



Fig. 3 BSE micrograph showing complex nature of interlayering in a chlorite-smectite stack. The delicate growth projection at the right-hand end of the stack is unlikely to have survived long-distance transport.



Fig. 4 BSE micrograph showing authigenic intergrowth of illite-smectite (I-S), kaolinite (K) and chlorite (C).

appear to have been incorporated during growth. Finally, groups of chlorite, illite and kaolinite crystals sometimes show complex textural intergrowths with each other and with quartz, feldspars, and authigenic dolomite-ankerite crystals (Fig. 4). We feel that the most likely explanation of these textural intergrowths is authigenic development of the clay stacks. The relatively large size and apparent fragility of the aggregates makes a detrital origin unlikely, and it is difficult to see how such features could be produced by differential alteration of detrital micas.

Further evidence suggests that growth of the clay stacks may have occurred at shallow depths during early diagenesis. First, the long axes of the stacks show a general sub-parallelism to the bedding (Fig. 1), except in the vicinity of what appear to be small burrows where the sediment fabric has been disturbed. Second, the finer-grained matrix surrounding the larger stacks often shows signs of deformation, suggesting growth of the stacks in soft, uncompacted sediment. Third, the concentration of clay stacks is often highest just below organic-rich laminae, which probably represent periods when inorganic sedimentation slowed or ceased. Finally, in several cases clay stacks have been observed to be cemented by glauconite or pyrite which are probably of near-surface origin. Clay stacks have also been observed to occur within calcite concretions, features which are generally accepted on the basis of isotopic and other evidence to be early diagenetic^{8,9}. Although we consider that the hypothesis is not yet fully proven, it seems possible that most clay mineral stacks formed at, or very close to, the sediment-water interface during periods of slow sedimentation. Diagenetic reactions are generally considered to be of minor importance in explaining the pattern of clay mineral assemblages in the modern oceans¹⁰⁻¹³, although some authors have postulated large-scale neo-formation of clay minerals contemporaneous with deposition¹⁴. Early authigenic chamosite and glauconite are found in a variety of modern marine environments¹⁵⁻¹⁸, and there appears to be no reason why other clay mineral stacks should not form in the right geochemical conditions.

We have attempted to show that BSE-EDXA analysis of shale thin sections can provide useful information about the nature of interstratification in clays as well as textural data which help to elucidate their origin. The SEM provides a valuable link between the optical microscope and bulk chemical-mineralogical data on the one hand and TEM results on the other. Our observation that clay minerals may exist in Jurassic shales as silt or fine sand-size particles suggests that conventional XRD procedures need to be modified to obtain a fully representative picture. A tremendous variation exists in size, shape and internal structures of clay minerals, as well as other fine-grained constituents of shales, which has not formerly

been fully recognized. Although this creates problems for the mudrock petrographer, it also offers hope that very detailed physical and chemical changes with time can be observed and understood.

K.P. acknowledges financial support provided by a NERC Research Fellowship and Girton College. D.H.K. was supported partly by NASA-Ames research grant NAG 2-174 and the Planetary Geology Program, Office of Space Science, research grant NAGW24. We thank David Newling, Pat Trusty, Bill Porter and Brian Krinsley for technical assistance, and British Petroleum for provision of some offshore samples.

Received 25 April; accepted 15 June 1983.

