aromatics is $[(39 - 16)/39 \times 100] = 59$ percent.

Data from the 49 samples were used to prepare the graph shown in Fig. 2. The relative persistence of types of hydrocarbon in decreasing order are: cycloparaffins, isoparaffins, and aromatics. The *n*-paraffins were not plotted; they appear to be the least persistent of the hydrocarbons as indicated by their consistently low concentrations in ocean water.

There are numerous possible mechanisms that may account for the low relative aromatic hydrocarbon content of ocean water. Evidence available at present suggests that biogenic sources do not yield aromatic hydrocarbon mixtures (*5*). On this basis then, hydrocarbons from biogenic sources serve as a diluent to aromatics. In principle, for example, a 50/50 mixture of biogenic and petroleum hydrocarbons would cause the aromatics of the petroleum mix to be diluted by a factor of 2. Two different methods for estimating hydrocarbon sources (*3, 6*) were applied to our data, and the results from both methods suggest that hydrocarbons along tanker routes are primarily from petroleum. Based on available knowledge, then, it does not appear that low aromatic concentrations are caused by a dilution effect from the presence of biogenic hydrocarbons.

Our study provides no explanation of why the aromatics may be preferentially removed from ocean water. Numerous processes give rise to changes in hydrocarbons. An evaluation of these processes has been presented in a workshop on petroleum in the marine environment convened by the National Academy of Sciences (*4*, pp. 45–48 and 58–60). One conclusion was that evaporation accounts for extensive loss of C_{15} and lighter hydrocarbons from the environment. Dissolution of hydrocarbons into the water column is another mechanism for the disappearance of hydrocarbons, and this pathway seemed to be particularly applicable to C_{10} and lighter hydrocarbons.

Neither evaporation nor dissolution, however, explains the selective disappearances of C_{14} and heavier aromatics. Other processes that may contribute to this behavior include degradation of hydrocarbons caused by chemical or biological reactions, or both. Still another possibility is removal of the hydrocarbons by absorption onto particulate matter followed by settling of the particulate to the ocean bottom. There would appear to be sound reasons to investigate all of these possibilities.

R. A. BROWN
H. L. HUFFMAN, JR.
Exxon Research and Engineering Company, Linden, New Jersey 07036

References

1. R. A. Brown, T. D. Searl, J. J. Elliott, B. G. Phillips, D. E. Brandon, P. H. Monaghan, in *Proceedings of Joint Conference on Prevention and Control of Oil Spills* (American Petroleum Institute, Washington, D.C., 1973), pp. 505–519.
2. R. A. Brown, J. J. Elliott, J. M. Kelliher, T. D. Searl, *Adv. Chem. Ser.*, in press.
3. P. H. Monaghan, D. E. Brandon, R. A. Brown, T. D. Searl, J. J. Elliott, *Measurement and Interpretation of Nonvolatile Hydrocarbons in the Ocean: Part I, Measurements in Atlantic, Mediterranean, Gulf of Mexico and Persian Gulf* (Exxon report prepared for the U.S. Department of Commerce, Maritime Administration, July 1974; available from the National Technical Information Service, Springfield, Va., as Document COM-74-11-634).
4. *Petroleum in the Marine Environment*, workshop at Airlie House, 21–25 May 1973. (National Academy of Sciences, Washington, D.C., 1975).
5. C. W. Bird and J. M. Lynch, *Chem. Soc. Rev.* **3** (No. 3), 309 (1974); J. W. Farrington and P. A. Meyers, in *Environmental Chemistry*, G. Eglinton, Ed. (Chemical Society, London, 1975), vol. 1, chap. 5.
6. J. W. Farrington, M. Teal, J. Quinn, T. Wade, K. Burne, *Bull. Environ. Contam. Toxicol.* **10** (No. 3), 129 (1973).

15 September 1975; revised 3 November 1975

Mineral Inclusions in Diamond: Temperature and Pressure of Equilibration

Abstract. *Two distinct suites of minerals included in natural diamond occur and probably represent different physical and chemical conditions during diamond growth. Minerals of the ultramafic suite appear to have equilibrated in the range 1000° to 1300°C between 45 and 65 kilobars, whereas the temperature range for minerals of the eclogitic suite is 850° to 1250°C. At present, models relating the partitioning of magnesium and iron between coexisting phases are not sufficiently rigorous to determine a value for the pressure of equilibration of these eclogitic suite inclusions.*

The occurrence of large, clear, and well-formed diamonds has led to the general belief that natural diamond has formed as a stable phase within the upper mantle of the earth (*1, 2*). Accordingly, detailed mineralogical and chemical study of the minerals included within diamond during its growth can provide significant data regarding the chemistry and physics of the upper mantle, as well as providing an insight into the genesis of diamond.

At the present time there is considerable interest in the use of chemical relationships among coexisting minerals as a means of elucidating the temperatures and pressures of formation (*3–6*). Perhaps the most interesting result of such studies to date has been the development of petrological models for the upper mantle based upon the study of xenoliths from kimberlite and basalt (*5, 7–9*). These models have been criticized (*10–12*) but do represent a major step forward in petrological studies and interpretation of mantle xenoliths.

