point it is appropriate to comment that use of the olivine-clinopyroxene geothermometer (*23*) for mineral inclusions of the eclogitic suite is invalid because olivine has not yet been observed to coexist in a diamond with either pyrope-almandine garnet or the associated clinopyroxene of the eclogitic suite.

The above results for both the ultramafic and eclogitic suites of inclusions illustrate the information that can be obtained from investigation of these minerals in diamond. Unfortunately, the relatively simple models used in the determination of pressure and temperature do not consider the effect of several important element substitutions, notably chromium, on the various partitionings. Nevertheless, as in other studies (*5*, *8*) the pressures and temperatures calculated in these models are internally consistent and fall within the anticipated ranges for mantle material.

It has been observed that specific kimberlite diatremes often contain multiple intrusions of kimberlite, each with possible characteristic suites of diamond morphologies. Such a phenomenon may also be reflected in the mineral inclusions in diamond, thus one particular pipe may contain considerably more minerals of one suite than the other. For example, in diamonds from the Premier mine eclogitic garnet and clinopyroxene are the major phases, whereas mineral inclusions of the ultramafic suite are less common. However, the diamonds examined from this pipe may have been obtained from one particular kimberlite facies in the mine. Since several distinct lithologies of kimberlite occur in the Premier Pipe (*24*), obviously more detailed sampling is necessary. This problem of sampling is a major factor in almost all studies of inclusions in diamond to date, but it is hoped that future investigations will be undertaken on diamonds from known areas within specific kimberlite pipes. The results of such studies would then be directly comparable with current investigations of the xenoliths from kimberlite (*25*) and should add considerably to our understanding of mantle mineralogy and chemistry.

HENRY O. A. MEYER
HSIAO-MING TSAI
Department of Geosciences, Purdue University, West Lafayette, Indiana 47907

