Structurally Adaptable Chain Silicates

By David A. Jefferson* and John M. Thomas*
(*Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge* CB2 1EP)

Summary A new approach to the interpretation of the structures of single-chain silicates is proposed, which rationalises the relationships between known regular structures and the occurrence of recently discovered defective structures in the pyroxenoid family ($MSiO_3$) and also predicts new structures.

Several structural types consisting of linear arrays of corner-sharing SiO_4 tetrahedra have been identified[1,2] amongst the naturally occurring single-chain silicates, general formula $MSiO_3$. The back-bone repeat distance (*i.e.* the identity period of the chain) varies amongst this family of so-called pyroxenoids, which include enstatite ($MgSiO_3$, a typical pyroxene), wollastonite ($CaSiO_3$). rhodonite [$(Mn,Fe,Ca)SiO_3$], and other members possessing longer repeat units (see Figures 1b and 1c).

High resolution electron microscopy (h.r.e.m.) can reveal directly[3–5] the unit-cell content and back-bone repeat units of these individual pyroxenoids, but the technique also brings to light the remarkable ease with which various members of the pyroxenoid family may co-exist, and probably interconvert, for a given silicate composition (*i.e.* an arbitrary mixture of cations M^{2+} within the formula $MSiO_3$). A particular repeat pattern and spacing is taken up because of the size of the template of edge-sharing octahedra on to which the chains are bound (Figure 1). The smaller Mg^{2+} ions (r_+ 0·72 Å) in enstatite 'dictate' a 5·2 Å repeat distance, whereas the larger Ca^{2+} ions (r_+ 1·00 Å) require a 7·3 Å back-bone repeat distance.

By preparing a series of synthetic chain silicates containing controlled (spatially averaged) amounts of Fe^{2+}, Mn^{2+}, and Ca^{2+} we have confirmed, by h.r.e.m., that the rhodonite structure is favoured in the Mn^{2+}-rich varieties. We have also established that coherent intergrowths, at the unit cell level, of wollastonite, rhodonite, and pyroxmangite

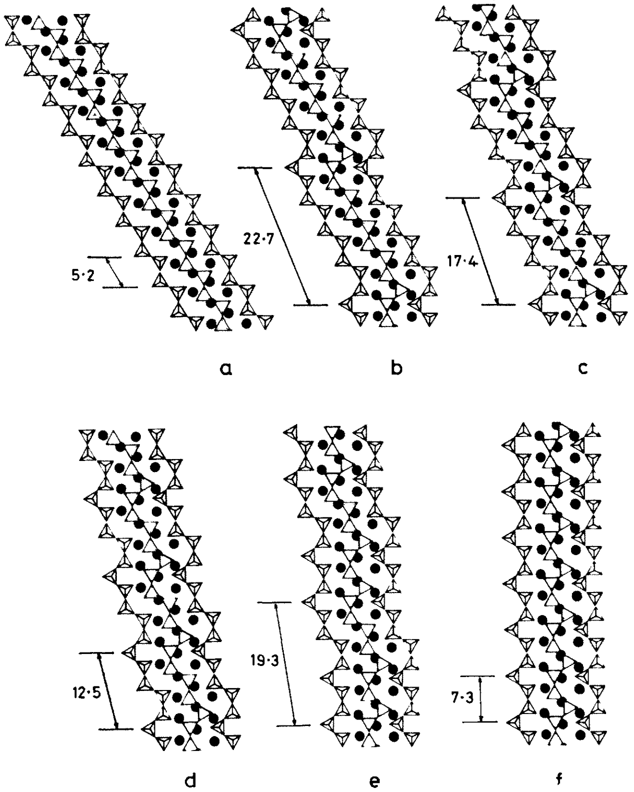

Figure 1. Schematic structural illustration of five known and one predicted member of the pyroxenoid family. (a) Pyroxene, (b) ferrosilite III, (c) pyroxmangite, (d) rhodonite, (e) predicted WWPy.... sequence, (f) wollastonite. The metal cations (shown as filled circles) occur in octahedra that are edge-shared and which form ribbons parallel to the chain (see text). The repeat distances are given in Å.