1. Shaw, D. B. & Weaver, C. E. *J. sedim. Petrol.* **35**, 213-222 (1965).
2. Hower, J., Eslinger, E. V., Hower, M. E. & Perry, E. A. *Bull. geol. Soc. Am.* **87**, 725-737 (1976).
3. Hall, M. G. & Lloyd, G. E. *Am. Miner.* **66**, 362-368 (1981).
4. Pye, K. & Krinsley, D. H. *Nature* **301**, 412-413 (1983).
5. Krinsley, D. H., Pye, K. & Kearsley, A. T. *Geol. Mag.* **120**, 109-114 (1983).
6. Pye, K. & Krinsley, D. H. *J. sedim. Petrol.* (in the press).
7. Hemingway, J. E. & Riddler, G. P. *Trans. Instn. Min. Metall. B. appl. Earth Sci.* **91**, B175-B186 (1982).
8. Raiswell, R. *Chem. Geol.* **18**, 227-244 (1976).
9. Coleman, M. L. & Raiswell, R. *Geochim. cosmochim. Acta* **45**, 329-340 (1981).
10. Weaver, C. E. *Bull. Am. Ass. petrol. Geol.* **42**, 254-271 (1958).
11. Biscaye, P. E. *Bull. geol. Soc. Am.* **76**, 803-832 (1965).
12. Griffin, J. J., Windom, H. & Goldberg, E. D. *Deep Sea Res.* **15**, 433-459 (1968).
13. Rateev, M. A., Gorbunova, Z. N., Lisitzyn, A. P. & Nosov, G. L. *Sedimentology* **13**, 21-43 (1969).
14. Jeans, C. V. *Clay Min.* **9**, 209-217 (1971).
15. Porrenga, D. H. *Mar. Geol.* **5**, 495-501 (1967).
16. Rohrlieh, V., Price, N. B. & Calvert, S. E. *J. sedim. Petrol.* **39**, 624-631 (1969).
17. Hein, J. R., Allwardt, A. O. & Griggs, G. B. *J. sedim. Petrol.* **44**, 562-571 (1974).
18. Birch, G. F., Willis, J. P. & Richard, R. S. *Mar. Geol.* **22**, 271-284 (1976).

Compression, nonstoichiometry and bulk viscosity of wüstite

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Wüstite (Fe_{1-x}O) is a complex oxide that is invariably nonstoichiometric ($0.04 \geq x \geq 0.12$). Point defects associated with this nonstoichiometry are clustered and result in a modulated crystal structure that has been extensively studied, but is not well understood¹⁻⁴. Many of the properties of these compounds, such as chemical diffusivity, electrical conductivity and magnetic transitions, seem to be significantly affected by the non-

stoichiometry and resulting ordering of defects⁵⁻⁸. We summarize here new and existing data on the elasticity of wüstite; these data indicate virtually no correlation between the bulk modulus and stoichiometry. There appears, however, to be a systematic difference between static and dynamic measurements. This behaviour suggests the presence of a frequency dependence to the bulk modulus that can be ascribed formally to a finite bulk viscosity of Fe_{1-x}O. Such an effect has not previously been described in oxide or silicate minerals, and it is presumably caused by pressure-induced changes in defect ordering and subsequent relaxation within the incommensurate structure of wüstite.

The bulk modulus of wüstite has been determined by several techniques, as illustrated in Fig. 1. Dynamic measurements include ultrasonic and shock-wave experiments that probe the sample on time scales of microseconds or less. In contrast, static determinations are carried out over periods of 10⁵-10⁶ s. Jackson *et al.*⁹ extrapolated ultrasonic data on polycrystalline (Mg, Fe)O samples to yield a bulk modulus of FeO that is in agreement with Mizutani's earlier determination on polycrystalline wüstite^{9,10} and the more recent single-crystal measurement of Sumino *et al.*¹¹ (based on cube-resonance interferometry). These results are consistent with the shock-compression data of Jeanloz and Ahrens¹² on polycrystalline wüstite in defining a dynamic value for the zero-pressure isothermal bulk modulus of wüstite:

$$K_{OT}^{\text{Dynamic}} = 178(\pm 6) \text{ GPa}$$

The hydrostatic compression of wüstite has recently been studied in two independent experiments^{13,14}. The measurements are in agreement with previous, nonhydrostatic determinations of the bulk modulus of wüstite¹⁵⁻¹⁷. Thus, we find a value of the static bulk modulus:

$$K_{OT}^{\text{Static}} = 155(\pm 5) \text{ GPa}$$

Nonhydrostatic conditions, which obtain in some of these experiments, do not seem to affect the results, contrary to what might be expected from previous static-compression studies¹⁸. Note that three pressure calibrations were utilized: Mao *et al.*¹⁷ and Will *et al.*¹⁶ used NaCl and Fe, respectively, as pressure standards, whereas the ruby-fluorescence technique was employed in the hydrostatic experiments¹³⁻¹⁷. This multiplicity of pressure standards reduces the possibility of systematic bias among the static-compression studies. We have used Eulerian finite-strain theory (Birch equation of state) to reduce the data of Will *et al.* and Mao *et al.* in accord with the analysis of the hydrostatic-compression data^{14,19}. Only the low-pressure data of Mao *et al.* have been considered because of the evidence for distortion of the crystal structure of wüstite that is associated with a second-order transition at high pressures (at or above about 10-20 GPa, depending on the degree of uniaxial stress)^{14,20}.

There is no compelling evidence among either the dynamic or static data for any change in bulk modulus with stoichiometry. In particular, we note the results of Hazen's experiment that was carried out simultaneously on three samples ($x = 0.055, 0.07$ and 0.10)¹³. The relative values of the compression of these samples (which are more precisely determined than their absolute values) yield $dK_{OT}/dx \sim 64$ GPa, as shown by the dot-dash curve in Fig. 1. This slope is in agreement with several model calculations¹⁴ that lead to predictions of a value for $dK_{OT}/dx \sim \pm 0.5 K_{OT}$, as illustrated by the shaded region in Fig. 1. Continuum models, on the one hand, lead to predictions of an increase in K_{OT} with increasing x , because the volume of wüstite decreases with increasing nonstoichiometry^{11,21,22}. Atomistic models^{23,24}, on the other hand, lead to predictions of a slight decrease of the bulk modulus as x increases, as does a model that treats the defect clusters in wüstite as magnetite-like microdomains¹⁴. The relative change in bulk modulus can be as large as $\pm 100\%$ of the change in x (ref. 14); the sign and

