Linear and Planar Defects in Wollastonite

By **J. Morales Palomino, David A. Jefferson,* John L. Hutchison,** and **John M. Thomas,** Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth SY23 1NE

Wollastonite from various sources has been examined by high-resolution electron microscopy and lattice images are presented which show a wide range of defect structures. Although these images do not show a one-to-one correspondence with the structure, it is shown that they can be used in the observation and characterisation of planar and linear defects.

HIGH-RESOLUTION electron microscopy (h.r.e.m.) is now established as one of the most powerful techniques for the study of the ultrastructure of minerals. Its principal achievements are that the local order (or disorder) may be ascertained for a region of a crystal that contains as few as 10^3 unit cells; almost all other techniques yield results that are in general ' averaged ' over some 10^{18} unit cells. Special conditions, relating to sample thickness, orientation, and ' openness ' of structure as well as various instrumental factors, have to be met, however, before reliable information may be extracted from the high-resolution micrographs. A summary of these preconditions, as well as an indication of the wealth of data that may be obtained from h.r.e.m., has been given previously.[1-7] It is to be noted that, in particular, with current instruments, the resolution limit at which the correspondence between object structure and observed image breaks down has been shown [8] to be *ca.* 3.8 Å. For heavy-metal oxides this figure is comparable to metal–metal atom distances, but, for the majority of inorganic materials, a successful h.r.e.m. study would only be possible with greater resolution than currently available. However, lattice images of many materials at this order of resolution can be used to clarify our knowledge of their ultrastructural characteristics, particularly defects, if the limitations of the technique are appreciated, and this is particularly appropriate to silicate minerals, the broad structural principles of which have been established, almost exclusively, on the basis of *X*-ray studies.

In so far as the chain silicate wollastonite ($CaSiO_3$) is concerned, the idealised structure may be regarded as quasi-layered, in that contiguous slabs [on (100)] may be visualised as being stacked along the a^* direction [Figure 1(*a*) and (*b*)]. There appear to be two operative

---

[1] P. R. Buseck and S. Iijima, *Amer. Min.*, 1974, **59**, 1.

[2] D. A. Jefferson and J. M. Thomas, *J.C.S. Faraday II*, 1974, 1691.

[3] J. E. Chisholm, in ' Surface and Defect Properties of Solids,' eds. M. W. Roberts and J. M. Thomas, 1975, vol. 4, p. 126.

[4] E. L. Evans and J. M. Thomas, *J. Solid-state Chem.*, 1975, **14**, 99.

[5] M. R. Wenk, W. F. Muller, N. A. Liddell, and P. P. Phakey, in ' Electron Microscopy in Mineralogy,' Springer–Verlag, Berlin, 1976, ch. 5.

[6] M. A. O'Keefe, Ph.D. Thesis, University of Melbourne, 1973.

[7] J. L. Hutchison, M. C. Irusteta, and E. J. W. Whittaker, *Acta Cryst.*, 1975, 794.

[8] D. A. Jefferson, G. R. Millward, and J. M. Thomas, *Acta Cryst.*, 1976, **A32**, 823.

displacement vectors relating a slab to its predecessor: either a slab is displaced by $+ 0.25b - 0.10c$ (designated V_1), or by $- 0.25b - 0.10c$ (V_2). These stacking possibilities consequently lead to two principal polytypic variants: in the one, a triclinic polytype,[9] the stacking sequence is $V_1V_1V_1 \ldots$ (or its twin-related form $V_2V_2V_2 \ldots$), whereas in a monoclinic polytype, parawollastonite,[10] with two slabs contained within the unit cell, the sequence is $V_1V_2V_1V_2V_1V_2 \ldots$

