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## INFLUENCE OF "DISPLACIVE-SHEARING" STRESSES ON THE KINETICS OF RECONSTRUCTIVE TRANSFORMATIONS EFFECTED BY PRESSURE IN THE RANGE 0-100,000 BARS

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Earlier results showed that ordinary laboratory grinders and mixers were able to convert several phases (*e.g.*  $\text{PbO}_2$ ,  $\text{MnF}_2$ ,  $\text{CaCO}_3$ ,  $\text{BeF}_2$ , etc.) into their respective high-pressure forms, which at equilibrium require 10-15,000 atmospheres at room temperature. Hence, experiments were devised to attempt to separate the effect of hydrostatic pressure from those of shearing stresses and "bond-breakage".

A study of the influence of shearing stresses superimposed upon quasi-hydrostatic pressures of up to 100,000 bars at temperatures below  $550^\circ\text{C}$  has been made possible by the development of a simple apparatus. This consists of the Bridgman uniaxial-type apparatus—with a provision for continuous rotation of the bottom piston very slowly back and forth through a  $2^\circ$  arc. The sample is heated externally; and displacive-shearing runs with pressure and temperature automatically controlled can be made for periods exceeding several days if desired. The results clearly separate the influence of "hydrostatic" pressure itself upon reaction rates from the effect of the added "displacive-shearing" stresses. Further, from the results it becomes clear that equilibrium relations between phases are not altered by the shearing stresses. The influence of this type of stress is illustrated for the transformations  $\text{SiO}_2 \text{ quartz} \rightleftharpoons \text{SiO}_2 \text{ coesite}$ ;  $\text{PbO}_2(\text{MnF}_2)_{\text{rutile}} \rightleftharpoons \text{PbO}_2(\text{MnF}_2)_{\text{orthorhombic}}$ ;  $\text{PbO}_{11\text{tharge}} \rightleftharpoons \text{PbO}_{\text{masseicot}}$ ;  $\text{CaCO}_3 \text{ calc.} \rightleftharpoons \text{CaCO}_3 \text{ arag.}$  and the formation of  $\text{NaAlSi}_2\text{O}_6$  (jadeite). Reactions which cannot usually be made to proceed below  $300\text{--}350^\circ\text{C}$  can be performed at temperatures between  $0\text{--}150^\circ\text{C}$ .

Increases in rates of reaction of two or three orders of magnitude can be attained at a given pressure and temperature. It is not clear whether this should be ascribed to strain energy stored in the lattice or merely to breakage of bonds.

### INTRODUCTION

It has recently been thoroughly demonstrated in our laboratory<sup>1</sup> that the combination of pressure, "shearing stresses" and bond breakage found in a variety of laboratory grinders is very effective in forming high-pressure phases of all types. These results are briefly summarized first. Using ordinary "automatic" laboratory grinders it was possible to convert the low pressure forms of  $\text{PbO}_2$ ,  $\text{MnF}_2$ ,  $\text{CaCO}_3$ ,  $\text{PbO}$ ,  $\text{Sb}_2\text{O}_3$ , and  $\text{BeF}_2$  into their corresponding high pressure polymorphs in a matter of hours of grinding at room temperature. The identification of the phases was established in all cases by powder X-ray diffractometry. Furthermore, the same effects, *i.e.* with neither fewer nor more substances, could be obtained by using the common vibrator-shaker mills (trade name: Wig-L-Bug) used in spectroscopic laboratories or dentists' offices. From earlier independent phase-diagram studies of these phases in our laboratory, it was shown that if the high-pressure phases were being formed in their respective regions of thermodynamic stability, then the pressures involved in these simple laboratory devices are of the order of 15,000 bars.

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hydrostatic pressure by runs in our apparatus. This has been done for some eight or nine substances. In Fig. 2 we have combined some of the information obtained on five phases. The general pattern of the data is as follows: On each sub-diagram is presented as a heavy line the equilibrium  $p-t$  curve (determined in separate studies in

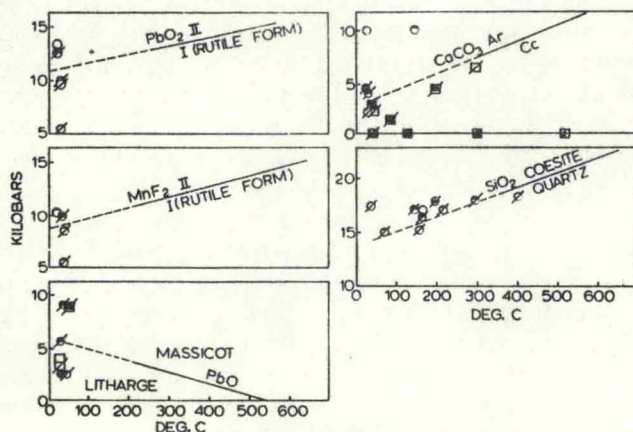


Fig. 2. The  $p-t$  equilibrium lines for five polymorphic pairs determined by phase equilibrium studies are shown as heavy lines. Note that the equilibrium work ends at temperatures near  $300^{\circ}\text{C}$ . The light dashed lines are extensions to low temperature of the equilibrium curves, and are independent of the results of the shearing experiments shown with diagonal bars. It can clearly be seen that within the limits of experimental error the application of these shearing stresses does not displace the position of equilibrium. Symbols: black filling for high-pressure forms. In respective plots squares are for massicot or aragonite, circles are for litharge or calcite, starting materials.

