of the continental shelf but largely on the rate at which the river can supply sediments to the nearshore zone. In summary, wave forces are the primary mechanism whereby the sea reworks and molds deltaic sediments; the construction of flat offshore profiles is the basic mechanism by which the river is able to overcome wave effects.

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9. Supported by Geography Programs, Office of Naval Research, under contract N00014-69-A-0211-0003, project NR 388 002, with the Coastal Studies Institute, Louisiana State University.

13 December 1971; revised 25 February 1972 ■

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# Pressure Measurement Made by the Utilization of Ruby Sharp-Line Luminescence

*Abstract.* *A rapid, convenient technique for precision pressure measurement in the diamond-anvil high-pressure cell, which makes use of the sharp-line* (R*-line) luminescence of ruby, has been developed. The observed shift is −0.77 ± 0.03 reciprocal centimeters per kilobar for* $R_1$ *and −0.84 ± 0.03 reciprocal centimeters per kilobar for* $R_2$ *to lower energy and is approximately linear in the range studied (to 22 kilobars). Line-broadening has been observed in some instances and has been tentatively identified with nonhydrostatic conditions surrounding the ruby sample.*

A persistent deficiency in the routine use of the high-pressure diamond cell (*1*) has been the inability to determine with simplicity and accuracy the pressure on the sample contained between the diamond anvils. In many reports pertaining to the diamond cell, pressures have been determined generally from the applied load on the anvils with no other factors taken into consideration (*2*). This procedure usually results in an unsatisfactory estimate of the pressure, particularly in the higher pressure ranges where errors as large as ± 30 percent have been estimated. Less frequently, pressures in the diamond cell have been determined from lattice parameters of powdered NaCl measured by x-ray diffraction techniques (*3*), and, in at least one instance, pressures were determined from shifts in the optical absorption bands in nickel dimethylglyoxime (*4*). These methods for measuring pressure in the diamond cell are either grossly inaccurate, insensitive, or extremely inconvenient, and it is for these reasons that we think the diamond pressure cell has not realized its full potential as a research tool.

Table 1. Fixed points used to calibrate measurements of pressure in the diamond cell at room temperature.

| Substance | Transition* | Transition pressure (kbar) |
|---|---|---|
| $CCl_4$ | L-I | 1.3 |
| $CCl_4$ | III-IV† | 40 |
| $H_2O$ | L-VI | 9.6 |
| $H_2O$ | VI-VII | 22.3 |
| $n$-$C_7H_{16}$ | L-I | 11.4 |
| $C_2H_5Br$ | L-I | 18.3 |

* The abbreviation L refers to the liquid state, and the Roman numerals designate solid phases. † The III-IV transition point of $CCl_4$ was not included in the data reported in Fig. 2 because of the nonhydrostatic character of the medium surrounding the ruby sample.

We have discovered what appears to be a new technique for continuous pressure measurement based on the the shift in wavelength of the sharp-line (*R*-line) luminescence in ruby samples. In all of our experiments to date we have used the diamond-anvil apparatus with metal gaskets (*5*), but the method is applicable to any pressure system with optical access. In practice a small fragment of pink ruby crystal (0.05 percent $Cr^{3+}$, by weight) is placed in the diamond cell with the material under study. The sample is excited by radiation from a super-high-pressure mercury arc which is filtered to eliminate the red wavelengths. A photoelectric detection system is used with a grating monochromator and a strip-chart recorder. A typical luminescence spectrum of a small fragment of ruby contained in the diamond pressure cell at ambient atmospheric pressure and room temperature is shown in Fig. 1, curve A. A similar spectrum is shown in curve B, except that here the pressure on the ruby crystal is approximately 22.3 kbar. The ruby sample from which this spectrum was obtained was enclosed in the diamond cell with an equilibrium mixture of ices VI and VII, a point known to be at 22.3 kbar and room temperature on the equilibrium phase diagram (*6*). The sample chamber, which is defined by the gasket wall and the two diamond anvils, is a right circular cylinder approximately 0.3 mm in diameter and 0.15 mm high. Readily measurable signals can be obtained from ruby samples occupying 20 percent of the cell volume. This amount of ruby does not interfere with other measurements in the cell.

In order to calibrate our measurements in the diamond cell, we have used the freezing points of the liquids listed in Table 1 along with two solid-solid transition points. These materials were selected because they have well-characterized transition pressures and

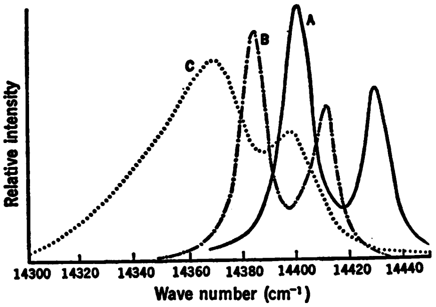

Fig. 1. The *R*-line luminescence spectra of a crystal of ruby in the diamond cell: curve A, ruby sample at ambient atmospheric pressure; curve B, ruby sample in a mixture of ices VI and VII at approximately 22.3 kbar; and curve C, ruby sample in a mixture of $CCl_4$ III and IV at an average pressure of 40 kbar (nonhydrostatic environment). (Peak heights are arbitrary.)

also because they were used in an earlier report which described the calibration of nickel dimethylglyoxime as a pressure standard (*4*). The data were treated by least-squares curve-fitting and were plotted on the graphs shown in Fig. 2. The graphs indicate that the line shift is linearly proportional to the pressure up to the highest calibration point used with a slope of $-0.77 \pm 0.03$ $\text{cm}^{-1}$/kbar for $R_1$ and $-0.84 \pm 0.03$ $\text{cm}^{-1}$/kbar for $R_2$. The standard deviations shown here represent the statistical variations.

