COWLEY, J. M. (1972). *Physical Aspects of Electron Microscopy and Microbeam Analysis*, ch. 1, edited by B. SIEGEL & D. R. BEAMAN, pp. 3–15. New York: John Wiley.
GLAESER, R. M. (1975). *Physical Aspects of Electron Microscopy and Microbeam Analysis*, edited by B. SIEGEL & D. R. BEAMAN, ch. 12, pp. 205–229. New York: John Wiley.
JOHANSEN, B. V. (1977). *Ultramicroscopy*, **2**, 229–239.
KITAIGORODSKY, A. I. (1961). *Organic Chemical Crystallography*, pp. 94–105. New York: Consultants Bureau.
KOBAYASHI, T. & REIMER, L. (1975). *Bull. Inst. Chem. Res. Kyoto Univ.* **53**, 105–116.
KUO, I. A. M. & GLAESER, R. M. (1975). *Ultramicroscopy*, **1**, 53–66.
MCLACHLAN, D. (1958). *Proc. Natl. Acad. Sci. USA*, **44**, 948–956.
MURATA, Y., FRYER, J. R. & BAIRD, T. (1976). *J. Microsc.* **108**, 261–275.
MURATA, Y., FRYER, J. R., BAIRD, T. & MURATA, H. (1977). *Acta Cryst.* A**33**, 198–200.
MURATA, Y., FRYER, J. R. & BAIRD, T. (1977). *Proc. EMAG '77, Glasgow. Inst. Phys. Conf. Ser.* 36. ch. 3, pp. 127–130.
REIMER, L. (1960). *Z. Naturforsch. Teil A*, **15**, 405–411.
REIMER, L. (1961). *Z. Naturforsch. Teil B*, **16**, 166–170.
REIMER, L. (1965). *Lab. Invest.* **14**, 1082–1096.
ROSE, H. (1977). *Ultramicroscopy*, **2**, 251–267.
SMITH, G. W. & STALLEY, J. C. (1975). *Acta Cryst.* A**31**, S122.
UYEDA, N., KOBAYASHI, T., SUITO, E., HARADA, Y. & WATANABE, M. (1972). *J. Appl. Phys.* **43**, 5181–5189.
VON BORRIES, B. & KAUSCHE, G. A. (1940). *Kolloid Z.* **90**, 132–141.
WILLIAMS, R. C. & FISHER, H. W. (1970). *J. Mol. Biol.* **52**, 121–123.

Acta Cryst. (1978). A**34**, 607–609

Mixed-Layer Characteristics in Real Humite Structures

BY W. F. MÜLLER

Fachbereich 11, *Mineralogie, Technische Hochschule Darmstadt, Schnittspahnstrasse* 9, *D* 6100 *Darmstadt, Federal Republic of Germany*

AND H.-R. WENK

Department of Geology and Geophysics, University of California, Berkeley, California 94720, *USA*

(*Received* 20 *December* 1977; *accepted* 21 *February* 1978)

Transmission electron micrographs resolving (100) lattice fringes of clinohumite revealed faults parallel to (100). A simplified model of humite minerals, which interprets them as layers of forsterite and brucite–sellaite, was used for analysis of the faults. These compositional faults produce one or two unit layers of humite and/or chondrodite interlayered between the regular sequence of clinohumite along **a***. Thus, non-stoichiometric compositions of humite minerals can be explained as mixed layers.

Introduction

The structure of humite minerals with formula $n.\mathrm{Mg_2SiO_4}.\mathrm{Mg(OH,F)_2}$ consists basically of a slightly distorted hexagonal close packing of anions similar to olivine with an ordered O, F, and OH arrangement (Taylor & West, 1929). Octahedral interstices are partially filled with Mg(Ti,Fe), and tetrahedral ones with Si. The various structures can be classified by emphasizing either tetrahedral or octahedral building elements. Tetrahedral interstices are filled in alternate layers parallel to (100). Such a structure resembles the stacking of forsterite ($\mathrm{Mg_2SiO_4}$) layers F with a spacing of 3·0 Å and brucite–sellaite [$\mathrm{Mg(F,OH)_2}$] layers B with a spacing of 1·4 Å (Taylor & West, 1929). The stacking scheme applies only to the cations, anions are distributed over all layers equally. In norbergite the sequence is FB ($d_{100} = 2 \times 4{\cdot}36$ Å), in chondrodite FFB ($d_{100} = 7{\cdot}44$ Å) (Fig. 1), in humite $FFFB$ ($d_{100} = 2 \times 10{\cdot}43$ Å) and in clinohumite $FFFFB$ ($d_{100} = 13{\cdot}44$ Å). This model was shown to be oversimplified because order of octahedral positions which occupy half of the interstices is different in the various humite minerals (Ribbe, Gibbs & Jones, 1969). Octahedra filled with