References and Notes

1. G. C. Kennedy and B. E. Nordlie, *Econ. Geol.* **63**, 495 (1968).
2. H. O. A. Meyer and F. R. Boyd, *Geochim. Cosmochim. Acta* **36**, 1255 (1972).
3. B. J. Wood and S. Banno, *Contrib. Mineral. Petrol.* **42**, 109 (1973).
4. B. J. Wood, *ibid.* **46**, 1 (1974).
5. F. R. Boyd, *Geochim. Cosmochim. Acta* **37**, 2533 (1973).
6. I. D. MacGregor, *Am. Mineral.* **59**, 110 (1974).
7. P. H. Nixon and F. R. Boyd, in *Lesotho Kimberlites*, P. H. Nixon, Ed. (Lesotho National Development Corp., Maseru, 1973), p. 67.
8. I. D. MacGregor and A. R. Basu, *Science* **185**, 1007 (1974).
9. E. D. Jackson and T. L. Wright, *J. Petrol.* **11**, 405 (1970).
10. H. G. Wilshire and E. D. Jackson, *J. Geol.* **83** 313 (1975).
11. J. C. Mercier and N. L. Carter, *J. Geophys. Res.* **80**, 3349 (1975).
12. L. Thomsen, *Science* **188**, 1130 (1975).
13. N. V. Sobolev, *Trans. Inst. Geol. Geophys.*, Issue 183, Akademiia Nauk SSSR (Siberian Branch) (1974).
14. M. Prinz, D. V. Manson, P. F. Hlava, K. Keil, *Phys. Chem. Earth* **9**, 797 (1975).
15. H. O. A. Meyer, *Science* **160**, 1446 (1968).
16. J. J. Gurney and G. S. Switzer, *Contrib. Mineral. Petrol.* **39**, 103 (1973).
17. B. T. C. Davis and F. R. Boyd, *J. Geophys. Res.* **71**, 3567 (1966).
18. J. Akella, *Carnegie Inst. Washington Yearb.* **73**, 273 (1974). Akella has also studied the solubility of Al_2O_3 in enstatite, but unfortunately the data are only useful above 1100°C, and would thus be only applicable to one of the inclusion assemblages.
19. R. D. Warner and W. C. Luth, *Am. Mineral.* **59**, 98 (1974). A major problem in all current studies of using the diopside-enstatite solvus for determining temperatures is the uncertainty in the exact location of the solvus. Recent determinations by C. E. Nehru and P. J. Wyllie [*Contrib. Mineral. Petrol.* **48**, 221 (1974)], T. Mori and D. H. Green [*Earth Planet. Sci. Lett.* **26**, 277 (1975)], and D. H. Lindsley and S. A. Dixon [*Geol. Soc. Am. Abstr. with Programs* **7**, 1171 (1975)] are available but give conflicting results. Accordingly, we have used the Davis and Boyd (*17*) data to be consistent with previously published studies on xenoliths from kimberlite.
20. J. Akella and F. R. Boyd, *Carnegie Inst. Washington Yearb.* **73**, 269 (1974).
21. H. J. Milledge, *Nature (London)* **190**, 1181 (1961).
22. A. Raheim and D. H. Green, *Contrib. Mineral. Petrol.* **48**, 179 (1974).
23. M. Powell and R. Powell, *ibid.* **48**, 249 (1974).
24. C. Frick, *Extended Abstracts, International Conference on Kimberlites*, Cape Town (1973), p. 119.
25. F. R. Boyd and P. H. Nixon, *Phys. Chem. Earth* **9**, 431 (1975); I. D. MacGregor, *ibid.*, p. 455; J. J. Gurney, B. Harte, K. G. Cox, *ibid.*, p. 507.
26. H.-M. Tsai and H. O. A. Meyer, unpublished data.
27. R. Berman, in *Physical Properties of Diamond*, R. Berman, Ed. (Clarendon, Oxford, 1965), p. 371.
28. A. Akimoto and Y. Syono, in *Accurate Characterization of the High Pressure Environment*, E. C. Lloyd, Ed. (Special publication, National Bureau of Standards, Washington, D.C., 1971). p. 273.
29. F. R. Boyd and J. L. England, *J. Geophys. Res.* **65**, 749 (1960),
30. K. Ito and G. C. Kennedy, *Mineral. Soc. Am. Spec. Pap.* **3**, 77 (1970).
31. A. E. Ringwood, I. D. MacGregor, F. R. Boyd, *Carnegie Inst. Washington Yearb.* **63**, 147 (1964).
32. V. S. Sobolev, N. V. Sobolev, Yu. G. Lavrent'yev, *Dokl. Akad. Nauk SSSR* **207**, 164 (1972).
33. N. V. Sobolev, A. I. Botkunov, Yu. G. Lavrent'yev, L. N. Pospelova, *Zap. Vses. Mineral. Ova.* **100**, 558 (1971).
34. N. V. Sobolev, M. A. Gnevushev, L. N. Mikhailovskaya, S. I. Futergendler, E. I. Shemanina, Yu. G. Lavrent'yev, L. N. Pospelova, *Dokl. Akad. Nauk SSSR* **198**, 190 (1971).
35. We thank Dr. H. J. Milledge for providing the diamonds used in this study, and also Dr. J. Moreau for the analysis of Jag.-4 inclusion. Support for this investigation is provided by NSF grants GA-36141 and GA-43990. H.M.T. acknowledges support from a David Ross fellowship, Purdue Research Foundation. Dr. R. H. McCallister provided constructive criticism of the manuscript, for which we are grateful.

23 December 1975

High-Pressure Physics: The 1-Megabar Mark on the Ruby R_1 Static Pressure Scale

Abstract. *Ruby crystals were subjected to a static pressure greater than 1 megabar in a diamond-windowed pressure cell. The pressure was monitored continuously by observing the spectral shift of the sharp fluorescent* R_1 *ruby line excited with a cadmium-helium gas-diffusion laser beam. One megabar appears to be the highest pressure ever reported for a static experiment in which an internal calibration was employed.*

Until recently, the limit to most high-pressure experimentation was approximately 300 kbar. That was the pressure to which internal calibration extended (for example, the volume equation of state of sodium chloride); it was also the pressure at which mechanical failure of apparatus usually occurred. In 1975 there were two reports of internally calibrated experiments at 500 kbar (*1*, *2*), both of which employed extensions of the National Bureau of Standards (NBS) calibration (*3*) of pressure dependence of the wavelength of the R_1 ruby fluorescence line. The NBS calibration showed the spectral shift to be linear to 291 kbar, and required serious revision (a factor of 2 at 500 kbar) of previous fixed point scales (*4*), from which pressures had earlier been estimated (*5*).