freely occur.[6,7] Thus, typically, over a distance along the back-bone of *ca.* 120 Å, the following sequence occurs RPRRWWWWWWRR...... where W, R, and P refer, respectively, to unit cell repeat distances (7·3 Å, 12·5 Å, and 17·4 Å) of the wollastonite, rhodonite, and pyroxmangite structures. The implications are clear. The lattice energy differences between various members of the pyroxenoid family are probably very small and variation in the cation composition during growth can readily be accommodated, again at the unit-cell level, by minor structural adaptation such as the rotation of some SiO_4 tetrahedra. More significantly, it suggests a logical interpretation for the occurrence of such intergrowths (unit-cell level stratigraphy) and the interconversion of one pyroxenoid into another, although this may require more extensive structural reassignment. We may picture (Table) any member of the pyroxenoid family to be composed of an appropriate admixture of wollastonite (W) and pyroxene (Py) building units, which contribute the segments (i) and (ii) (Figure 2), respectively, to the chains.

TABLE. Various combinations of the pyroxene (Py) and wollastonite (W) building blocks.

Structural type	Idealized formula	Representation of structure in terms of Py(2) and W(3) building blocks	
Pyroxene	$Mg_2(Si_2O_6)$	Py	2.
Wollastonite	$Ca_3(Si_3O_9)$	W	3.
Rhodonite	$(Ca,Fe,Mn)_5(Si_5O_{15})$	PyW	2.3.
Pyroxmangite	$(Ca,Mn,Fe)_7(Si_7O_{21})$	PyPyW	2.2.3.
Ferrosilite III	$(Fe)_9Si_9O_{27}$	PyPyPyW	2.2.2.3.
Predicted new members:	$M_8Si_8O_{24}$	PyWW	2.3.3.
	$M_{11}Si_{11}O_{33}$	PyWWW	2.3.3.3.


(i) (ii)

FIGURE 2.

The advantages of this building block picture are several. First, it enables the pyroxenoid structural types to be formulated in much the same way as the homologous members of the so-called shear structures[8] (in, say, Ti_nO_{2n-1} where, depending on the value of *n*, there is an appropriate admixture of crystallographic shear and antiphase boundaries). Second, as we show in detail elsewhere,[6,9] grossly defective synthetic and naturally occurring metasilicates, composed of many kinds of extended planar faults, can be 'seen' (by h.r.e.m.) to be made up of various non-regular admixtures of the Py and W building blocks. Third, this interpretation has a predictive value and it is now expected that a new series of single-chain silicates exists in which, by analogy, the numbers would be: PyWW ($M_8Si_8O_{24}$) (as shown in Figure 1e); PyWWW ($M_{11}Si_{11}O_{33}$); and PyWWWW ($M_{14}Si_{14}O_{42}$). Attempts to synthesize such structures are under way.

The double-chain silicates (amphiboles) adapt to local (unit-cell level) and grown-in compositional variation in rather different ways; see refs. 5, 10. Intergrowths of triple-, quadruple-, and other multiple-chains are less easily interconverted into one another.

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[1] F. Liebau, 'Handbook of Geochemistry,' Vol. II/3, Chapter 14, Springer-Verlag, Berlin, (1972).

[2] M. Alario Franco, D. A. Jefferson, N. J. Pugh, J. M. Thomas, and A. C. Bishop, *Mater. Res. Bull.*, 1980, **15**, 73.

[3] J. M. Thomas and D. A. Jefferson, *Endeavour*, 1978, **2**, 127.

[4] L. G. Mallinson, D. A. Jefferson, J. M. Thomas, and J. L. Hutchison, *Philos. Trans. R. Soc. London, Ser. A*, 1980, **295**, 537.

[5] J. M. Thomas, D. A. Jefferson, L. G. Mallinson, D. J. Smith, and E. Sian Crawford, *Chem. Scr.*, 1978–79, **14**, 167 (Nobel Symposium, Stockholm, August 1979).

[6] D. A. Jefferson, N. J. Pugh, M. Alario Franco, L. G. Mallinson, G. R. Millward, and J. M. Thomas, *Acta Crystallogr., Ser. A*, 1980, **36**, in the press.

[7] D. A. Jefferson and N. J. Pugh, *Acta. Crystallogr.*, submitted for publication.

[8] L. A. Bursill and B. G. Hyde, *Prog. Solid State Chem.*, 1972, **1**, 177.

[9] D. A. Jefferson, N. J. Pugh, and J. M. Thomas, in preparation.

[10] D. A. Jefferson, L. G. Mallinson, J. L. Hutchison, and J. M. Thomas, *Contrib. Mineral. Petrol.*, 1978, **66**, 1.

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