- 20. H. E. Landsberg and J. M. Albert, Weatherwise H. E. Landsberg and J. M. Albert, *Weatherwise* (April 1974), p. 63.
 J. A. Eddy, *Clim. Change* 1, 173 (1977).
 J. P. Kennett and P. Huddlestun, *Quat. Res.* (N.Y.) 2, 38 (1972).
- 23. D. Ninkovich and W. L. Donn, Science 194, 899
- 24. Eruptions listed are from the better-studied re-
- gions of the world; eruptions from many areas have not vet been documented

- have not yet been documented.
 25. C. Sancetta, J. Imbrie, N. G. Kipp, Quat. Res. (N.Y.) 3, 110 (1973).
 26. N. G. Pisias, *ibid.* 10, 366 (1978).
 27. M. I. Budyko, *Tellus* 21, 611 (1969).
 28. R. S. J. Sparks, S. Self, G. P. L. Walker, *Geology* 1, 115 (1973).
 29. J. W. Drexler, W. I. Rose, Jr., R. S. J. Sparks, M. T. Ledbetter, *Eos* 59, 1104 (1978); M. T. Ledbetter, R. S. J. Sparks, W. I. Rose, Jr., *ibid.*, p. 312.
- D. Diradovich, R. S. S. Sparks, W. I. Rose, Ji., ibid., p. 312.
 D. Ninkovich, N. J. Shackleton, A. A. Abdel-Monem, J. D. Obradovich, G. Isett, *Nature (London)* 276, 574 (1978).
 S. Yumi and Y. Wako, in *Earthquake Dis-* 30.
- 31. placement Fields and the Rotation of the Earth, piacement Fields and the Rotation of the Larth,
 L. Mansinha, D. E. Smylie, A. E. Beck, Eds.
 (Springer-Verlag, New York, 1970), p. 82.
 D. L. Anderson, Science 186, 49 (1974).
 J. Chappell, Earth Planet. Sci. Lett. 26, 370 (1975).
- 33.
- (1975) 34. M. Golombek and M. J. Carr, J. Volcanol. Geo-
- M. Golombek and M. J. Carr, J. Volcanol. Geo-therm. Res. 3, 299 (1978); W. L. Hamilton, J. Geophys. Res. 78, 3363 (1973); F. M. Mauk and M. J. S. Johnston, *ibid.*, p. 3356.
 R. K. Matthews, Earth Planet. Sci. Lett. 5, 459 (1969).
 J. C. Eichelberger, Nature (London) 275, 21 (1978); R. S. J. Sparks, H. Sigurdsson, L. Wil-son, *ibid.* 267, 315 (1977).
 J. D. Hays, I. Umbria, N. J. Shaeklaton, Science,
- 37.
- J. D. Hays, J. Imbrie, N. J. Shackleton, *Science* 194, 1121 (1976). 38
- J. W. King, Nature (London) 245, 443 (1973); H. H. Lamb, Climate, Present, Past and Future, vol. 1, Fundamentals and Climate Now (Meth-39.
- Vol. 1, Fundamentals and Climate Now (Meth-uen, London, 1972).
 T. J. Cohen and P. R. Lintz, Nature (London)
 250, 398 (1974); J. Gribbin, *ibid.* 246, 453 (1973);
 P. D. Jose, Astron. J. 70, 193 (1965); K. D.
 Wood, Nature (London) 240, 91 (1972).
- G. H. (1968). H. Curtis, Geol. Soc. Am. Mem. 116, 153 40.
- 41. R. D. M. Verbeek, Nature (London) 30, 10 42.
- K. D. M. Velcek, Value (Establish) 50, 16 (1884).
 J. F. Lerbekmo, J. A. Westgate, D. G. W. Smith, G. H. Denton, in *Quaternary Studies*, R. P. Suggate and M. M. Cresswell, Eds. (Royal Society of New Zealand, Wellington, 1975), p. 2022 203
- P. D. Sheets, Univ. Mus. Stud. South. Ill. Univ. No. 9 (1976); V. C. Steen-McIntyre and P. D. Sheets, Geol. Soc. Am. Abstr. Programs 10, 497
- J. Healy, N.Z. Geol. Surv. Bull. 73 (1964), part 44. 1; C. G. Vucetich and W. A. Pullar, N.Z. J. Geol. Geophys. 16, 745 (1973); C. G. Vucetich Geol. Geophys. 16, 745 (1973); C. G. Vuceticn and R. Howorth, Abstr. 10th INQUA (Int. Quat. Assoc.) Congr. (1977), p. 491.
 45. J. Keller, W. B. F. Ryan, D. Ninkovich, R. Al-therr, Geol. Soc. Am. Bull. 89, 591 (1978).
 46. R. W. van Benmelen, in Acta of the 1st Inter-terrational control of the 1st Inter-
- national Scientific Congress on the Volcano Thera (Archaeological Service of Greece,
- Athens, 1971), p. 5.
 A. Bond and R. S. J. Sparks, J. Geol. Soc. London 132, 1 (1976); N. D. Watkins, R. S. J. Sparks, H. Sigurdsson, T. C. Huang, A. Federman, S. Carey, D. Ninkovich, Nature (London) 122 (1978).
- 48. H. Machida, Geogr. Rep. Tokyo Metrop. Univ. 11, 109 (1976).
- H. Williams and G. G. Goles, Min. Ind. Bull. 62, 37 (1968); L. R. Kittleman, Geol. Soc. Am. Bull. 49. (1973
- G. Vucetich and W. A. Pullar, N.Z. J. Geol. 50. Geophys. 12, 784 (1969); S. Self and R. S. J. Sparks, Bull. Volcanol., in press. S. Aramaki and T. Ui, Bull. Volcanol. 29, 29
- 51. S S. Alaman and T. C., Zan. Control (1966).
 S. N. Carey and H. Sigurdsson, Geol. Soc. Am. Abstr. Programs 10, 377 (1978).
 C. G. Vucetich and R. Howorth, N.Z. J. Geol. Control (1974). 52. S
- 53.
- Geophys, **19**, 43 (1976) 54.
- Geophys. 19, 43 (1976). I. A. Nairn, *ibid.* 15, 251 (1972); _____ and B. P. Kohn, *ibid.* 16, 299 (1973). C. G. Newhall and S. Self, unpublished data. We acknowledge valuable discussions with R. W. Decker and J. E. Hansen. Supported by NASA grant NSG 5145 (S.S.); M.R.R. was an NRC-NAS research associate at the Goddard Institute for Space Studies during this cutdu Institute for Space Studies during this study.