In principle, the room-temperature luminescence line width of 11.0 $\text{cm}^{-1}$ (*7*) allows a calibration of pressure to within a fraction of a kilobar. In this work, however, a standard deviation of 1.5 kbar was calculated, which means that other uncertainties of approximately 1 kbar exist.

In the case of $Cr^{3+}$ in $Al_2O_3$ the dependence of the wavelength on pressure probably cannot be calculated theoretically at this time. Our measurements indicate that the shift is, however, linear, at least to 22 kbar, under the assumption of the fixed points listed in Table 1. The small compressibility of the sapphire host lattice (*8*) makes it unlikely that there will be a great departure from this observed linearity in the usable range of the diamond cell.

We have chosen the *R*-lines of ruby for the measurement for several reasons. In earlier pressure measurements made by optical means broad lines or bands have been involved (*4*). In the case of broad lines, one must assume that the band shape does not change with pressure, but this, in the previous cases studied, is obviously not the case. In ruby purely electronic transitions are responsible for the *R*-lines, and there is no Stokes shift present. The transitions take place between the $^2E$ and $^4A_2$ crystal field split states of the $Cr^{3+}$ ion. The $^2E$ state is split into two states $\bar{E}$ and $2\bar{A}$, and it is this splitting which is responsible for the two peaks. Actually each peak in the spectra of Fig. 1 is a doublet with a splitting of 0.38 $\text{cm}^{-1}$ coming from the splitting of the ground state $^4A_2$ into Kramer's doublets. This splitting is observable only at low temperatures.

Our values for the shift of the $^2E$ levels ($-0.77 \pm 0.03$ and $-0.84 \pm 0.03$ $\text{cm}^{-1}$/kbar are in fair agreement with earlier results. Langer and Euwema (*9*) reported a constant of $-0.90 \pm 0.05$ $\text{cm}^{-1}$/kbar for the pressure coefficient of the ruby *R*-lines up to 10 kbar obtained by an absorption method. However, in that report it is not clear at what temperature this result was obtained, and neither is it clear to which line this constant refers. Paetzold (*10*) reported similar data up to 1 kbar also by an absorption method. His values at 290°K are $-0.93$ $\text{cm}^{-1}$/kbar for $R_1$ and $-0.82$ $\text{cm}^{-1}$/kbar for $R_2$. Because ruby *R*-lines have a large temperature coefficient [approximately $-0.14$ $\text{cm}^{-1}$/°K at room temperature (*7*)], the sample temperature is of vital importance in all measurements made by this technique. The thermal shift at room temperature corresponds to a pressure shift of approximately 0.17 kbar/°K. Hence, care should be taken that the excitation light does not heat the ruby sample, although it must be of sufficient intensity to provide detectable signals.

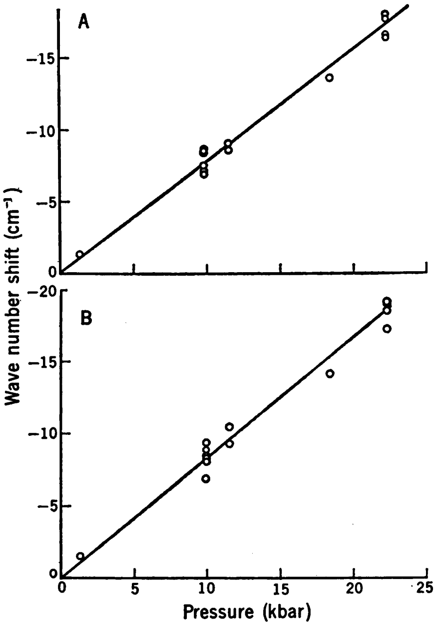

Fig. 2. The shift in the *R*-line luminescence of a crystal of ruby as a function of pressure to 23 kbar: (A) $R_1$ shift; (B) $R_2$ shift.

The spectrum for a sample of ruby placed in the cell with $CCl_4$ and at a pressure which produced an equilibrium mixture of phases III and IV is shown in Fig. 1, curve *C*. A large broadening is observed for the luminescence lines which we think is an indication of a nonhydrostatic environment. The transition III-IV in $CCl_4$ is known to be sluggish and usually requires thermal energy in order for it to occur. The shifts indicate an average pressure of 40 kbar, a pressure at which we know from other measurements that no broadening of the ruby lines occurs in a hydrostatic environment. This example illustrates the potential of the technique in identifying and studying nonhydrostatic phenomena.

Preliminary measurements at higher pressures in which lattice parameters of NaCl were used to calibrate the pressures indicate no significant departure from linearity to 70 kbar and no degradation of the line shape of the luminescence. We are also extending the range of measurements with the ruby to determine its temperature limitations. On the basis of data in the literature, it appears that the luminescence is useful to approximately 200°C. Above this temperature line-broadening effects become dominant. At low temperatures the technique should be somewhat more precise because the lines become somewhat sharper (*7*). The thermal shifts of the peaks will require accurate temperature control to give precise pressure measurements. Because $Al_2O_3$ is chemically quite inert, it is almost an ideal material for an internal pressure sensor and, after accurate calibration, may be useful as a secondary pressure standard. The inertness of the ruby makes it likely that experiments involving temperature cycling above 200°C will not destroy the usefulness of this measurement technique.

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28 January 1972