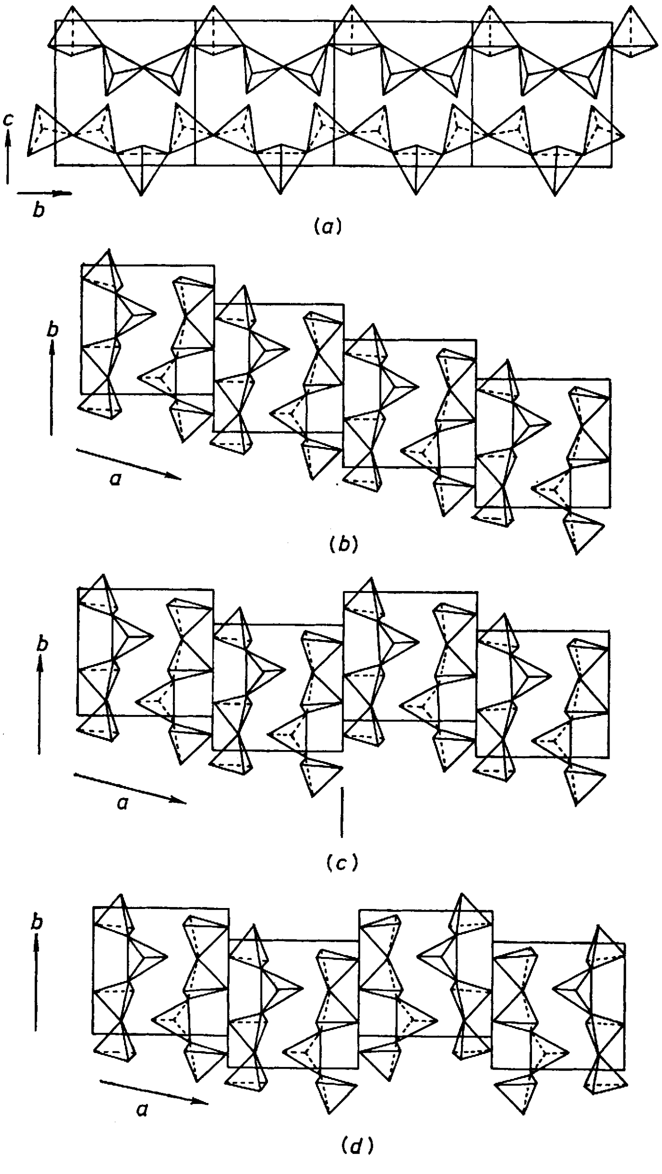

FIGURE 1 (a) Schematic representation of wollastonite structure projected on to (100). (b) Wollastonite structure viewed along [001]. (c) A simple displacement fault in triclinic wollastonite viewed down [001]. (d) Reflection twinning in wollastonite, accompanied by 0.25b shift, viewed down [001]. In this case there is no obvious stacking fault but the direction of the tetrahedra are inverted at the planar fault

In the course of extensive h.r.e.m. studies of wollastonite from various geological origins, we have discovered several distinct types of defective structure, the details of which we now summarise. These fall into two categories, planar faults, which have been reported in earlier studies,[11] and linear faults, and we discuss each separately. Whereas the general structural and chemical features associated with some of these defects seem clear, for others they are, at present, enigmatic.

RESULTS AND DISCUSSION

Planar Faults.—Of the numerous types (*i.e.* distinct geological sources) of samples investigated none was found to be perfectly ordered at the ultrastructural unit-cell level. Indeed, the degree of ' interfusion ' or coexistence of triclinic and monoclinic polytypes varied widely from one sample to another, as illustrated in Figure 2(*a*) and (*b*). Samples emanating from Finland (see Experimental section) exhibited large domains (average width in the a^* direction of 100—150 Å) of the triclinic structure interrupted (at AA, BB, *etc.*) by extended stacking faults [Figure 2(*a*)] where the second kind of displacement vector has intervened. Californian samples, however, frequently consisted of rather finely intergrown domains of both the mono- and tri-clinic polytypes [Figure 2(*b*)]. Here the number of extended stacking faults is very large.

Occasionally a different kind of (and as yet incompletely characterised) planar defect occurs; an example is shown in Figure 2(*c*). The most noteworthy feature of this micrograph is the abrupt change of contrast at the boundary FF, but there is no apparent accompanying stacking fault, the presence of which might lead to a change of contrast. One possible explanation is that (as suggested by Wenk *et al.*[5]) reflection twinning on (100) combined with an $0.25b$ shift has occurred at the interface. [Schematic representations of an accepted displacement fault and this postulated type are given in Figure 1(*c*) and (*d*).] Since the usual V_1 or V_2 displacements involve $+ 0.25b - 0.10c$ and $-0.25b - 0.10c$ respectively, such a twin may or may not interrupt the stacking sequence when viewed down [001]. If, however, a true reflection occurs then the $-0.10c$ component of the shift would be reversed and this could produce a change of contrast. Independent evidence that this type of interpretation may be valid is afforded by single-crystal X-ray studies. The precession photograph of Figure 3 may be rationalised in terms of the reflection twin plus $0.25b$ shift outlined above. The absence of diffuse streaks parallel to a^* at the $l = 1, 2,$ *etc.* rows indicates that in this sample (from California) the twinning, whilst definitely present, is not recurrent on a fine scale (polysynthetic).

Linear Faults.—Three distinct kinds of linear faults (dislocations) have been detected. The most commonly occurring is one which has been reported previously[12] and is illustrated in Figure 4(*a*). This type of fault must

---

[9] K. S. Mamedov and N. V. Belov, *Doklady Akad. Nauk S.S.S.R.*, 1956, **107**, 463.

[10] F. J. Trojer, *Z. Krist.*, 1968, **127**, 291.

[11] D. A. Jefferson and J. M. Thomas, *Mat. Res. Bull.*, 1975, **10**, 761.