11 June 1979

SCIENCE, VOL. 206, 16 NOVEMBER 1979

B1-B2 Transition in Calcium Oxide from Shock-Wave

and Diamond-Cell Experiments

Abstract. Volume and structural data obtained by shock-wave and diamond-cell techniques demonstrate that calcium oxide transforms from the B1 (sodium chloride type) to the B2 (cesium chloride type) structure at 60 to 70 gigapascals (0.6 to 0.7 megabar) with a volume decrease of 11 percent. The agreement between the shockwave and diamond-cell results independently confirms the ruby-fluorescence pressure scale to about 65 gigapascals. The shock-wave data agree closely with ultrasonic measurements on the B1 phase and also agree satisfactorily with equations of state derived from ab initio calculations. The discovery of this B1-B2 transition is significant in that it allows considerable enrichment of calcium components in the earth's lower mantle, which is consistent with inhomogeneous accretion theories.

Calcium oxide, initially in the B1 (NaCl type) structure, is expected to transform to the B2 (CsCl type) structure at high pressure, by analogy with the B1-B2 transitions found in alkali halides (1, 2). There is considerable interest in such transitions both in theoretical studies of oxide structures (3-5) and because of their possible occurrence in the earth's lower mantle. We have carried out shock-wave experiments on CaO to determine its equation of state (Hugoniot) (6), as well as x-ray diffraction, under static high pressures, through a diamond cell (7); both techniques demonstrate a B1-B2 transition in CaO at 60 to 70 GPa (0.6 to 0.7 Mbar). To our knowledge this is the first documentation of the B2 structure in an oxide of direct geophysical interest.

Our new data are given in Table 1 and Fig. 1 along with previous results for CaO (8). For comparison, theoretical Hugoniots based on finite strain theory and ab initio [modified electron gas (4)] calculations for the B1 and B2 phases are also given (9). The shock data provide an accurate dynamic compression curve for CaO and the x-ray data from the diamond cell confirm the nature of the structural transition. The diamond-cell

experiments indicate that the transition begins at 60 (± 2) GPa on the ruby-fluorescence pressure scale (7) and at room temperature (295 K), whereas the shockwave data indicate a slightly higher transition pressure: about 63 to 70 GPa, but at approximately 1350 K (10). A volume decrease of 11 ± 1 percent is found at the transition in both sets of experiments, which is in agreement with simple systematics among the data for B1-B2 transitions in halides (11) and provides additional support for applying such systematics to oxides. The consistency of the shock-wave and diamond-cell results for the transition pressure in CaO provides an approximate but independent confirmation of the ruby-fluorescence scale calibration at about 65 (± 5) GPa. Thus the B1-B2 transition in CaO may be a convenient and readily reversible pressure-calibration point for ultrahigh-pressure static experiments.