these or other laboratories). It will be noticed that this  $p-t$  phase boundary usually is determined experimentally only in the region above about  $300^{\circ}\text{C}$ ; below this the line is extrapolated down to room temperature as a dashed line. Note that the experimental runs with the displacive shear apparatus are not the basis for drawing the curve. We are attempting to present in each case a comparison between the extrapolated curve and the displacive shear runs. All such runs are shown with a diagonal across the symbol. Each of the phases in Fig. 2 can be briefly discussed in turn:

**$\text{PbO}_2$ .** The equilibrium curve reported by White, Dachille and Roy<sup>5</sup> was based on points from  $300\text{--}550^{\circ}\text{C}$ . It will be recalled that grinding in a mortar or Wig-L-Bug easily produces the high pressure form at room temperature. However, it can clearly be seen that shearing runs at  $9\text{--}10,000$  bars (below the extrapolated equilibrium curve) failed to convert the rutile form; as soon as the hydrostatic ambient pressure is raised to  $12,000$  bars (above the curve) conversion to the high form takes place rapidly. In general, therefore, the data from the shearing runs fit rather well with the equilibrium data within experimental limits.

**$\text{MnF}_2$ .** The study by Azzaria and Dachille<sup>6</sup> has shown that this phase acts as a nearly perfect model for  $\text{PbO}_2$  with two structurally analogous polymorphs in equilibrium along a  $p-t$  line which is close to that for  $\text{PbO}_2$  itself. Here again the shearing experiments fit in with the extrapolated curve. The presence of small amounts of one phase in the stability field of the other is attributed here both to failure of

quenching as well as to the pre-pelleting procedure. (The transition for  $MnF_2$  is much faster than the analogous one for  $PbO_2$ .)

*PbO*. The rather peculiar phase relations in this system, reported elsewhere<sup>5</sup>, are due to the negative slope for the transition which also has the remarkably small enthalpy of transition of less than 0.25 cal/g for a reconstructive phase change. The shearing runs will convert litharge to massicot at room temperature only above the pressure required by the curve but not below it. Similarly, massicot will convert to litharge at room temperature at pressures below the curve by the action of displacive shear. Without this action the massicot will not revert to the stable form, as shown by the black-without-diagonal circle in the figure. A number of shearing runs in the region of 6000 bars at room temperature, using either litharge or massicot, showed that rapid changes to the appropriate form occurred. These runs are represented by the barred circle which falls on the extension of the  $p-t$  equilibrium line.

*CaCO<sub>3</sub>*. The calcite-aragonite transition of this compound has been studied by others<sup>7-9</sup> and from their work it is reasonable to place the equilibrium pressure at room temperature in the region of 3000 bars. Jamieson used heat of solution data at temperatures below 100° C. MacDonald used the uniaxial high pressure apparatus and Clark used compressed nitrogen in an internally heated bomb. The high pressure experiments resulted in essentially the same  $p-t$  equilibrium although Clark's results place the pressures higher by about 1000 bars. Both workers had to restrict their data to runs made at temperatures above 250-350° C. The  $p-t$  line drawn in the  $CaCO_3$  sub-diagram of Fig. 2 is an average of their results. Our shearing experiments show very plainly that calcite will remain unchanged at room temperature below the equilibrium pressure but will form aragonite in a few hours when above this pressure.

*SiO<sub>2</sub>*. The quartz-coesite transformation is of considerable current interest. The equilibrium curve after Dacheille and Roy<sup>2</sup>, shown in Fig. 2, was based on runs from 350-650° C. Although considerable effort was made to produce coesite in shearing experiments at room temperature, no clear-cut evidence for coesite can be presented. At 70-100° C coesite is just detectable while it can be made well at 150° C and above. A very large number of shearing runs were made in the whole temperature range but none below the extrapolated curve produced coesite, while those above the curve did produce coesite easily.

From these results in five separate systems it becomes clear that the shearing action itself does not alter the equilibrium relations between the phases, at least not to an extent that it can be measured with our tools. Hence, the action of a mortar grinder and of a Wig-L-Bug is composed of two separable functions, each of them essential. The first is the generation of pressures of the order of 10-20,000 atmospheres sufficient to put substances in the stability field of a new polymorph. The second is to increase the rates of reaction due to the shearing stresses and/or the bond breakage involved. We shall turn our attention now to the question of the rates of the reactions involved.

#### INFLUENCE OF "DISPLACING SHEAR" ON RATES OF REACTIONS

In the above cases of polymorphism are several excellent qualitative examples of the effect of such shearing. A few data will be cited in each case, reserving the most extensive set on  $PbO_2$  for later discussion.

*MnF<sub>2</sub>*. A static pressure run of 60 hours at room temperature above the equi-

librium pressure will form none or very little of the II phase, but under the same conditions, the addition of shear will result in over 50 % conversion in only three hours. However, higher static pressures will drive the transition quite readily almost to completion at other conditions; for example, 72 hours, 25° C and 40,000 bars, or 10 minutes, 150° C, 80,000 bars.

*PbO*. Litharge only partially converts to massicot when held in the massicot field under static pressure at room temperature, but essentially complete conversion will occur at 9000 bars in four hours with the addition of shear. Freshly prepared massicot remains unchanged at room temperature at 2500 bars for 24 hours but the addition of shear produces 20 % litharge in only 30 minutes and more than 85 % in four hours. (It is of interest here to mention that in the equilibrium work on this transition under hydrothermal conditions—White, