# The crystal structure of manganoan kilchoanite, $Ca_{2.33}Mn_{0.67}Si_2O_7$: a site-preference rule for the substitution of Mn for Ca

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## Abstract

The crystal structure of a Mn-bearing kilchoanite, $Ca_{2.33}Mn_{0.67}Si_2O_7$, orthorhombic, $I2cm$, $a = 11.356(2)$, $b = 5.007(1)$, $c = 21.817(1)$Å, $Z = 8$, was refined using single-crystal X-ray data to an $R$ value of 3.1% for 1725 unique reflections. It is isostructural with kilchoanite, $Ca_3Si_2O_7$, and shows a partial disorder of Mn and Ca over the four octahedral sites. On a basis of occupancy refinement, the $M3$ site ($\langle M3-O \rangle = 2.307$ Å) contains 0.508Ca and 0.492Mn, and the $M4$ site ($\langle M4-O \rangle = 2.346$ Å) contains 0.822Ca and 0.178Mn, whereas the $M1$ and $M2$ sites ($\langle M1-O \rangle = 2.538$ Å, $\langle M2-O \rangle = 2.380$ Å) are occupied only by Ca. Substitution of Mn cations for Ca can be interpreted as taking place on the following sites in preferential order: (1) the smaller Ca site; (2) the less distorted Ca site; (3) the Ca site showing a loss in neutrality of formal electrostatic valence. A statistical survey of Si–O–Si angles observed in silicates containing [$Si_2O_7$] groups confirms that these angles become smaller with an increase in the coordination number of the bridging oxygen. Oversaturation of electrostatic bond-strength to the bridging oxygen in some groups of the crystal structures with two tetrahedra sharing a vertex (pyro-anion, $T_2O_7^{6-}$), which is caused by increase in the coordination number of the bridging oxygen and/or by $T$ cations with larger charge than 4+, results in longer $T-O_{br}$ bonds length and in smaller $T-O_{br}-T$ angles.

KEYWORDS: kilchoanite, manganese, crystal structure, site preference.

## Introduction

KNOWLEDGE of the crystal structures of disilicates is important to our understanding of the systematic generation of silicate minerals, because melilite $Ca_2(Al_{2x},Mg_{1-x})_2Si_{2-x}O_7$ ($0 \le x \le 1$) is possibly the first silicate mineral to have condensed and crystallized from a nebula of solar composition (Grossman, 1972). It is also of crystallo-chemical interest that large-cation silicates have the common structural unit of the [$Si_2O_7$]$^{-6}$ group (Liebau, 1985). The configuration of this unit is governed by the nature of the additional cation. Present information indicates that kilchoanite and rankinite are dimorphous (Agrell and Gay, 1961). Natural kilchoanite is almost pure $Ca_3Si_2O_7$ (Agrell, 1965; Henmi et al., 1975). Furthermore, from phase equilibrium data for the ternary system $CaO-MnO-SiO_2$, Glasser (1961) suggested that the $Ca_3Si_2O_7$ structure does not permit substitution of appreciable amounts of $Mn^{2+}$. Kimata (1986) synthesized Mn-bearing kilchoanite with the composition $Ca_{2.33}Mn_{0.67}$

$Si_{2.00}O_7$, accompanied by a small amount of manganoan åkermanite having the same composition. The structure of kilchoanite $Ca_3Si_2O_7$ has not been studied since the original structure determination by Taylor (1971). The structure of rankinite was first determined by Kusachi et al. (1975) and further refined by Saburi et al. (1976). The behaviour of the larger cation in disilicates is summarized by Liebau (1985), and is very useful in the discussion of the manganoan kilchoanite structure.

The present work was undertaken to determine the details of the substitution of $Mn^{2+}$ into kilchoanite, $Ca_3Si_2O_7$.

## Experimental

Characterization of the sample used for structure analysis has been already done by Kimata (1986). The chemical composition determined by EPMA confirmed the structure formula $Ca_{2.33}Mn_{0.67}Si_{2.00}O_7$, which is the same as that of melilite. The crystal appears homogeneous, as no

compositional zoning was detected. A spherically ground crystal 0.1 mm in diameter was prepared from one of the synthesized grains. Precession photographs showed systematic absences of the type $h + k + l = 2n + 1$ for general reflections. The solution of the structure was initiated using MULTAN 80 (Main, 1980) and referring to the structure of kilchoanite (Taylor, 1971) as a guide. Intensity statistics produced by MULTAN indicated the structure is non-centrosymmetric, fixing the space group as $I2cm$, which is also compatible with that used for the refinement of kilchoanite by Taylor (1971).

Data were collected on a RIGAKU AFC-5 four-circle automated diffractometer and on the rotating-anode X-ray generator (operating conditions: 160 mA, 50 kV), using the graphite-monochromatized Mo-$K\alpha$ X-radiation ($\lambda$ = 0.71069 Å). Unit-cell parameters were determined by least-squares refinement of 25 high-angle reflections with $2\theta = 25\text{--}45°$. Three standard reflections were monitored after every 50 reflections to check for crystal movement and electronic stability; everything was stable during data collection. An $\omega\text{--}2\theta$ scan was made with a constant scan rate of $2° 2\theta$ per minute. A total of 2566 reflections was measured over 1 asymmetric unit out to a maximum $2\theta$ of $90°$. A reflection was classed as observed if its intensity exceeded 3.0 standard deviations ($I > 3.0\sigma I$) based on counting statistics. Standard data reduction resulted in 1725 reflections which were considered as observed. A spherical absorption correction was made with the ACACA program (Wuensch and Prewitt, 1965). All relevant crystal data are represented in Table 1.

### Refinement

Full-matrix, least-squares refinement was done using the program RFINE2 (Finger and Prince, 1975). Scattering curves for neutral atoms were taken from Doyle and Turner (1968), and corrections for anomalous dispersion were taken from the International Tables for X-ray (Crystallography, Vol. IV (1974, p. 99, 149). Refinement was initiated using atomic coordinates and isotropic temperature factors from Taylor (1971); Mn was initially distributed equally over the $M2$, $M3$ and $M4$ sites. The final refinement, including all coordinates, anisotropic temperature factors and unconstrained site populations converged to $R$ = 0.031 ($R_w$ = 0.035). Final parameters are listed in Tables 2 and 3. Bond lengths are given in Table 4 and selected polyhedral edge lengths and angles are given in Table 5. A table of observed and

Table 1. Crystallographic data for manganoan kilchoanite.

| formula | $Ca_{2.33}Mn_{0.67}Si_{2.00}O_7$ |
|---|---|
| molar. wt. | 298.36 |
| symmetry | orthorhombic |
| S. G. | I2cm |
| a (Å) | 11.356(2) |
| b (Å) | 5.007(1) |
| c (Å) | 21.817(1) |
| Volume (Å³) | 1240.5(3) |
| z | 8 |
| Crystal size | 0.10 mm sphere |
| $D_{calc}$ (g.m⁻³) | 3.195 |
| F(000) | 1178.8 |
| $\mu$(MoK$\alpha$) | 36.86 |
| No. of non equivalent reflections | 1725 |
| R | 3.1 |
| wR | 3.2 |

calculated structure factors is available from the author on request.

### Discussion

Figure 1 emphasizes an alternative description of the structure of manganoan kilchoanite as consisting of isolated $SiO_4$ tetrahedra and $Si_3O_{10}$ clusters. As suggested by Liebau (1985), kilchoanite is a rare mixed-anion silicate with single and triple tetrahedral clusters: $Ca_6[SiO_4][Si_3O_{10}]$. The refined occupanies (Table 6) agree well with the EPMA values.

There is extensive substitution of Mn for Ca in many silicates, carbonates and phosphates (Peacor, 1972). In manganoan kilchoanite, taking account of all the anions within 2.7 Å, the coordination numbers are eight for $M1$ and six for the $M2$, $M3$ and $M4$ sites, the former two of which are occupied only by calcium. Among these, the largest is $M1$, which is coordinated by the bridging oxygens of two $Si_2O_7$ groups; this is the only doubly chelated polyhedron in the structure. The present structural analysis showed partial disorder of Ca and Mn at the $M3$ and $M4$ sites. The expanded crystal-chemical formula of the sample can be rewritten as $Ca_{0.5}Ca_{0.5}(Ca_{0.508}Mn_{0.492})$ $(Ca_{0.822}Mn_{0.178})Si_2O_7$; it consists of the following end-members: $Ca_{2.33}Mn_{0.67}Si_{2.00}O_7$ = $0.33Ca_3Si_2O_7 + 0.67Ca_2MnSi_2O_7$. The $M3$ and $M4$ sites are on or near the (001) plane (Fig. 1), and furthermore, the undersaturation of total bond strength at the $M3$ site (Table 7) represents the relative instability of the $M3$–$O$ bond. The
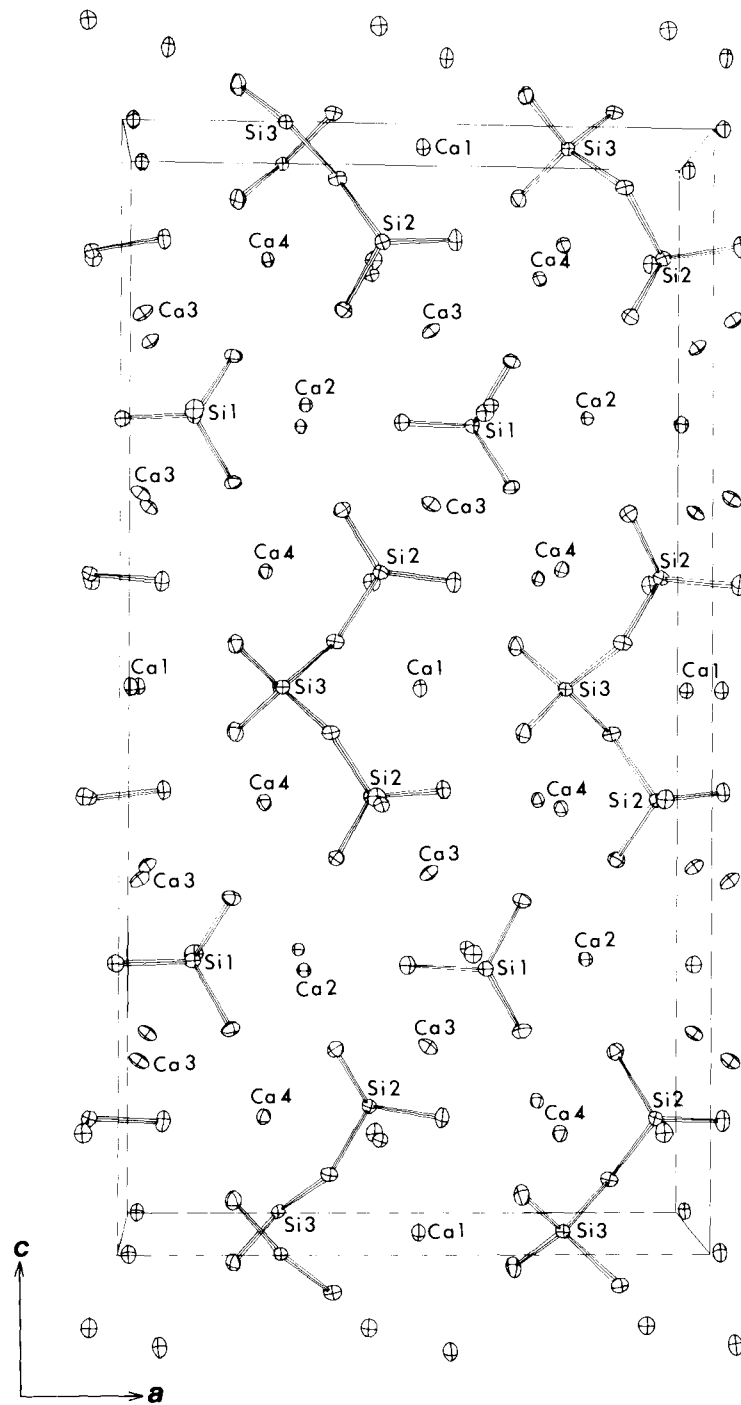
FIG. 1. A projection onto (010) of the manganoan kilchoanite structure showing probability ellipsoids of thermal vibration. Tetrahedral bond directions associated with [SiO₄] and [Si₃O₁₀] groups are represented as solid lines; the bonding of Ca to these groups is not shown.

Table 2. Final atomic co-ordinates (fractional) and isotropic
temperature factors (B, in Å²); estimated standard deviations
on last digit in parentheses.

| Atom | x/a | y/b | z/c | B | Site symmetry and multiplicity | |
|------|-----|-----|-----|---|---|---|
| Ca1 | 0.0173(1) | 0 | 0 | 0.86 | 2 | 4 |
| Ca2 | 0.3095(1) | 0.9943(2) | 1/4 | 0.64 | m | 4 |
| Ca3 | 0.03378(9) | 0.0028(2) | 0.17000(3) | 0.87 | I | 8 |
| Ca4 | 0.24432(9) | 0.4953(2) | 0.10580(3) | 0.75 | I | 8 |
| Si1 | 0.1194(2) | 0.4222(3) | 1/4 | 0.64 | m | 4 |
| Si2 | 0.4386(1) | 0.9384(2) | 0.10256(4) | 0.65 | I | 8 |
| Si3 | 0.2728(1) | 0 | 0 | 0.62 | 2 | 4 |
| O1 | 0.1864(3) | 0.2910(5) | 0.1908(1) | 0.85 | I | 8 |
| O2 | 0.9893(4) | 0.2836(8) | 1/4 | 0.91 | m | 4 |
| O3 | 0.1203(4) | 0.7450(9) | 1/4 | 0.96 | m | 4 |
| O4 | 0.3743(3) | 0.7953(6) | 0.1601(1) | 0.97 | I | 8 |
| O5 | 0.0664(3) | 0.7011(6) | 0.0956(1) | 1.03 | I | 8 |
| O6 | 0.3638(3) | 0.8127(5) | 0.0420(1) | 0.83 | I | 8 |
| O7 | 0.4354(3) | 0.2591(6) | 0.0987(1) | 0.91 | I | 8 |
| O8 | 0.1923(2) | 0.1878(5) | 0.0405(1) | 1.08 | I | 8 |

Table 3. Anisotropic temperature factors.

| Site | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|------|------|------|------|------|------|------|
| Ca1 | .00123(5) | .00919(27) | .00055(1) | 0 | 0 | .00020(7) |
| Ca2 | .00122(4) | .00693(25) | .00031(1) | .00045(13) | 0 | 0 |
| Ca3 | .00218(3) | .00597(13) | .00046(1) | -.00018(7) | -.00038(1) | -.00029(4) |
| Ca4 | .00127(3) | .00740(16) | .00044(1) | -.00002(9) | .00004(1) | -.00026(4) |
| Si1 | .00143(8) | .00522(41) | .00035(2) | .00060(16) | 0 | 0 |
| Si2 | .00143(6) | .00511(23) | .00037(1) | .00026(11) | -.000004(24) | -.00012(5) |
| Si3 | .00117(6) | .00630(35) | .00033(2) | 0 | 0 | .000003(87) |
| O1 | .00208(16) | .00776(86) | .00036(4) | .00122(35) | .00016(6) | .00017(14) |
| O2 | .00157(22) | .00936(132) | .00052(6) | .00038(47) | 0 | 0 |
| O3 | .00225(26) | .00556(6) | .00062(6) | .00030(48) | 0 | 0 |
| O4 | .00192(17) | .01033(90) | .00046(4) | .00006(33) | .00012(7) | -.00013(16) |
| O5 | .00127(15) | .01027(91) | .00074(5) | -.00004(32) | .00008(7) | .00046(17) |
| O6 | .00210(16) | .00665(73) | .00039(4) | .00026(31) | -.00008(6) | -.00002(14) |
| O7 | .00182(16) | .00574(65) | .00063(4) | .00022(33) | -.00001(8) | -.00016(15) |
| O8 | .00156(15) | .01109(86) | .00069(5) | .00055(32) | .00002(7) | -.00109(17) |

characteristic configuration of this $Mn^{2+}$ cation provides an explanation for the strong (001) cleavage of synthetic kilchoanite $Ca_3Si_2O_7$ (Taylor, 1971).

It is now clear that in a number of disilicates, the bridging oxygen atoms do indeed reside on special positions (Liebau, 1985). For example, in both melilite (Kimata and Ii, 1981) and hemimorphite (McDonald and Cruickshank, 1967), the disilicate groups are arranged across a mirror plane. By contrast, the bridging O6 oxygen in manganoan kilchoanite is on a general position. Such a configuration is unusual. The electrostatic valency rule is not followed exactly in another kilchoanite structure (Taylor, 1971), in which the Si–O bond lengths are similar to those in manganoan kilchoanite. One of the tetrahedra in the present sample shows considerable distortion, with Si–O bonds ranging from 1.692 to 1.608 Å, and the normal length of the Si1–O3 bond (1.616 Å) differs from the abnormal one (1.70 Å) in natural kilchoanite. Inasmuch as the formal bond strength (Pauling, 1960) of O3 atoms is equal to 2, this is justified on crystal chemical