The shock-wave data corresponding to the B1 phase are in excellent agreement (Fig. 1) with the theoretical Hugoniot calculated from recent ultrasonic data for CaO (9) and compare favorably with the theoretical Hugoniot based on the modified electron gas theory (4). Hence, the equation of state of CaO in the B1 structure appears to be very well constrained both experimentally and theoretically. Although the ab initio results underestimate somewhat the density of the B2 phase, they predict its compressional behavior quite well. Our Hugoniot data are consistent with essentially iden-

Fig. 1. New shock-wave data for CaO compared with previous, static compression data (8) and theoretical Hugoniots based on finitestrain (P_{3H}) and ab initio [modified electron gas (MEG)] calculations (9). Also shown are two seismological models for the lower mantle (15). Error bars for the shock-wave data are approximately the size of the symbols (or smaller); the datum in parentheses is considerably less certain. The open symbol represents an alternative interpretation of the 70-GPa result (6).

0036-8075/79/1116-0829\$00.50/0 Copyright © 1979 AAAS



tical zero-pressure bulk moduli (and pressure derivatives) for the B1 and B2 phases of CaO, as expected from systematics (9).

Similar B1-B2 transitions are also considered to be plausible in the geophysically important (Mg,Fe)O series. From simple concepts involving ratios of ionic radii (12), the B1 monoxides might be expected to transform at successively higher pressures in the following order (cation/anion radius ratios are given in parentheses): BaO (0.97), SrO (0.83), CaO (0.71), and MgO (0.51). Barium oxide is known to transform from a B1 to a B2related structure at about 14 GPa (2), and hence SrO is expected to transform at about 45 (± 10) GPa and MgO above 100 to 110 GPa, from the present results for CaO combined with these systematics. No B1-B2 transitions have been found in SrO up to 34 GPa and MgO up to 95 GPa or higher pressures (13), and the only other oxide for which a B1-B2 transition is known is EuO (but after it undergoes an electronic transition) (14). Hence, CaO appears to be the only oxide for which an uncomplicated B1-B2 transition has been found to date. Despite the relatively simple nature of B1-B2 transitions, however, their theoretical characterization is still imperfect, particularly for the purpose of predicting their occurrence. This conclusion is illustrated by the data for CaO, which disagree with the B1-B2 transition pressure of 120 GPa expected from ab initio calculations (4) and with the transition pressure of 28 to 40 GPa based on a semiempirical latticeinstability model (5).

A significant consequence of the B1-B2 transition in CaO is that the resulting density increase allows a considerable amount of CaO component within the earth's lower mantle, at least below a depth of about 1550 km (corresponding to a pressure of 65 GPa). As shown in Fig. 1, the Hugoniot of the B2 phase of CaO is within 1 to 2 percent of the seismologically determined pressuredensity relation for the lower mantle (15). Reduction of this Hugoniot to estimated mantle temperatures results in only a small correction, which, if anything, improves the comparison (16). Although calcium might well occur in a complex oxide or silicate mineral, simple oxidemixing models have proved rather successful in modeling the properties of the mantle and candidate minerals at high pressure (17). Hence, from purely geophysical considerations, a significant enrichment of refractory, calcium-bearing phases is allowed within the earth's deep interior. Such enrichment might, for exTable 1. Calcium oxide diamond-cell results.

Run	Pres- sure* (GPa)	Molar volume† (cm ³)		Rela- tive
		B1 phase	B2 phase	sity† (B1/B2)
14 Y 1	60.6	12.44	11.10	1.7
14Y2	61.2	12.36	11.06	0.7
14Y3	63.4	12.26	10.90	0.5
14Y4	63.7	12.28	10.87	0.5
14Y5	66.8	12.18	10.91	0.2

*The precision is ± 2 GPa; the absolute accuracy of the calibration is within 6 percent (7). †Based or 200 and 110 x-ray lines for B1 and B2 patterns, re †Based on spectively; the estimated precision of the molar volume is about ± 0.7 percent. Relative intensities of x-ray lines are based on visual estimates.

ample, be consistent with inhomogeneous accretion theories of the terrestrial planets and would imply that the mantle is not chemically homogeneous throughout (18).

