

To maximize the displacement, the magnetic disturbance field is assumed perpendicular to the average or undisturbed field. Consider first the case where the disturbance at all levels equals its value measured at the surface; this implies a very extensive current source in the ionosphere. In this case it can be shown that the displacement of a field line, in the auroral zone, at 1,000 km. above the conducting core, is about 0.015Δ km., where Δ is the disturbance in γ (10^{-5} gauss) units.

In the case of more localized ionospheric currents Δ increases with altitude, and the overall effect of this, for a given surface value of the disturbance, is to give a smaller displacement than that above. Consider an overhead cylindrical current causing the disturbance. Then Δ is (A/d) , d being distance from the current and A a constant. Therefore, Δ is less than (A/h) where h is the vertical component of d . Taking Δ as (A/h) the desired displacement of a line in 1,000 km. height can readily be found, and it increases slowly as the current diameter is reduced. For a current of diameter greater than about 0.1 km. the calculated displacement is less than the 0.015 Δ km. found before. But for such small diameters, replacing (A/d) by (A/h) causes a gross overestimate of the displacement; and furthermore, ionospheric currents have a much larger scale than 0.1 km. Adding the disturbance due to the induced current in the core does not alter this result.

Thus the displacement of 0.015Δ km. (Δ in γ) is an upper limit to the movement of auroral phenomena due to field distortion. This distance is very small. It equals 50 km. (almost $\frac{1}{2}^\circ$ of latitude) only if Δ has the extreme value of $3,300\gamma$; while if Δ is less than $1,300\gamma$, as in most magnetic storms when the K index does not exceed 7, the displacement is less than 20 km. Only by very slow changes, such as those with the period of the sunspot cycle, can the lines of force be moved through great distances at low altitudes.

Observations of the radiation points of auroral coronæ⁴ show that the displacements of the field lines between the Earth's surface and the auroræ are well within the limits expected from the foregoing.

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¹ Rees, M. H., and Reid, G. C., *Nature*, **184**, 539 (1959).

² Alfvén, H., "Cosmical Electrodynamics", Chapter 2 (Oxford, 1950).

³ Lahiri, B. N., and Eriç, A. T., *Phil. Trans. Roy. Soc., A*, **237**, 509 (1939).

⁴ Abbott, W. N., *Canad. J. Phys.*, **36**, 643 (1958).

GEOCHEMISTRY

High-pressure Phase Transformations in Laboratory Mechanical Mixers and Mortars

THE mechanical action of simple laboratory grinders, mortars and similar devices has occasionally been used to assist in chemical reactions in addition to performing their primary physical functions. Among these chemical reactions are phase trans-

formations. That the effect is due to some kind of a pressure component in the mechanical action may appear obvious, but the magnitude of the pressures is not readily appreciated, nor can it be calculated or measured. However, in the course of work in this laboratory on the high-pressure polymorphism of lead dioxide (PbO_2), the information that a phase identical with the new high-pressure polymorph, which had been shown to be stable only in the region above 10,000 bars, had been formed by simple grinding¹ was noted with no little surprise. The observation was promptly confirmed by grinding a small amount (2 gm.) of the common rutile form (I) of lead dioxide in a mechanical mortar and pestle combination of laboratory pattern. Grinding in air for a few hours converted an estimated one-third to the denser orthorhombic form (II). After preliminary work, it transpired that nothing new in principle had been added to some similar results which had been reported by Burns and Bredig² on the transformation of calcite to aragonite by grinding in a mortar. The high-pressure phase was formed from the low-pressure one, the amount of change was dependent on time, and subsequent heating would form the low-pressure phase. A significant difference is that phase equilibrium and thermochemical studies³ place the calcite-aragonite transformation at about 3,000 bars at room temperature, which is considerably lower than the 10,000 bars necessary for the lead oxide I \rightleftharpoons II transformation.

The obvious question that arises is whether or not the high-pressure types are actually being formed in their field of stability, or whether the shearing stresses so dominant in such an environment either alter the relative free-energy relations of the two forms or permit metastable nucleation of the high-pressure phase. Therefore, other substances with known p - t relationships between polymorphs (work in this laboratory, with L. Azzaria and W. B. White) were chosen for further study: MnF_2 , BeF_2 , SiO_2 , PbO , Sb_2O_3 , B_2O_3 and BaSO_4 . Their transition pressures at room temperature (extrapolated from our equilibrium data obtained at higher temperatures) are near 9,500, 15,500, 13,500, 5,500, 10,000, 18,500 and 30,000 bars respectively. It was found that grinding for several hours in the mortar assembly under air or nitrogen (where oxidation was a possibility) would produce varying amounts (as determined in every case by X-ray diffraction) of the high-pressure phases of PbO , PbO_2 , CaCO_3 , MnF_2 , Sb_2O_3 and BeF_2 (questionable) in decreasing order. Also of new but related interest is our finding that the 'quenchable' transitions in calcium carbonate and lead dioxide and in many other selected phases could be effected (partially), in a few minutes to 2 hr., by the action of a small rapidly vibrating mixer-grinder. The type used (trade name 'Wig-L-Bug') is common in spectroscopic laboratories and was used with a metal vial and ball and 50-100 mgm. of sample. Furthermore, it was found that the same (*vide supra*) relative effectiveness in forming detectable amounts of the high-pressure phases was evident in the action of the 'Wig-L-Bug'. Of the highest-pressure phase, BeF_2 (cesite), only a trace was formed. Making allowances for the very sluggish nature of the quartz-cesite transition of silica and the more complex relation⁴ and serious hydration problem in the new high-pressure B_2O_3 polymorph, it appears that pressures in the region of 10-20,000 bars are being

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applied intermittently to the fine grains subjected to the 'grinding' actions in each of these types of apparatus.

