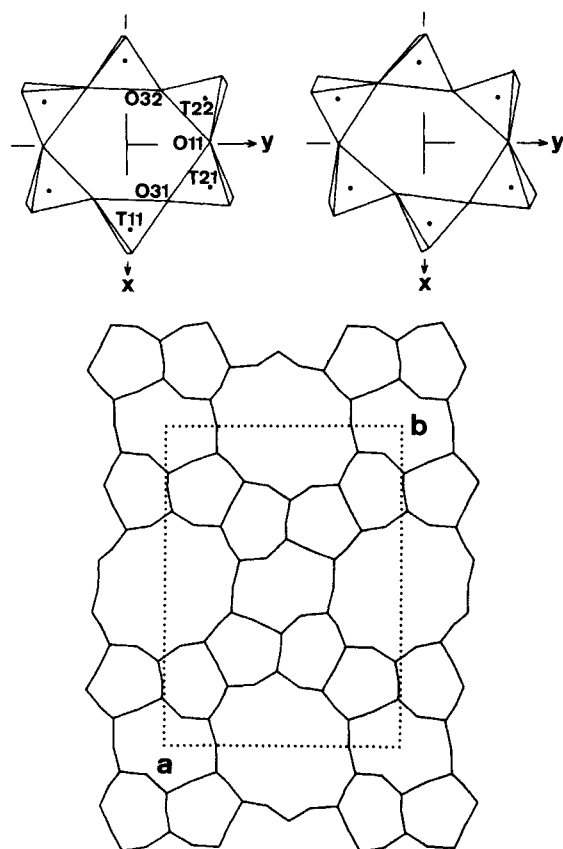


Fig. 2. Distortion of the framework in monoclinic ferrierite. (a) Six-membered rings at the origin after X-ray refinement (left) and DLS (right). (b) Schematic diagram of the DLS model structure showing enhanced deviations from orthorhombic symmetry.

were $R = 0.079$ and $wR = 0.060$. The values calculated separately for the a -reflections were $R = 0.061$ ($wR = 0.053$) and for the b -reflections $R = 0.156$ ($wR = 0.128$).

Discussion

The framework structure of monoclinic ferrierite deviates slightly and yet significantly from orthorhombic symmetry as can be seen in Figure 1. In contrast to the structure of the more abundant orthorhombic ferrierite monoclinic ferrierite from Altoona shows no T-O-T angles of 180° (at O51 and O52), nor planar six-rings in 0, 0, 0 etc. These features are an indication that the monoclinic framework conformation is energetically favorable (Meier and Ha, 1980; Gibbs, 1982).

The observed distortions of the framework structure were simulated by distance least squares (DLS) computations (Meier and Villiger, 1969; Baerlocher et al., 1977) which lend further support to the energy-related conjecture. DLS refinements were carried out in $P2_1/n$ starting with the positions of the $Immm$ model in which some atoms had been displaced arbitrarily to reduce the symmetry. The

prescribed cell constants were those determined by X-rays but no other constraints were applied. The resultant DLS model with the lowest mean residual was found to agree remarkably well with the results of the structure refinement. This is illustrated in Figure 2a which shows the conformation of the six-ring as determined by X-rays compared to that of the DLS framework model. Corresponding tetrahedra are all tilted in the same way. The DLS model structure, which is shown in projection along [001] in Figure 2b, illustrates the monoclinic distortion of the framework in a suitably enhanced manner.

The 5 Al atoms per unit cell do not appear to be concentrated in any one of the 9 T-sites of the Si-rich framework. In general, the T-O distances (Table 2) are shorter than expected (by about 0.02\AA on the average) as was already noted by Vaughan (1966). Their T-O-T angle dependence compares well with the relation given by Gibbs (1982) for pure Si-O bonds.

Wise and Tschernich (1976) found that the a cell constant is strongly correlated with the Si content of ferrierites. As was also noted by these authors the linear relationship between a and the Si content is not obeyed by the diamond shaped ferrierite from Altoona, the monoclinic variety dealt with in this paper. In their work Wise and Tschernich also mentioned that ferrierites with lower Si contents contain more divalent cations. This led us to compare the a cell constant with the Mg content. Figure 3 shows that these latter parameters are clearly correlated and that this correlation also holds for monoclinic ferrierite (Al).

In typical orthorhombic ferrierite, octahedral $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ ions are wedged in between six-rings of the framework. These hydrated Mg ions strongly interact with the framework as is indicated by short distances of $2.00(1)\text{\AA}$ between Mg- and O-atoms of the six-rings (Gramlich-

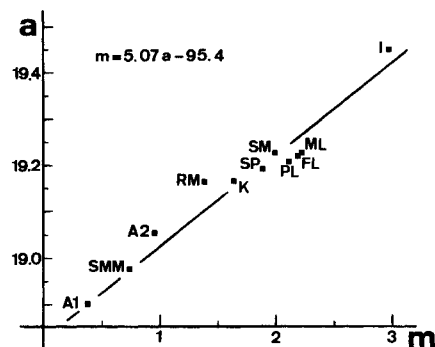


Fig. 3. Plot of lattice constants a (in Å) vs. number m of Mg ions per unit cell in ferrierites. Locality symbols: A1 and A2 Altoona, Washington; SMM Santa Monica Mountains; RM Rodope Mountains, Bulgaria; K Kamloops Lake B.C.; SP Sonora Pass, California; SM Silver Mountain, California; PL Pinaus Lake, B. C.; FL Francois Lake, B.C.; ML Monte Lake, B.C.; I Albergo Bassi, Vicenza, Italy (all data from Wise and Tschernich (1976) and references cited therein). Linear regression yielded $R = 0.97$.

Meier et al., 1985; Smith et al., in prep.). It is noteworthy, that monoclinic ferrierite contains only minor amounts of Mg. It appears, therefore, that the postulated low energy conformation of the monoclinic ferrierite framework structure is attained only at low Mg levels when cation-framework interaction is minor enough.

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