Table 4. Bond multiplicities and interatomic distances (Å).

| Distances | | Distances | |
|-----------|--|-----------|--|
| Ca1-O5 [x2] | 2.628(3) | Si1-O1 [x2] | 1.637(3) |
| -O6 [x2] | 2.516(3) | -O2 | 1.632(5) |
| -O7 [x2] | 2.638(3) | -O3 | 1.616(5) |
| -O8 [x2] | 2.369(3) | | |
| | | | |
| Ca2-O1 [x2] | 2.415(3) | Si2-O4 | 1.619(3) |
| -O2 | 2.325(5) | -O5 | 1.618(3) |
| -O3 | 2.485(5) | -O6 | 1.692(3) |
| -O4 [x2] | 2.320(3) | -O7 | 1.608(3) |
| | | | |
| Ca3-O1 | 2.301(3) | Si3-O6 [x2] | 1.669(3) |
| -O2 | 2.297(3) | -O8 [X2] | 1.581(3) |
| -O3 | 2.383(3) | | |
| -O4 | 2.357(3) | O-O (within tetrahedra) | |
| -O5 | 2.248(3) | Shortest: | |
| -O7 | 2.255(3) | O1-O1 | 2.580(4) |
| | | | |
| Ca4-O1 | 2.217(3) | Longest: | |
| -O4 | 2.416(3) | O4-O7 | 2.769(4) |
| -O5 | 2.279(3) | | |
| -O6 | 2.510(3) | | |
| -O7 | 2.476(3) | | |
| -O8 | 2.180(3) | | |

ground. The average Si–O bond length, 1.630 Å, is consistent with those for other silicates and calcium–manganese silicates (Peacor, 1972), but the range of bond lengths, 1.581 to 1.692 Å, is

Table 5. Polyhedral interatomic angles (°).

| Angles | | | | | | |
|---|---|---|---|---|---|---|
| At Si1: | O1-O1 | 104.3(2) | Smallest | in Ca-O | polyhedra | |
| | O1-O2 [x2] | 104.5(2) | At Ca1 | O5-O6 | 60.23(9) | |
| | O1-O3 [x2] | 113.5(1) | Ca2 | O1-O1 | 64.7(1) | |
| | O2-O3 | 115.5(3) | Ca3 | O1-O2 | 68.4(1) | |
| | | | Ca4 | O4-O6 | 63.14(9) | |
| At Si2: | O4-O5 | 106.6(2) | | | | |
| | O4-O6 | 102.4(2) | | | | |
| | O4-O7 | 118.2(2) | | | | |
| | O5-O6 | 102.5(2) | | | | |
| | O5-O7 | 116.5(2) | | | | |
| | O6-O7 | 108.7(2) | | | | |
| At Si3: | O6-O6 | 103.6(2) | | | | |
| | O6-O8a [x2] | 112.7(1) | | | | |
| | O6-O8b [x2] | 109.3(1) | | | | |
| | O8-O8 | 109.3(2) | | | | |
| At O6: | Si2-Si3 | 122.0(2) | | | | |

Table 6. Mean distances (Å), occupancies and distortions around Ca sites.

| Ca-polyhedron | Mean distance | | Occupancies | Distortion(x10-4)* | |
|---|---|---|---|---|---|
| | Kil | Mn-kil | Mn-kil | Kil | Mn-kil |
| Ca1-O [8] | 2.510 | 2.538 | Ca1.00 | 20.4 | 24.4 |
| Ca2-O [6] | 2.395 | 2.380 | Ca1.00 | 4.46 | 6.97 |
| Ca3-O [6] | 2.365 | 2.307 | Ca₀.₅₀₈Mn₀.₄₉₂ | 4.34 | 4.57 |
| Ca4-O [6] | 2.368 | 2.346 | Ca₀.₈₂₂Mn₀.₁₇₈ | 14.5 | 29.5 |

* Weiss et al. (1981)

rather large, and the Si2–O6 bond, 1.692 Å, is unusually long. This enlargement can be explained by oversaturation of the formal bond strength to O6 oxygen, as summarized in Table 7, while unusual shortening of the Si3–O8 bond is regarded as due to its undersaturation to O8. Using the parameters of Brown (1981), the following calculated bond strengths are obtained for Si1, Si2, and Si3, respectively: 4.00, 3.97 and 4.08 in valence units. All of these bond strengths around three Si cations are reasonably close to the ideal value for a cation coordination number of [4]. As stated above, the bond-length variations in the present silicate anion can be satisfactorily interpreted in terms of the bond-valence requirements of the individual oxygen anions.