In general the initial crystallization and subsolidus changes in silicate minerals are well documented from both experimental and naturally occurring systems. In contrast, little is known concerning the initial and subsequent stages of diamond growth; however, it is possible to suggest probable pressure and temperature conditions in which diamond crystallized by applying the knowledge of silicate systems to the pertinent minerals included in natural diamond.

Several silicate minerals occur as primary inclusions, and abundant among them are olivine, garnet, enstatite, and diopside (*2, 13, 14*). Depending upon their major element chemistry the minerals may be assigned to one of two distinct mineral suites. For example, olivine (Fo_{92-96}), enstatite (En_{94}), chrome-pyrope garnet (*15, 16*), and diopside belong to the ultramafic suite, whereas pyrope-almandine garnet and clinopyroxene with appreciable contents of Na and Al are assigned to the eclogitic suite. Although minerals of each individual suite may coexist in a single diamond, the presence of minerals from both suites together within the same diamond has not been observed. It is thus probable that these two suites represent either different chemical or physical conditions, or both, in which diamond has formed.

There is, at present, insufficient data for a statistical analysis of the relative abun-

Table 1. Temperature and pressure of equilibration for mineral inclusions of ultramafic suite in diamond.

Diamond No.	Assemblage	Temperature (°C)	Pressure (kb)	Reference
1 Pre-7-75	Diopside-enstatite-chrome pyrope	1270	65	(*26*)
2 Jag-4-75	Diopside-enstatite	1010	53	(*26*)
3 No. 1	Diopside-enstatite-pyrope almandine	1050	45	(*14*)
4 No. 3	Diopside-enstatite	970	60	(*14*)

dances of minerals in each suite, or of the abundance of either suite throughout the world. Undoubtedly olivine is the most common inclusion, followed closely by chrome-pyrope garnet. Both of these minerals belong to the ultramafic suite and thus there is a suggestion that this is more prevalent than the eclogitic suite. Unfortunately, at this time there are not enough data to discuss the abundance or restriction of either suite to a single diamond-bearing locality.

Boyd (*5*) and MacGregor and Basu (*8*) have used the enstatite-diopside solvus (*17*) to estimate temperatures of equilibration for diopsides occurring in garnet and spinel-lherzolites from kimberlitic and basaltic diatremes. This temperature being known, the pressure is determined from the Al_2O_3 content of the coexisting enstatite (*6, 18*) provided that both diopside and enstatite have formed in equilibrium with either garnet or spinel. A significant problem with the use of the diopside solvus to estimate temperature is the uncertainty of the magnitude of the shift of the solvus with increasing pressure (*11, 19*). However, with this problem in mind it is possible to make some assessment of the temperature and pressure of equilibration for the mineral inclusions of the ultramafic suite. The results obtained for four assemblages of the ultramafic minerals are presented in Table 1.

All four diamonds contain diopside and enstatite, whereas diamonds 1 and 3 also contain garnet. For the assemblage in diamond number 1 from the Precambrian Premier kimberlite pipe, South Africa, the temperature was determined with the Ca/(Ca + Mg) ratio of both diopside and enstatite (*18*) as well as the partitioning of Fe and Mg between garnet and diopside (*20*). The temperatures obtained by the different methods agreed to within 50°C. The garnet in this diamond is a chrome-pyrope and contains almost 7 percent Cr_2O_3 by weight. The effect of chromium on the partitioning of Al_2O_3 and Cr_2O_3 between garnet and enstatite is unknown. For this reason no correction for Cr_2O_3 in the enstatite has been made in determining the pressures.

Table 2. Temperature of equilibration for coexisting garnet-clinopyroxene inclusions of eclogitic suite in diamond.

Diamond No.	Temperature (°C)	Reference
5 Pre-12-75	1250	(*26*)
6 D15-G15	1130	(*2*)
7 No. 33	1005* 885*	(*14*)
8 No. 36	1080	(*14*)
9 No. 38	1000	(*14*)
10 No. 42	850	(*14*)
11 M-46	925	(*32*)
12 MB-1	905	(*33*)
13 880	1115	(*34*)

*See text for explanation.

The temperatures and pressures quoted in Table 1 should be taken, however, as estimates, since the effect of pressure on the diopside solvus is unknown and has thus not been considered in this study. The uncertainty in the temperature determined by means of a propagation of errors calculation is ±15°C for assemblage 1 and ±30°C for the others. These temperature ranges translate into an uncertainty of about ±4 kb in the pressure. Nevertheless, the values obtained do provide some indication of the conditions pertinent to the physicochemical history of diamond. It is important to note that these conditions represent the last equilibration temperatures recorded by the inclusions and host diamond, which may or may not correspond to the original conditions under which diamond crystallized. However, it is somewhat reassuring that the values of pressure and temperature listed in Table 1 all lie within the diamond stability field and close to the region previously suggested for diamond formation (Fig. 1) (*15*). Furthermore, as a general comment with regard to diamond and associated inclusions, two univariant equilibriums define a pressure-temperature region in which growth must have occurred: (i) the lower bound is the graphite-diamond stability curve (Fig. 1) and is based on the premise that diamond crystallizes within its stability field in nature, and (ii) the upper bound is the coesite-stishovite equilibrium curve (Fig. 1) and is pertinent in view of the occurrence of coesite as an inclusion in natural diamonds (*21*).