That a real pressure component is operative in the action of the mortar assembly was shown by increasing or reducing the weight of the pestle-head assembly by means of a suitable weight or counterpoise to twice or one-sixth the normal weight. Thus, although about 20 per cent conversion of calcite to aragonite was achieved by only 13 hr. of grinding under normal weight, and about 5 per cent in the same time under half the normal weight, more than 100 hr. under the one-sixth weight failed to produce detectable amounts of aragonite. Presumably the greatly reduced weight of pestle is not sufficient to generate pressures greater than 3,000 bars on the calcite, leaving it still in its equilibrium field. Another example is the litharge-massicot transition of lead oxide in which litharge is the low-pressure (and also low-temperature) form. The action of the light-weight pestle (under nitrogen) will drive massicot readily to the stable litharge (this being merely the effect on kinetics due to bond breakage), but if litharge is the starting material no change to massicot is observed. To accomplish the latter the heavier pestle is necessary, presumably since only then is enough pressure available to reach the massicot field. On the other hand, the heavy pestle will produce some litharge when acting on massicot, because all values of pressure up to the maximum must be encountered, since the apparatus of necessity produces a whole 'spectrum' of pressures. A similar example was found on grinding a mixture of the senarmonite and valentinite forms of Sb_2O_3 .

Thus it is clear that the stresses causing fracture generally operate to accelerate reactions, although the effect is larger in some pairs of structures than in others. Superimposed on this kinetic effect is a hydrostatic pressure effect. Detailed verification of the separability of the 'stress' and pressure effects has been effected⁶ in an uniaxial high-pressure device⁶ so modified that a slow continuous oscillating displacing shear action by the movement of one piston through 2° of arc is applied to samples (of the above compounds) simultaneously subjected to high pressures and temperatures. It is sufficient to mention here that it has been established that stresses in the form of displacing shear do not alter equilibrium pressures of transitions (within the experimental limits), although they do contribute enormously to the rates of such reactions.

Burns and Bredig² have already pointed out that the possibility of phase transformations taking place on grinding must be taken into account in explaining discrepancies in the behaviour of calcium carbonate. Our results show that: (1) 'grinding' or mixing, in both 'automatic mortars' and 'Wig-L-Bug'-type shakers not only can introduce appreciable amounts of surface and strain energy but also can quite generally cause the formation of high-pressure phases; (2) the effective maximum in the 'spectrum' of hydrostatic pressures obtained in such instruments is not less than about 15,000 bars; (3) in addition to the quasi-hydrostatic pressures exerted, the shearing stresses causing the breakage of bonds and/or the storage of strain energy result in a very marked acceleration on the kinetics of such transformations.

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¹ Zaslavsky, A. I., Kondrashov, Y. A., and Tolkachev, S. S., *Doklady Akad. Nauk.*, **75**, 559 (1950). Bode, H., and Voss, E., *Z. Elektrochem.*, **60**, 1053 (1956).

² Burns, J. H., and Bredig, M. A., *J. Chem. Phys.*, **25**, 1281 (1956). At the time of oral presentation (see ref. 5) of this work, Prof. J. Goldsmith directed our attention to his work with J. C. Jamieson on the grinding of magnesian calcites, etc., reported orally at the American Crystallographic Association, Milwaukee meeting, 1958.

³ MacDonald, G. J. F., *Amer. Min.*, **41**, 744 (1956). Jamieson, J. C., *J. Chem. Phys.*, **21**, 1385 (1953). Clark, S. P., *Amer. Min.*, **42**, 564 (1957).

⁴ Dachille, F., and Roy, R., *J. Amer. Ceram. Soc.*, **41**, 78 (1959).

⁵ Dachille, F., and Roy, R., oral presentation, Geol. Soc. Amer., Pittsburgh meeting, November 3 (1959).

⁶ Dachille, F., and Roy, R., *Z. Krist.* (in the press).

Strontium-90 in the 'Mixed Layer' of the Atlantic Ocean

OCEANOGRAPHY and marine geochemistry have only relatively recently been able to take advantage of isotopic tracer techniques; unfortunately, the conceptual framework devised for isotope studies in biochemistry and physiology is not readily applicable to systems of very large spatial extension.

In considering the significance of the ocean reservoirs in the geochemistry of carbon dioxide, and in using the distribution of carbon-14 to derive rates of ocean mixing in both vertical and horizontal planes, it has been conventional¹ to divide the oceans into shallow surface reservoirs assumed to be well mixed, and deep reservoirs assumed to be only slowly renewed from the surface. Since, in some applications, the quantitative expression of this picture is extremely sensitive to the assumed depth of the surface reservoir, and to its rate of renewal from below, it seems important to point out that these parameters are measurable by using relatively short-lived radioisotopes, which are added to the system at the surface. In the case of the Atlantic Ocean, North and South, this condition is well met by radioactive strontium-90 from bomb test fall-out. To the Atlantic, strontium-90 has been added, measurably, only as fall-out to the ocean surface. In this form the isotope is wholly soluble in water²; and in sea water, the dilution of the radioisotope by both stable strontium and stable calcium in solution is so great that neither biological nor chemical processes produce significant changes in strontium-90 concentration. Thus, its vertical transport depends wholly on vertical movement of the water in which it is dissolved.

As a part of an extended study of the marine geochemistry of long-lived radioisotopes from fall-out, we are obtaining a number of series of measurements of the change in strontium-90 concentration with depth in the ocean. Some of these measurements, together with descriptions of the methods employed, have been published³. We now present (Table 1) seven series of strontium-90 analyses, all but one previously unreported. These series agree in showing very significant concentrations of radiostrontium at depth in the open ocean, both north and south of the equator. The number of analyses is still too few to justify very precise integration of the curves of strontium-90 versus depth, but an average concen-