> **RAYMOND JEANLOZ*** T. J. Ahrens

Seismological Laboratory, California Institute of Technology, Pasadena 91125

H. K. MAO, P. M. BELL Carnegie Institution of Washington, Washington, D.C. 20008

References and Notes

- 1. C. W. F. T. Pistorius, Prog. Solid State Chem. 11, 1 (1976).
- I. L. Liu, J. Appl. Phys. 42, 3702 (1971); and W. A. Bassett, J. Geophys. Res. 77, 4934 1972)
- M. Tosi and T. Arai, Adv. High Pressure Res. 1, 265 (1966).
- 4. A. J. Cohen and R. G. Gordon, *Phys. Rev. B* 14, 4593 (1976).
- 435 (1970).
 5. H. Demarest, R. Ota, O. L. Anderson, in *High Pressure Research*, M. Manghnani and S. Akimoto, Eds. (Academic Press, New York, 1970).
- 1977), p. 281.
 Shock experiments were performed on synthetic, single crystals in {100} orientation, which were prepared under controlled conditions to prevent hydration. Samples were impacted by projectiles launched from either a two-stage light-gas gun or a 40-mm propellant gun. H Experi mental techniques are described by R. Jeanloz and T. J. Ahrens [*Proc. Lunar Planet. Sci. Conf. 9th* (1978), p. 2789] and further details will be given by Jeanloz and Ahrens (in preparation). The datum in parentheses in Fig. 1 results from a partially successful experiment and hence has a considerable uncertainty, estimated as ± 1 to 2 percent in density and pressure. The open symbol represents an alternative (and less preferred) interpretation of the results of the 70-GPa shock experiment. In the preferred interpretation, a two-wave structure is inferred for the shock front, the first wave $(70.2 \pm 0.4 \text{ GPa})$ being associated with the phase transition. The alternative interpretation yields a transition pressure of about 63 (± 3) GPa.
- Powdered CaO from the sample material used in 7. the shock experiments was mounted in a gas-keted, high-pressure diamond cell in a 4:1 mix-ture of methanol and ethanol [H. K. Mao and P. ture of methanol and ethanol [H. K. Mao and P. M. Bell, Carnegie Inst. Washington Yearb. 76, 644 (1977); *ibid.* 77, 904 (1978); G. J. Piermarini, S. Block, J. D. Barnett, J. Appl. Phys. 44, 5377 (1973)]. Lattice parameters and structures were determined by x-ray diffraction (Ag K_{α} and Mo K_{α} radiation) at pressures between 60 and 67 GPa (precision, ±2 GPa) as determined on the ruby-fluorescence scale [J. D. Barnett, S. Block, G. J. Piermarini, *Rev. Sci. Instrum.* 44, 1 (1973); H. K. Mao, P. M. Bell, J. W. Shaner, D. J. Steinberg, J. Appl. Phys. 49, 3276 (1978)]. The B2 structure was identified by its 100, 110, 111, and 200 x-ray lines. and 200 x-ray lines.