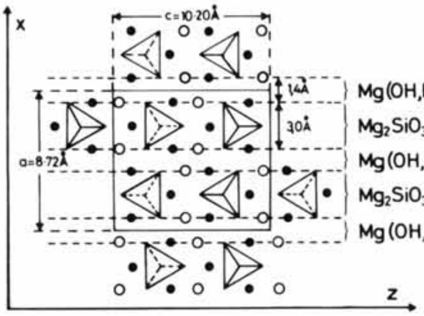

Fig. 1. Projection of norbergite on (010). Simplified model which interprets the humite structures in terms of layers of 'forsterite', $Mg_2SiO_3(OH,F)$, and 'brucite', Mg(OH,F)O. Solid circles Mg, open circles (OH,F).

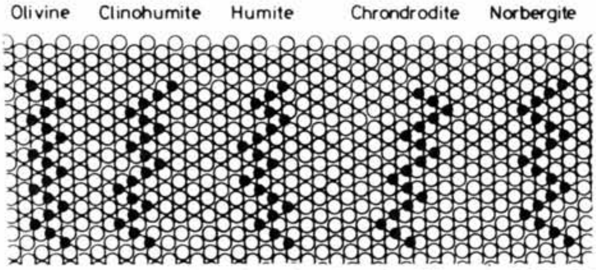

Fig. 2. Projection of humite minerals and olivine on (010). The difference in the octahedral chains of the various structures is shown schematically. Solid circles are octahedral cations in the (010) plane which is the plane of the close-packed anion layer indicated by open circles.

magnesium extend as chains parallel to *x* [a view on the close-packed plane (010) is shown in Fig. 2]. New X-ray refinements of humite structures have confirmed that relations are more complicated than a pure stacking but the stacking model may nevertheless constitute the most basic principle (Gibbs & Ribbe, 1969; Gibbs, Ribbe & Anderson, 1970; Ribbe & Gibbs, 1971; Robinson, Gibbs & Ribbe, 1973). In this case we might expect to find stacking faults in the real humite structures because the fault energy on close-packed planes is obviously low. Transmission electron microscopy is the obvious technique with which to study the microstructure of humite minerals.

Experimental and results

We analyzed two samples of clinohumite, a pure Mg clinohumite from a wollastonite fels in Death Valley, California (1-DV 12) and a titano clinohumite from serpentinites of Val Malenco, Italian Alps (Mal 58). Electron-transparent foils were prepared from petrographic thin sections by ion-beam thinning and then analyzed in bright field and dark field with a JEM 100B electron microscope equipped with a side-entry high-angle tilt stage. The micrograph shown in Fig. 3 displays fringes with a 13·4 Å spacing which correspond to (100) lattice planes in clinohumite with *FFFFB*