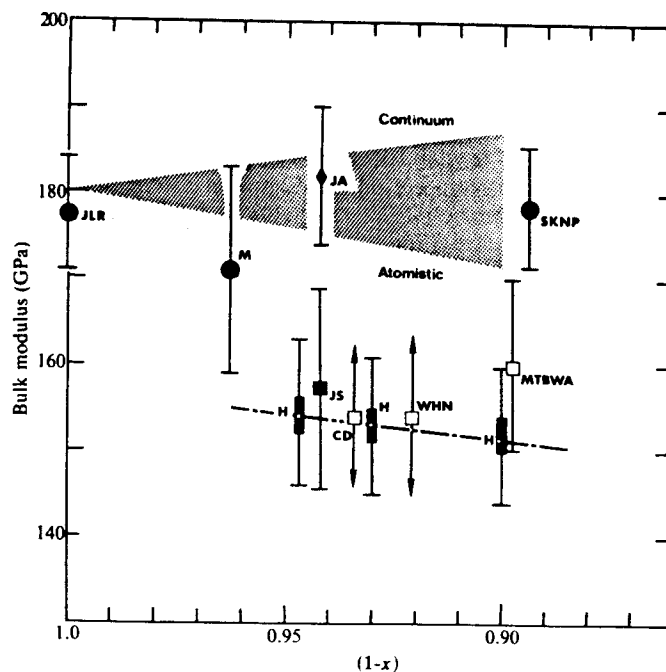


Fig. 1 Isothermal bulk modulus of wüstite as a function of composition or nonstoichiometry. Dynamic measurements are indicated by circles and a diamond, whereas static measurements are shown as squares and rectangles. Composition was determined from the lattice parameter quoted in each study^{29,30}. The techniques used include ultrasonic and cube-resonance interferometry (circles: JLR, Jackson *et al.*⁹; M, Mizutani¹⁰; SKNP, Sumino *et al.*¹¹), shock-wave compression (diamond: JA, Jeanloz and Ahrens¹²), hydrostatic compression (filled square and rectangles: H, Hazen¹³; JS, Jeanloz and Sato-Sorenson¹⁴) and nonhydrostatic compression (open squares: CD, Clendenen and Drickamer¹⁵; WHN, Will *et al.*¹⁶; MTBWA, Mao *et al.*¹⁷). The shaded region illustrates the effect of nonstoichiometry on the bulk modulus that is expected according to several theoretical and empirical models discussed in the text. (A value of 180 GPa at $x = 0.0$ is assumed.¹¹) The dependency of the bulk modulus on x observed by Hazen¹³ is shown by the dotted-dashed line (relative uncertainties among these determinations of bulk moduli are indicated by the sizes of the rectangles). Adiabatic moduli have been corrected to isothermal values, and static-compression measurements are all reduced according to finite-strain theory. Also, the data of Mao *et al.*¹⁷ have been reanalysed, as discussed in the text.

magnitude of the calculated change depend on the choice of parameters used in these calculations. In the light of data shown in Fig. 1, however, it appears that the bulk modulus of wüstite is essentially independent of stoichiometry. It is not possible, therefore, to ascribe the systematic difference between static and dynamic values of the bulk modulus to a dependency of K_{OT} on sample composition, x . This conclusion is supported by the differing results of the experiments of Jeanloz and Ahrens¹², and Jeanloz and Sato-Sorenson¹⁴, that were carried out on the same sample material.

The difference between static and dynamic moduli can be interpreted as a modulus defect, $\Delta K \sim 23$ GPa (ref. 25). If this interpretation is correct, then the data summarized in Fig. 1 imply that wüstite exhibits a bulk viscosity of magnitude $\kappa \sim \Delta K \tau$, where τ is the characteristic time for the relaxation mechanism that is involved. We cannot distinguish between anelastic and viscoelastic types of relaxation from these data, so we refer to bulk viscosity in only a loose sense without necessarily implying that finite volumetric strains of any significant magnitude need occur. As structural relaxation is observed in experiments lasting days to weeks, the magnitude of τ would be expected to be about 10⁵-10⁶ s, or less. In fact, a value $\tau \sim 10^6$ s is consistent with the data of Hazen *et al.*, which suggest that wüstite undergoes an irreversible (thus,

viscoelastic) change in lattice parameter at high pressures²⁶. A rough estimate of τ can be made from high-temperature diffusivity measurements, which may be used to determine the atomic jump frequency Γ . An extrapolation of the data of Chen and Peterson⁶ from $\sim 1,100$ K (activation energy $Q = 123$ kJ mol⁻¹) combined with the assumption that the diffusive length scale is the shortest distance between sites in the defect clusters (~ 0.03 nm) yields a predicted value of $\tau = \Gamma^{-1} \sim 10^7$ s at room temperature. (We use Morin's²⁷ value of ~ 0.6 for the correlation factor.) Alternatively, τ is $\sim 10^6$ s if the activation energy of defect migration $Q \sim 115$ kJ mol⁻¹, which is within the range that has been reported^{15,6,28}. Therefore, we can estimate the magnitude of the bulk viscosity in wüstite $\kappa \sim 10^{16} - 10^{17}$ Pa s. Similar effects might be observed in the magnesiowüstite series (Mg, Fe)O, because samples with as much as 40% Mg substitution for Fe display nonstoichiometric characteristics^{9,29}.

The unusual occurrence of bulk viscosity in a simple oxide is consistent with the complex defect structure that is found in wüstite^{2,4}. We infer that defect clusters are rearranged under hydrostatic compression, such that the bulk viscosity is a macroscopic description of what is, on a microscopic level, a pressure-induced, order-disorder transformation of the defect structure. This phenomenon is not a polymorphic transition; the main NaCl-type crystal structure of wüstite remains unchanged to pressures of ~ 10 GPa or more^{14,20,26}. Consequently, we would expect no difference between static and dynamic moduli for a hypothetical defect-free FeO. (Note that defects can occur in stoichiometric wüstite if equal numbers of vacancies and interstitials are present; bulk relaxation may thus be observed even for $x = 0$.) We therefore consider the dynamic modulus, rather than the static modulus, to be representative of interatomic bonding forces in wüstite. The observed modulus defect provides a new constraint on models of the defect-ordering behaviour within this nonstoichiometric compound.