Tables 6 and 8 show that the substitution of $Mn^{2+}$ for $Ca^{2+}$ decreases the distortion of Si-tetrahedra and increases that of Ca-polyhedra. Thus the regularity of the Si-tetrahedron is enhanced by the size and charge of the non-tetrahedral cation. Concomitant distortion about the Ca and Si sites is an important factor in maintaining the stability of the kilchoanite structure with varying solid solution; such a compensation mechanism is also observed in the melilite structure (Kimata,

1984). There is no doubt that the sizes of the cations constrain the distortions in a given structure type.

The frequency distribution of Si–O–Si angles in silicates (Bauer, 1980) has a maximum at 139°, energetically the most favourable angle for a strain-free Si–O–Si bond (Liebau, 1985). Large deviations from 139° can be attributed to strain due to the forced accommodation of non-tetrahedral cations of unfavourable size and/or electronegativity. Moreover, it is clear from the work of Gibbs (1982) that shift of the maximum in histograms of Si–O–Si angles is associated with changes in the coordination numbers of the bridging oxygen atoms. A statistical survey of Si–O–Si angles in silicates containing [$Si_2O_7$] groups (Liebau, 1985) verifies that the bond angle for three-coordinated oxygen ranges between 124 and 137°, whereas the angle for two-coordinated oxygen is more variable, ranging between 130 and 180°. The Si–O–Si angle of 122° in the present manganoan kilchoanite is slightly larger than the value of 117° observed in natural kilchoanite (Taylor, 1971). This observation is apparently contradictory, as the ionic radius of $Mn^{2+}$ is smaller than $Ca^{2+}$. The difference in Si–O–Si angles between these

Table 7. Bond strength (Po) of the oxygens and calcium sites.

|     | Ca1 | Ca2 | Ca3   | Ca4 | Si1 | Si2 | Si3 | Total Po |
|-----|-----|-----|-------|-----|-----|-----|-----|----------|
| O1  | /   | 2/6 | 2/6   | 2/6 | 4/4 | /   | /   | +2.00    |
| O2  | /   | 2/6 | 2x2/6 | /   | 4/4 | /   | /   | +2.00    |
| O3  | /   | 2/6 | 2x2/6 | /   | 4/4 | /   | /   | +2.00    |
| O4  | /   | 2/6 | 2/6   | 2/6 | /   | 4/4 | /   | +2.00    |
| O5  | 2/8 | /   | 2/6   | 2/6 | /   | 4/4 | /   | +1.917   |
| O6  | 2/8 | /   | /     | 2/6 | /   | 4/4 | 4/4 | +2.583   |
| O7  | 2/8 | /   | 2/6   | 2/6 | /   | 4/4 | /   | +1.917   |
| O8  | 2/8 | /   | /     | 2/6 | /   | /   | 4/4 | +1.583   |

|     | O1 | O2 | O3 | O4 | O5 | O6 | O7 | O8 | Total Po |
|-----|----|----|----|----|----|----|----|----|----------|
| Ca1 | /  | /  | /  | /  | 2x | 2x | 2x | 2x | 16.00    |
| Ca2 | 2x | 1x | 1x | 2x | /  | /  | /  | /  | 12.00    |
| Ca3 | 1x | 1x | 1x | 1x | 1x | /  | 1x | /  | 11.834   |
| Ca4 | 1x | /  | /  | 1x | 1x | 1x | 1x | 1x | 12.00    |

n in nx is multiple of each bond strength.