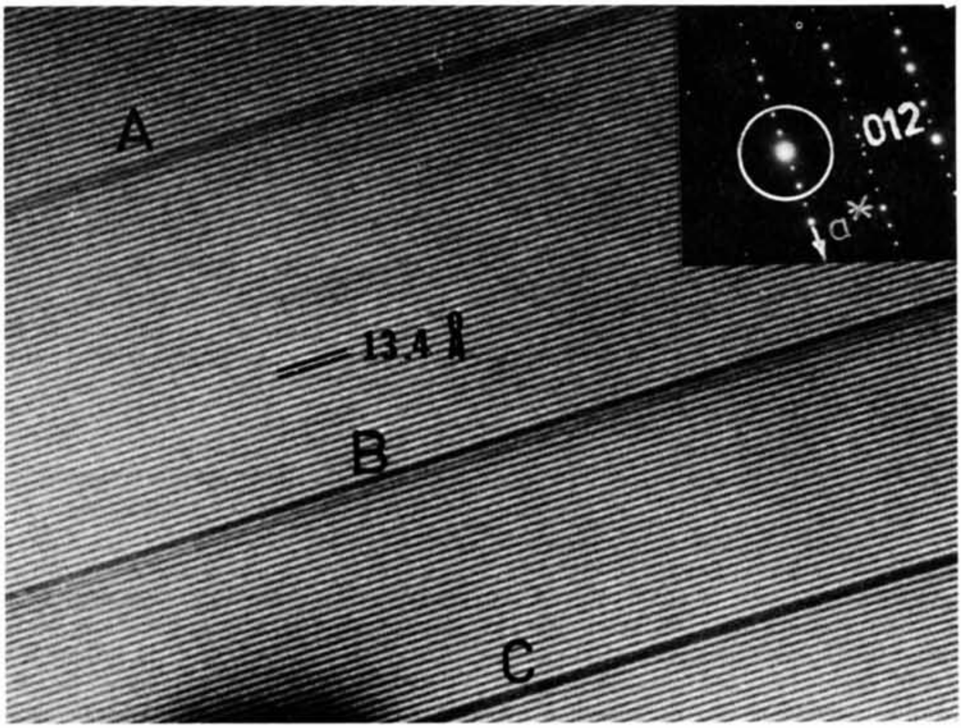

Fig. 3. Transmission electron microscopy lattice image of titano clinohumite from Val Malenco, Italian Alps. The (100) lattice fringes are interrupted by the faults *A*, *B*, and *C*. The corresponding electron diffraction pattern is inserted and the objective-aperture area, including the imaging beams, indicated.

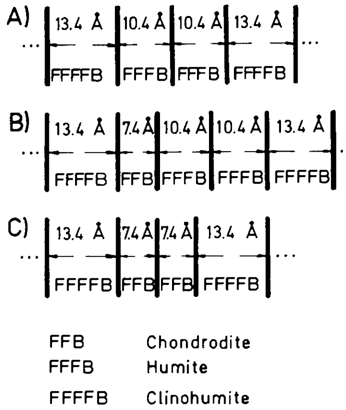

Fig. 4. Schematic representation of the faults *A*, *B*, and *C* shown in Fig. 3 and their interpretation.

stacking. But we observe faults which interrupt the regular sequence. A schematic representation of the line spacings across the faults at *A*, *B*, and *C* of Fig. 3 and their interpretation is given in Fig. 4. We note that the regular sequence of clinohumite (13·4 Å; *FFFFB*) is interrupted by layers of humite (10·4 Å; *FFFB*) and chondrodite (7·4 Å; *FFB*). The structure shown here is directly analogous to another mixed-layer mineral bastnaesite–synchisite (Van Landuyt & Amelinckx, 1975). Following the nomenclature of Amelinckx & Van Landuyt (1976) the faults found in clinohumite are compositional faults because they do change the composition locally. Because of these faults we can obtain any nonstoichiometric intermediate compositions in the humite series. So far we have not been able to identify sequential faults but they may also exist and give rise to polytypes. The fault density is much lower than in wollastonite which contains conservative stacking faults (Wenk, Müller, Liddell & Phakey, 1976); therefore, streaking parallel to **a*** observed in electron diffraction patterns is much less intense.

Compositional faults were observed in both clinohumite samples. In addition, a preliminary study of a chondrodite sample revealed faults parallel to (100), but these have not yet been studied in detail.

Conclusions

Electron microscopy establishes that natural clinohumites have a mixed-layer structure which may, however, deviate from the ideal model with forsterite and brucite units (Taylor & West, 1929). Based on evidence from line-resolution experiments we cannot determine the exact nature of the structure in the narrow *FB* and *FFB* layers, particularly the arrangement of octahedra. This would require *n*-beam point-resolution experiments which we could not do with the available equipment (Cowley & Iijima, 1976). In any case, clinohumite emerges as another mineral example where the real structure deviates from the ideal structure and where it becomes difficult to evaluate the significance of an X-ray structure refinement which averages over thousands of unit cells, even though atomic parameters may have refined to great precision.

Support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

Amelinckx, S. & Van Landuyt, J. (1976). *Electron Microscopy in Mineralogy*, edited by H.-R. Wenk, pp. 68–112. Berlin, Heidelberg, New York: Springer.

Cowley, J. M. & Iijima, S. (1976). *Electron Microscopy in Mineralogy*, edited by H.-R. Wenk, pp. 123–136. Berlin, Heidelberg, New York: Springer.

Gibbs, G. V. & Ribbe, P. H. (1969). *Am. Mineral.* **54**, 309–313.

Gibbs, G. V., Ribbe, P. H. & Anderson, C. W. (1970). *Am. Mineral.* **55**, 1182–1194.

Ribbe, P. H. & Gibbs, G. V. (1971). *Am. Mineral.* **56**, 1155–1173.

Ribbe, P. H., Gibbs, G. V. & Jones, H. W. (1969). *Mineral. Mag.* **36**, 966–975.

Robinson, K., Gibbs, G. V. & Ribbe, P. H. (1973). *Am. Mineral.* **58**, 43–49.

Taylor, W. H. & West, J. (1929). *Z. Kristallogr.* **70**, 461–474.

Van Landuyt, J. & Amelinckx, S. (1975). *Am. Mineral.* **60**, 351–358.

Wenk, H.-R., Müller, W. F., Liddell, N. A. & Phakey, P. P. (1976). *Electron Microscopy in Mineralogy*, pp. 324–331. Berlin, Heidelberg, New York: Springer.