We thank D. Heinz, M. S. T. Bukowinski, L. W. Finger, H. K. Mao and H. S. Yoder Jr, for helpful comments. This work was supported by NASA grant NAGW-439, NSF grant EAR 81-15517 and the A. P. Sloan Foundation.

Received 25 April; accepted 15 June 1983.

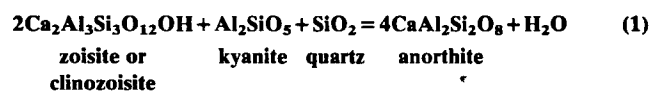
- Koch, F. & Cohen, J. B. *Acta crystallogr.* B25, 275-287 (1969).
- Andersson, B. & Sletnes, J. O. *Acta crystallogr.* A33, 268-276 (1977).
- Gavarrí, J., Carel, C. & Weigel, D. *J. Solid State Chem.* 29, 81-95 (1979).
- Yamamoto, A. *Acta crystallogr.* B38, 1451-1456 (1982).
- Kofstad, P. *Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides* (Wiley, New York, 1972).
- Chen, W. K. & Peterson, N. L. *J. phys. Chem. Solids* 36, 1097-1103 (1975).
- Koch, F. B. & Fine, M. F. *J. appl. Phys.* 38, 1470-1471 (1966).
- Greenwood, N. N. in *Perspectives in Mössbauer Spectroscopy* (eds Cohen, S. G. & Pasternak, M.) 27-39 (Plenum, New York, 1973).
- Jackson, I., Liebermann, R. C. & Ringwood, A. E. *Phys. Chem. Miner.* 3, 11-31 (1978).
- Mizutani, H., Hamano, Y. & Akimoto, S. *J. geophys. Res.* 77, 3744-3749 (1972).
- Sumino, Y., Kumazawa, M., Nishizawa, O. & Pluschkell, W. *J. Phys. Earth* 28, 475-495 (1980).
- Jeanloz, R. & Ahrens, T. J. *Geophys. J. R. astr. Soc.* 62, 505-528 (1980).
- Hazen, R. M. *Yb. Carnegie Instn Wash.* 80, 277-280 (1981).
- Jeanloz, R. & Sato-Sorensen, Y. *EOS* 63, 1097 (1982).
- Clendennan, R. L. & Drickamer, H. G. *J. chem. Phys.* 44, 4223-4228 (1966).
- Will, G., Hinze, E. & Nuding, W. *Phys. Chem. Miner.* 6, 157-167 (1980).
- Mao, H. K., Takahashi, T., Bassett, W., Weaver, J. S. & Akimoto, S. *J. geophys. Res.* 74, 1061-1069 (1969).
- Wilburn, D. R. & Bassett, W. A. *Am. Miner.* 63, 591-596 (1978).
- Birch, F. *Phys. Rev.* 71, 809-824 (1947).
- Zou, G. T., Mao, H. K., Bell, P. M. & Virgo, D. *Yb. Carnegie Instn Wash.* 79, 374-376 (1980).
- Holder, J. & Granato, A. V. *Phys. Rev.* 182, 729-741 (1969).
- Holder, J. & Granato, A. V. in *Physical Acoustics* Vol. 8 (eds Mason, W. P. & Thurston, R. N.) 237-277 (Academic, New York, 1971).
- Ludwig, W. *Natn. Bur. Stand. Misc. Publ.* 287, 151-156 (1966).
- Pistorius, M. Z. *angew. Phys.* 29, 145-152 (1970).
- Norwick, A. S. & Berry, B. S. *Anelastic Relaxation in Crystalline Solids* (Academic, New York, 1972).
- Hazen, R. M., Mao, H. K., Finger, L. W. & Bell, P. M. *Yb. Carnegie Instn Wash.* 80, 274-277 (1981).
- Morin, F. *Scripta metall.* 10, 553-556 (1976).
- Chen, W. K. & Peterson, N. L. *J. Phys. Chem. Solids* 41, 335-339 (1980).
- Simons, B. *Yb. Carnegie Instn Wash.* 79, 376-380 (1980).
- Hentschel, B. *Z. Naturf.* 25a, 1996-1997 (1970).