[12] J. L. Hutchison and A. C. McLaren, *Contr. Min. Pet.*, 1976, **55**, 303.

exist if a stacking fault on (100) does not extend entirely across that (100) plane. In the language of dislocation theory, a sessile partial dislocation occurs in the structure. Such a fault has been previously schematised [13] and, if, as seems probable, it were a pure edge dislocation it would be of the type (100)[010]. Major chemical changes must occur at the dislocation core to accommodate the structural demands for the existence of a twinned triclinic region on one side of the fault and its absence on the other. We do not yet have direct evidence for the existence of the short strip of pyroxene structure (or alternative pyroxenoid structures such as rhodonite or pyroxmangite) which could be present in every wollastonite chain that crosses the dislocation core.

In Figure 4(*b*) we ' see ' that an extra incomplete layer, parallel to (100), has been inserted into the wollastonite structure, thereby giving rise to a dislocation in which the Bergers vector is parallel to [100]. This is a sessile Frank dislocation of type (010)$\frac{1}{2}$[100], not hitherto reported; and here there is no necessity for the wollastonite chains to undergo such a drastic structural and compositional modification, unless some chain ' branching ' takes place, as was required for the (100)[010] type of linear fault.

A third kind of linear fault (seen very infrequently to date) was detected from the micrograph shown in Figure 4(*c*), where the electron-beam direction is normal, rather than parallel (as in all previous micrographs), to the (100) planes. The defect seems, in this case, to be associated with a pronounced tilt of the crystal, and it is possible that we have here a disclination rather than a dislocation.

In addition to the extended defects described so far, another structurally anomalous feature has been noted. In a relatively perfect monoclinic sample from Tanzania, one region was observed with an apparent 0.5*b* displacement at each layer rather than the 0.25*b* of the accepted structure. This is indicated in the circumscribed region of Figure 5. Conceptually, it is very difficult to understand how such a stacking arrangement can be reconciled with the accepted structure, unless there is associated with it an appreciable displacement parallel to [001]. Indeed it seems very likely, especially in the light of preliminary lattice-image calculations (see below), that this apparent ' structure ' arises from the fact that the high-resolution image is merely a ' lattice ' image bearing no obvious relation to the projected charge density, and that the structure in this part of the micrograph is the accepted monoclinic form, but owing to differences in defocus over the range of the image the arrangement of fringes is altered.

Significance of Micrographs.—It must be emphasised that the high-resolution micrographs shown here do not accurately reflect the projected charge density [14] of the various wollastonite specimens. Rigorous *N*-beam dynamical calculations of the type fully described elsewhere [15] demonstrate that this is so. Wollastonite is a very strong scatterer of electrons, so that the actual image seen is profoundly affected by the multiple scattering events within the thin specimen. Nevertheless the fringe contrast has a validity and meaningfulness, and it has already been amply demonstrated that h.r.e.m. images of wollastonite are interpretable in terms of the structural models we have utilised above. There is no doubt that previous h.r.e.m. micrographs taken by us and other workers do convey the correct shape and size of the appropriate unit cells. In view of this fact, it should be possible, with the aid of further *N*-beam calculations (now under way), to characterise more fully the various defects that have been discussed here. Such characteristics will be further aided by (*i*) obtaining micrographs of ion-beam thinned samples, orientated such that the chain axis is parallel to the electron beam so that reflection twinning, if present, can be observed directly, and (*ii*) the use of ultrasensitive microanalytical techniques (based on energy dispersion of *X*-rays emitted from structurally defective regions). Experiments of this kind are in progress.

EXPERIMENTAL

All the samples were examined in the form of finely crushed grains supported on ' holey ' carbon films after deposition from acetone suspension. Specimens were examined in a Philips EM300 electron microscope fitted with a high-resolution stage and image-intensification system, or on a Siemens Elmiskop 102A fitted with a double-tilt (45°) stage. Images were recorded with the electron beam either parallel to [001] or normal to (100), at magnifications ranging from 2×10^5 to 5×10^5. Single crystals of several samples were examined on an *X*-ray precession instrument, using filtered copper radiation. The range of samples examined included wollastonite from California, Devon, Finland, Tanzania, New York State, and Mexico. In addition, two samples of laboratory-synthesised material were studied.

We thank the Royal Society Exchange Scheme and the S.R.C. for support (to J. M. P. and J. L. H.), and the S.R.C. for the electron microscopes.

[7/065 *Received*, 13*th January*, 1977]

---

[13] D. A. Jefferson and J. M. Thomas, *EMAG–75 Proceedings*, Bristol, 1975, p. 275.

[14] D. F. Lynch, A. F. Moodie, and M. A. O'Keefe, *Acta Cryst.*, 1975, **A31**, 300.

[15] J. G. Allpress, E. A. Hewatt, A. F. Moodie, and J. V. Sanders, *Acta Cryst.*, 1972, **A28**, 528.