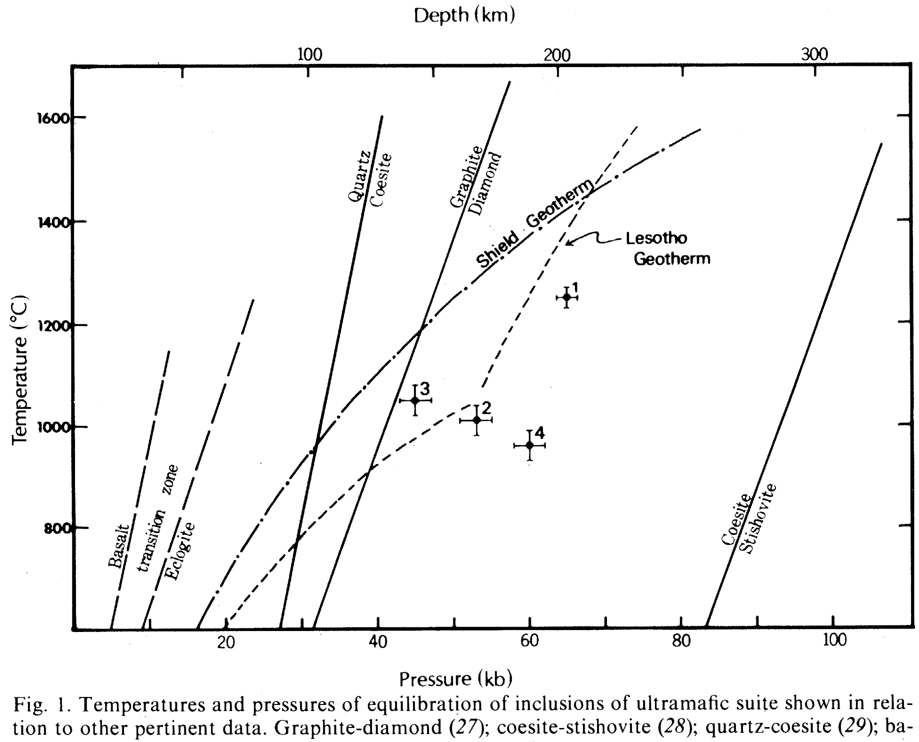

Fig. 1. Temperatures and pressures of equilibration of inclusions of ultramafic suite shown in relation to other pertinent data. Graphite-diamond (*27*); coesite-stishovite (*28*); quartz-coesite (*29*); basalt-eclogite (*30*); shield geotherm (*31*); Lesotho geotherm (*5*).

Several diamonds contain coexisting garnet and clinopyroxene inclusions that belong to the eclogitic suite. Using the models of Akella and Boyd (*20*), and Raheim and Green (*22*), which are based on experimental data between 30 and 44 kb, we have determined possible temperatures of equilibration. In general, both models produce similar temperatures, and the results are shown in Table 2.

The temperatures obtained range between 850° and 1250°C but are on average similar to those of the ultramafic suite. The range of temperatures may be due to the diamonds having been obtained from different geographic localities and also from different horizons within the upper mantle. Furthermore, some of the inclusions are not in direct contact with each other and thus the partitioning of Fe/Mg does not always represent final equilibration temperature, but probably represents the initial Fe/Mg ratio frozen-in at the time of incorporation of the assemblage into the diamond. This is perhaps exemplified by the garnet-clinopyroxene assemblage in diamond number 7. This diamond contained ten isolated pyroxenes and one garnet-pyroxene pair in contact (*14*). The temperature determined from the phases in contact is lower than that obtained from the chemistry of the isolated minerals. At this 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).

→ 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*).

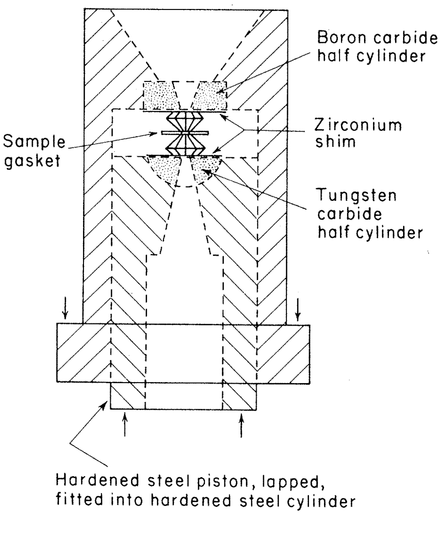

Fig. 1. Simplified diagram of diamond pressure cell, after Mao and Bell (*6*). The two half-cylinders shown are of identical shape. The axis of the lower one is normal to the page; the axis of the upper one lies in the plane of the page. An upper half-cylinder of boron carbide is used for x-ray diffraction 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.