Fe-free clinozoisite stability relative to zoisite

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Orthorhombic zoisite, Ca₂Al₃Si₃O₁₂OH, and its monoclinic polymorph, clinozoisite, are key indicator minerals in low- and middle-grade basic and calcareous metamorphic rocks, and often occur together in apparent equilibrium¹. Both minerals contain variable amounts of Fe³⁺ replacing Al, but clinozoisite always contains more Fe³⁺, with as much as 30-40% substitution in typical epidote. Interpretations of their relative stabilities, based on field relations¹⁻³ and experimental studies^{4,5}, have conflicted markedly. No unambiguous experimental demonstrations of reversibility of a zoisite-clinozoisite equilibrium have yet been performed, and it may well be that such an equilibrium relation, if it exists, lies in a portion of the *P, T* plane which is inaccessible to direct investigation. We present here experimental reversals of the Fe-free equilibrium:



using both clinozoisite and zoisite. At 550 °C, the reaction with zoisite is in equilibrium at 6.30±0.25 kbar and the reaction with clinozoisite is in equilibrium at 7.30±0.15 kbar. Therefore, clinozoisite is considerably less stable than zoisite at this temperature, and the reaction with clinozoisite, though reversible, is metastable. Reliable thermodynamic data for the phases show, with the present experimental data, that zoisite has lower Gibbs free energy at 550 °C by 1,020±400 cal mol⁻¹. Published composition data of natural coexisting zoisite and clinozoisite, together with first-order assumptions as to the equilibrium temperatures of the parageneses, suggest that zoisite entropy is ~ 2.5 cal mol⁻¹ K⁻¹ higher than that of clinozoisite and that Fe-free clinozoisite becomes stable relative to zoisite below about 200 °C.

An internally-heated gas-pressure vessel with Ar medium was used to investigate reaction (1). Pressures were measured accurately to ±50 bar with both a manganin pressure cell and a bourdon-tube gauge. Two Cr-Al thermocouples at the ends of the sample showed 1-2 °C differences. Run durations were 4 days.

Starting materials were, with the exception of clinozoisite and quartz, crystalline phases synthesized from reagent-grade oxides or hydroxides. Natural quartz was from Lisbon, Maryland. Clinozoisite plus quartz was synthesized from a natural scolecite, CaAl₂Si₃O₁₀ · 3H₂O at 500 °C and 15 kbar for 4 h. The scolecite contained <0.01 wt% Na₂O as the principal impurity. Two homogenized reversal mix powders were made which consisted of nearly equal proportions of reactants and products in reaction (1), one mix with zoisite and the other with clinozoisite. Portions of each mix were sealed in Pt tubes with $\sim 25\%$ H₂O and placed side-by-side in the pressure vessel. The direction of a reaction produced during a run was deduced from changes of X-ray diffraction peak heights.

The experimental results at 550 °C are shown in Fig. 1. Only diffraction patterns showing large apparent changes, $\sim 30\%$ in the relative amounts of product and reactant phases, are shown as defining the directions of reaction. Between 6.6 and 7.2 kbar, zoisite grew relative to anorthite, but clinozoisite broke down. Therefore, zoisite is stable with kyanite and quartz to lower pressures than clinozoisite by at least 600 bar and at most 1,400 bar at 550 °C.

Run charges with the clinozoisite mix were checked for the spontaneous appearance of zoisite by searching for the distinct