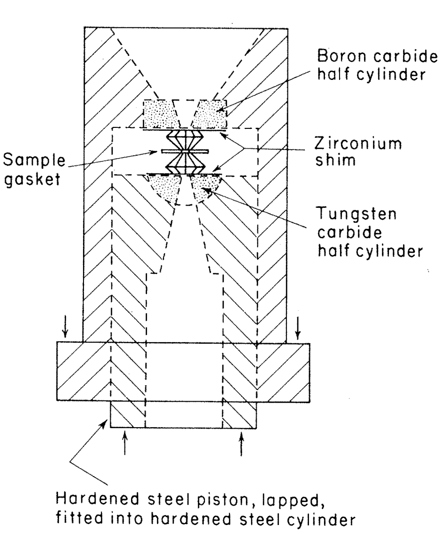

Fig. 1. Simplified diagram of diamond pressure cell, after Mao and Bell (*6*). The two half-cylinders shown are of identical shape. The axis of the lower one is normal to the page; the axis of the upper one lies in the plane of the page. An upper half-cylinder of boron carbide is used for x-ray diffraction of the sample under pressure; it was replaced with a tungsten carbide half-cylinder for the experiments reported here. The upper portion of the outer cylinder is 3.2 mm in diameter. The work area of the diamonds (not drawn to scale) is 1.5×10^{-3} cm^2.

We report here experiments in which pressures of 1 Mbar were reached, as measured by a further extension of the new NBS scale. The data are reproducible and can be easily compared with other types of calibration. The estimated uncertainty in pressure is no greater than 10 percent. To the best of our knowledge, this is the highest static pressure ever reached in an experiment in which an internal calibration was employed.

The difference between external and internal calibration of pressure is fundamental. External procedures usually involve monitoring mechanical loading of high-pressure apparatus. However, the loading is not transmitted to an internal sample because the apparatus deforms, and as parts begin to yield it is not possible to determine the internal pressure.

In the experiments reported here, it was possible to monitor the sample being pressurized with a new diamond-windowed cell. The cell was designed for static experimentation in the megabar pressure range, which was inaccessible with previous apparatus. Ruby fluorescence in the cell was excited by a laser beam, and its wavelength was monitored continuously with a spectrometer linked to the pressure cell by a fiber optic bundle.

The improved diamond pressure cell used in the experiments has been described in detail by Mao and Bell (*6*) and is shown diagrammatically in Fig. 1. The apparatus consists of two single-crystal diamonds opposed as pressure anvils. A scissors-shaped lever-block assembly is spring-loaded to apply a mechanical advantage of 2. The diamonds are supported by half-cylinder seats of tungsten carbide with a zirconium shim (0.001 inch thick) placed between the low-pressure-bearing surfaces. The half-cylinders are adjusted to achieve and maintain excellent alignment of the diamonds (to better than one-half a Newton color fringe interference of the diamond faces) during an experiment. A sheet (0.010 inch thick) of work-hardened steel (*7*) is placed between the high-pressure diamond faces, and then a crystal of ruby is placed on the steel and pressed into it as the diamond anvils are squeezed together. Blue laser light (*8*), wavelength 441 nm, is used to excite fluorescence in the ruby. Spectrometer and detector systems are the same as previously described (*6*), except that the photomultiplier tube in the experiments was cooled to –50°C to reduce dark noise (*9*).

Before the experiments were done we observed the sodium chloride B1–B2 (NaCl-CsCl structure types) transition at 291 kbar (*1*) and simultaneously measured the wavelength of the R_1 ruby line. A single ruby fragment was monitored each time an experiment was done. The observed spectral shift of the R_1 ruby line in a typical experiment and the corresponding pressures from a linear extension of the NBS scale are listed in Table 1. The intensity of the R_1 ruby line appeared to diminish slightly as the pressure was increased to the megabar range. No sign of mechanical failure was observed in the diamonds, and with improved support it should be possible to increase the pressure to at least 1.5 Mbar.