- E. A. Perez-Albuerne and H. G. Drickamer, J. Chem. Phys. 43, 1381 (1965); Y. Sato, Y. Ida, S. Akimoto, High Temp. High Pressures 5, 679 (1973).
- 9. Theoretical Hugoniots based on third-order fi-Theoretical Hugoniots based on third-order fi-nite strain theory were constructed [G. F. Davies and E. S. Gaffney, *Geophys. J. R. As-tron. Soc.* 33, 165 (1973)] from the ultrasonic data of Z. P. Chang and E. K. Graham [J. Phys. *Chem. Solids* 38, 1355 (1977)] for the B1 phase, using the following values: $\rho_0 = 3.345$ Mg/m³, $K_{0s} = 112.5$ GPa, $K_0' = 4.79$, $\gamma_0 = 1.505$ (γ/V V = constant); where ρ_0 is the density, K_{0s} is the adiabatic bulk modulus and K_0' its pressure deadiabatic bulk modulus and K_0 its pressure de-rivative, and V is volume. All necessary parame-ters are experimentally constrained except for ters are experimentally constrained except for the volume dependence of the Grüneisen param-eter (γ), which introduces only a minor uncer-tainty. These parameters were estimated for the B2 phase, guided by systematics [G. F. Davies, *Geophys. J. R. Astron. Soc.* **44**, 625 (1976); (11)]: $\rho_0 = 3.76$ Mg/m³, $K_{0s} = 115$ GPa, $K_0' = 5$, $\gamma_0 = 1.51$ ($\gamma/V = \text{constant}$); the transition ener-ever E = 80 k/m³ ($R_{0s} = 100$ k/m³). $\gamma_0 = 1.51$ ($\gamma/\nu = constant$); the transition energy $E_{tr} = 80$ kJ/mole. Theoretical Hugoniots for the B1 and B2 phases based on the modified electron gas theory (4) were constructed with the same thermal properties as above, correcting the theoretical bulk moduli according to H. E. Hite and R. J. Kearney [J. Appl. Phys. 38, 5424 (1967)] and R. A. Bartels and V. H. Vetter [J. Phys. Chem. Solids 33, 1991 (1972)]. Shock temperatures were estimated by determining the thermal offset between abiabat and Hugoniot, based on the finite strain calculations and a Debye-Grüneisen model for the specific heat [T. J. Ahrens, C. F. Petersen, J. T. Rosenberg, J. Geophys. Res. 74, 2727 (1969)].
- 10. The apparent difference in transition pressures may be due to either thermal or kinetic effects: may be due to either thermal or kinetic effects: for example, an offset of a few gigapascals due to kinetics is found for the {100} orientation of NaCl transforming under shock [J. N. Fritz, S. P. Marsh, W. J. Carter, R. G. McQueen, Natl. Bur. Stand. (U.S.) Spec. Publ. 326 (1971), p. 201]. Alternatively, this difference in transition pressures could be due completely to the higher temperatures achieved under shock, implying an outcome of the order of the 13 Urople opy decrease on the order of 4 to 13 J/mole-K at the transition.
- K at the transition.
 I. C. Jamieson, in *High Pressure Research*, M. Manghnani and S. Akimoto, Eds. (Academic Press, New York, 1977), p. 209; H. H. Demarest, Jr., C. R. Cassell, J. C. Jamieson, *J. Phys. Chem. Solids* 39, 1211 (1978).
 Z. A. F. Wells, *Structural Inorganic Chemistry* (Oxford Univ. Press, Oxford, ed. 4, 1975); R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Soci. B* 25, 975 (1969); see also (1, 2).
- Snanon and C. 1. Prewit, Acta Crystallogr. Sect. B 25, 925 (1969); see also (1, 2). L. Liu and W. A. Bassett, J. Geophys. Res. 78, 8470 (1973); H. K. Mao and P. M. Bell, 84, 4533 (1979); W. J. Carter, S. P. Marsh, J. N. Fritz, R. G. McQueen, Natl. Bur. Stand. (U.S.) Spec. Publ. 336 (1971) p. 146 13.
- 16
- (19), w. J. Caltel, S. F. Malsh, J. N. Filz, K. G. McQueen, Nail. Bur. Stand. (U.S.) Spec. Publ. 326 (1971), p. 146.
 A. Jayaraman, Phys. Rev. Lett. 29, 1674 (1972).
 A. M. Dziewonski, A. L. Hales, E. R. Lapwood, Phys. Earth Planet. Interiors 10, 12 (1975); D. L. Anderson and R. S. Hart, J. Geophys. Res. 81, 1461 (1976).
 For example, at 110 GPa the temperature on the Hugoniot, about 2850 K (10), is identical to estimated mantle temperatures [F. D. Stacey, Phys. Earth Planet. Interiors 15, 341 (1977)].
 F. Birch, J. Geophys. Res. 57, 227 (1952); R. G. McQueen, S. P. Marsh, J. N. Fritz, *ibid.* 72, 4999 (1967); L. V. Al'tshuler and I. I. Sharipdzhanov, Izv. Acad. Sci. USSR Earth Phys. No. 3 (1971), p. 167; D. L. Anderson, C. Sammis, T. Jordan, Science 171, 1103 (1971); L. Liu and A. E. Ringwood, Earth Planet. Sci. Lett. 17. and A. E. Ringwood, Earth Planet. Sci. Lett. 28, 209 (1975).
- 18. K. K. Turekian and S. P. Clark, Jr., Earth Plan-K. K. Turekian and S. P. Clark, Jr., Earth Plan-et. Sci. Lett. 6, 346 (1969); L. Grossman and J. W. Larimer, Rev. Geophys. Space Phys. 12, 71 (1974); A. E. Ringwood, Composition and Pe-trology of the Earth's Mantle (McGraw-Hill, New York, 1975).
- New York, 1975). We are very grateful to R. A. Bartels, M. M. Abraham, and Y. Chen for generously providing sample material. We thank R. G. Gordon and J. C. Jamieson for helpful comments and dis-cussions. Work supported by NSF grants EAR 75-15006A01 (California Institute of Technology) and EAR 76-81703 (Carnegie Institution of Washington). This is contribution 2328 from the Washington). This is contribution 3258 from the Division of Geological and Planetary Sciences,
- California Institute of Technology. Present address: Department of Geological Sci-ences, Harvard University, Cambridge, Mass. 02138.

21 May 1979

SCIENCE, VOL. 206