two kilchoanites seems to be ascribed to the larger electronegativity of the $Mn^{2+}$ cation (Pauling, 1960). Moreover, these two smaller values are below the bond angle range of three-coordinated oxygen; the bridging O6 oxygen in the kilchoanite structure is four-coordinated. Increase in the coordination number of the bridging oxygen in disilicate groups leads to a reduction of the Si–O–Si angle. This correlation can be developed more extensively in connection with the observation that the Si2–O6 bond distance is the largest of all the Si–O bonds in manganoan kilchoanite. The decrease in the (Si–$O_{br}$) distance with increasing the Si–$O_{br}$–Si angle in silicates has been demonstrated by Liebau (1985). Hawthorne and Calvo (1978) suggested that longer $\langle V-O_{br}\rangle$ bond lengths of the divanadate groups in a series of structures are generally associated with smaller V–$O_{br}$–V angles. The same geometrical character is perceived also in other rare mixed-anion silicates with single and triple tetrahedral clusters: ardennite (Donnary and Allmann, 1968) and $Ho_4[SiO_4]$ $[Si_3O_{10}]$ (Felsche, 1972), and in some disphosphates: $\alpha$-$Cu_2P_2O_7$ (Calvo, 1967), $\alpha$-$Zn_2P_2O_7$ (Robertson and Calvo, 1970) and $SiP_2O_7$ (Bissert and Liebau, 1970). Such a relationship between the $T-O_{br}$ distances and the $T-O_{br}-T$ angles may be common to some groups of the crystal structures with two tetrahedra sharing a vertex (pyro-anion, $T_2O_7^{q-}$): pyrosilicates, pyrovanadates, pyrophosphates and so on. Oversaturation of electrostatic bond-strength to the bridging oxygen in $T_2O_7^{q-}$-bearing crystalline groups, which is caused by increase in the coordination number of the bridging oxygen and/or by $T$ cations with charge greater than 4+, results in longer $T-O_{br}$ bonds length and finally in smaller $T-O_{br}-T$ angles.

As a rule, $Mn^{2+}$ cations are situated with low point symmetry. Eight-fold coordination is not found for the 'pure' $Mn^{2+}$ cation (Belov et al.,

Table 8. Mean distances (Å) and distortion of Si-tetrahedra.

|        | Mean distance | | distortion[*] | |
|--------|-------|--------|-------|--------|
|        | Kil  | Mn-kil | Kil   | Mn-kil |
| Si1–O  | 1.65 | 1.631  | 5.541 | 5.386  |
| Si2–O  | 1.65 | 1.634  | 7.556 | 4.970  |
| Si3–O  | 1.64 | 1.625  | 4.970 | 3.329  |

[*] Robinson et al. (1971)

1984). It does, however, arise when the other larger cations are statistically 'diluted' by $Mn^{2+}$ cations, for which this type of polyhedron is usual. As $Mn^{2+}$ has no CFSE (crystal field stability energy), its structural role is controlled principally by local electrostatic charge and ionic radius. If only Ca and $Mn^{2+}$ disorder over various sites, $Mn^{2+}$ should preferentially order on those sites at which their average bond lengths are shorter. This preference can be verified in olivine (glauco-chroite, $CaMnSiO_4$) and pyroxene (johannsenite, $CaMnSi_2O_6$); Freed and Peacor, 1967. Inasmuch as the $M1$ and $M2$ sites in the manganoan kilchoanite structure are rather larger than the $M3$ and $M4$ sites, the above explanation can be applied to occurrence of $Mn^{2+}$ at both the $M3$ and $M4$ sites. In kilchoanite (Taylor, 1971), the mean Ca–O distances in $M3$ and $M4$ sites are equal to each other, and the $Mn^{2+}$ cation prefers the less distorted $M3$ site (Table 6). Moreover total formal bond-strength at the $M3$ site is undersaturated, whereas that at $M4$ is ideal. Entry of $Mn^{2+}$ (smaller than Ca) into the $M3$ site causes an apparent increase of its bond-strength, because according to Brown's formula (1981), shortening of the bond distance in a site leads to increase of the bond-strength. The difference in potential energy between the $M3$ and $M4$ sites is presumably ascribed to deviations from ideality of the formal

bond-strengths. The conclusion is that the order of preferential substitution of Mn for Ca is as follows: (1) the smaller Ca sites; (2) the Ca sites showing less distortion; (3) the Ca sites showing a loss in neutrality of formal electrostatic valence.

Inasmuch as concentration of $Mn^{2+}$ cations into the $M3$ site with lower bond-strength accords with preference of the cations for the less distorted octahedral site, order of preferences (2) and (3) may sometimes reverse corresponding to the degree of their deviations. Other applications of this substitution rule are recognized in $Mn^{2+}$-bearing fluorapatite (Warren and Mazelsky, 1974) and harstigite $MnCa_6Be_4[SiO_4]_2[Si_2O_7]_2(OH)_2$ (Hesse and Stumpel, 1986), and we conclude that this order of preference may be widely applied to the distribution of other cations. A rule governing substitution of $Mn^{2+}$ for smaller isovalent cations has not yet been established. Judicious combination of the above three rules can lead to significant improvement in establishing a general rule for such substitutions.

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