Table 1. Observed spectral shift ($\Delta\lambda$) of the R_1 line of a ruby crystal at high pressure. The shift of 106 Å (values in italics) corresponds to the B1–B2 transition in NaCl. Pressures below 291 kbar were determined from the NBS calibration curve (*2*). Pressures above 291 kbar were determined from a linear extension of the NBS curve.

$\Delta\lambda$ (Å)	Pressure (kbar)
30	83
75	206
106	*291*
180	495
225	619
290	797
310	823
320	880
370	1018

The capability of routinely experimenting at pressures in the megabar range has far-reaching applications. It will be possible to study insulator-metal transitions and numerous other proposed physical and chemical changes in materials at high pressures (*10*). The accessibility of this pressure range coupled with the high temperatures already reached (*2*) makes it possible to experiment directly at the conditions of the earth's core.

H. K. Mao
P. M. Bell

Geophysical Laboratory,
Carnegie Institution of Washington,
Washington, D.C. 20008

References and Notes

1. G. J. Piermarini and S. Block, *Rev. Sci. Instrum.* **46**, 973 (1975).
2. P. M. Bell and H. K. Mao, *Carnegie Inst. Washington Yearb.* **74**, 399 (1975).
3. G. J. Piermarini, S. Block, J. O. Barnett, R. A. Forman, *J. Appl. Phys.* **46**, 2774 (1975).
4. H. G. Drickamer, *Rev. Sci. Instrum.* **41**, 1667 (1970).
5. N. Kawai and S. Mochizuki, *Phys. Lett. A* **36**, 54 (1971).
6. H. K. Mao and P. M. Bell, *Carnegie Inst. Washington Yearb.* **74**, 402 (1975).
7. This material was kindly supplied by L. C. Ming, University of Rochester.
8. Meterologic Instruments, Inc., Bellmawr, N.J., He-Cd laser ML 442.
9. Products For Research Inc., Danvers, Mass., Carnot-cycle cooler.
10. P. M. Bell and H. K. Mao, *Carnegie Inst. Washington Yearb.* **73**, 507 (1974).
11. We wish to thank G. J. Piermarini and S. Block of the National Bureau of Standards and A. Van Valkenburg of the Geophysical Laboratory for useful suggestions and assistance in this project.

29 December 1975; revised 8 January 1976

Surface Predominance of Trace Elements in Airborne Particles

Abstract. *A number of minor and trace elements including Be, C, Ca, Cr, K, Li, Mn, Na, P, Pb, S, Tl, V, and Zn present in coal fly ash are found to be preferentially concentrated on the particle surfaces. Environmentally effective concentrations of these elements are thus much higher than indicated by conventional bulk analyses.*

It is now well established that toxic trace elements such as As, Be, Cd, Cr, Mn, Ni, Pb, Sb, Se, Tl, V, and Zn are being mobilized in the atmosphere in association with particles emitted from fossil fuel combustion and conversion (*1*). It has also been shown (*1–3*) that the specific concentrations of many of these elements (in micrograms per gram of fly ash) increase with decreasing particle size in fly ash derived from coal combustion. Consequently, the highest trace element concentrations are encountered in small particles which most readily pass through control devices, which remain suspended in the atmosphere for long periods, and which deposit in the innermost regions of the human respiratory tract when inhaled (*2, 4*).

Recently, it has been suggested (*5*) that this dependence of elemental concentration on particle size occurs because certain elements (or their compounds) are volatilized in the high-temperature coal combustion zone and then condense uniformly onto the surfaces of entrained fly ash particles as the temperature falls. Such surface deposition would give rise to the observed inverse dependence of specific concentration on the diameter of the approximately spherical fly ash particles (*2, 3*).

If surface deposition does occur, either as a result of the postulated mechanism or otherwise, then the actual concentrations of toxic material present at the point of contact of a particle with living tissues may be substantially higher than hitherto supposed on the basis of bulk analyses. To establish whether the surface concentrations of toxic elements are higher, we have determined the dependences of several elemental concentrations as a function of depth in individual coal fly ash particles.

The fly ash samples studied were collected in the stack systems of two coal-fired power plants burning midwestern U.S. bituminous coals. One plant was of small capacity and obsolete design utilizing a chain grate stoker; the other was a large modern plant with an input of pulverized coal.