Chain–Ring Interconversion in Metasilicates

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Summary Theoretical studies indicate that lattices of the chain and ring varieties of $CaSiO_3$ fit together with only slight mis-match; high resolution electron microscopic studies of a sample undergoing conversion from chain- to ring-structure, however, indicate that intergrowths do not occur and, instead, the chain structure recrystallises *via* a glassy phase into ring silicate of the same composition.

RECENT high resolution electron microscopic studies of single-chain metasilicates (pyroxenoids) indicate that different structural types can be intergrown on a very fine scale.[1] In view of the structural adaptability demonstrated, the possibility that chain silicates of the wollastonite type can transform topotactically into pseudowollastonite ring structures could not be discounted. Recent calculations of lattice matching between both phases of composition $CaSiO_3$ (Table) have indicated that mis-match along certain lattice planes is only slight, further suggesting the possibility of intergrowths. In order to investigate whether such features can occur, even if only on a fine scale, high resolution electron microscopic investigations of a natural sample of wollastonite have been undertaken, after annealing at a temperature high enough to produce partial conversion into the ring structure.

TABLE. Calculated mutual planes of contact and overall mis-match between lattice meshes for chain and ring varieties of $CaSiO_3$.

Directions defining plane of contact[a]	Plane of contact	% Mis-match (long diagonal)	% Mis-match (short diagonal)	Angles between defined diagonal
I [101], [111]	(121)	1·4	1·7	79·86
II [111], [200]	$(0\bar{1}1)$			79·70
I [010], [101]	(101)	5·2	4·5	80·50
II [100], $[0\bar{1}1]$	(011)			81·97
I $[0\bar{1}1]$, [101]	(111)	3·1	9·6	68·31
II [101], $[0\bar{1}1]$	$(\bar{1}11)$			74·87
I $[\bar{1}01]$, [020]	(101)	6·9	3·4	80·50
II $[\bar{1}11]$, $[\bar{1}\bar{1}1]$	(101)			83·14
I [002], [020]	(100)	4·0	7·8	89·94
II $[2\bar{1}0]$, $[\bar{1}\bar{1}1]$	(123)			87·75
I [110], $[1\bar{1}0]$	(001)	7·5	10·0	85·22
II [010], [002]	(100)			86·62

[a] I = wollastonite: $a = 7{\cdot}94$, $b = 7{\cdot}32$, $c = 7{\cdot}07$ Å, $\alpha = 90{\cdot}03$, $\beta = 95{\cdot}37$, $\gamma = 103{\cdot}42°$; II = pseudowollastonite: $a = 6{\cdot}695$, $b = 9{\cdot}257$, $c = 6{\cdot}666$ Å, $\alpha = 86{\cdot}63$, $\beta = 76{\cdot}13$, $\gamma = 70{\cdot}38°$.

The wollastonite sample used was extensively characterised by X-ray powder diffraction and analytical electron microscopy, the latter study confirming that the sample was almost pure $CaSiO_3$. Previous X-ray and electron microscopic investigations[2] indicated a high degree of stacking disorder. After annealing for 20 h at 1250 °C, the X-ray powder diffraction pattern indicated the presence of both chain- and ring-structures; no appreciable degree of particle size or disorder broadening of the lines was noted. Upon examination by high resolution microscopy, the particles present could be divided into three categories. Much of the sample appeared to consist of crystals of the chain structure, usually imaged with the electron beam parallel to [100], but in some cases images down the [001] axis were obtained, and these indicated a high degree of crystal perfection. Frequently, however, such crystals possessed amorphous edges, rather than the well developed cleavages normally observed. This was also true of crystals of the ring structure, but these showed, in addition to the two- and four-layer polytypes observed in Ca–Sr metasilicates,[3] a high degree of disorder, and a tendency for amorphous regions to develop during exposure to the electron beam. The third category of particles appeared to be truly amorphous, and had not been noted in examination before heat treatment. No intergrowths of chain and ring structures, or other postulated chain structures,[4] were observed.

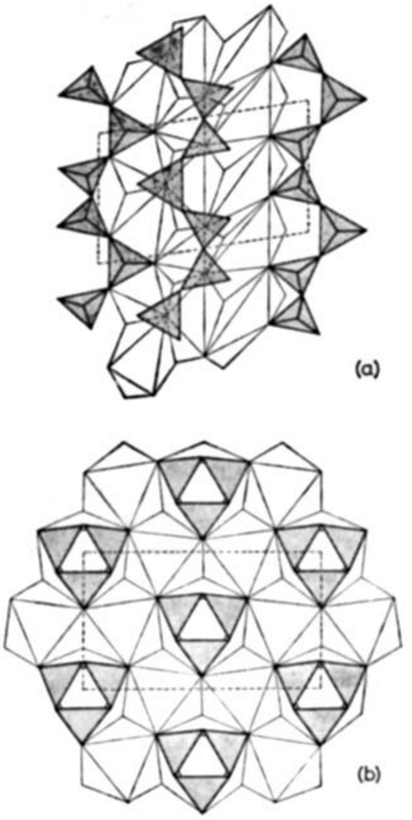

FIGURE. Schematic representations of the structures of (a) wollastonite and (b) pseudowollastonite, projected onto the planes of the Ca atoms. In each case the SiO_4 tetrahedral arrangement is idealised.

The chain- and ring-structure variants of $CaSiO_3$ are indicated in the Figure, both projected onto the plane containing the Ca atoms. Although the configuration of the SiO_4 tetrahedral network is the most apparent distinguishing feature, the differences between the Ca–O octahedral networks are also considerable. These are fully occupied in the ring structure but vacant octahedra are required in the chain variety, to avoid octahedra and tetrahedra sharing a face. Although the breaking of the silicate chain to form rings can be envisaged as a relatively easy process, with every third Si atom having only to move to an adjacent site, the overall movement of Ca atoms in the structural conversion is considerable. In the light of the experimental data, therefore, it appears that the latter is the determining factor in the transformation, the migration of Ca^{2+} ions creating a glassy intermediate state, from which recrystallisation in the ring structure occurs.

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[1] M. Alario-Franco, D. A. Jefferson, N. J. Pugh, and J. M. Thomas, *Mater. Res. Bull.*, 1980, **15**, 73; M. Reid and M. Korekawa, *Phys. Chem. Miner.*, 1980, **5**, 365; D. J. Smith, D. A. Jefferson, and L. G. Mallinson, *Acta. Crystallogr., Sect. A*, 1981, **37**, 273; D. A. Jefferson and N. J. Pugh, *ibid.*, p. 281.

[2] D. A. Jefferson and M. G. Bown, *Nature (London) Phys. Sci.*, 1973, **245**, 43; D. A. Jefferson and J. M. Thomas, *Mater. Res. Bull.*, 1975, **10**, 761.

[3] Wen Shu-Lin, D. A. Jefferson, and J. M. Thomas, *Mater. Res. Bull.*, 1980, **15**, 1643.

[4] D. A. Jefferson and J. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1980, 743.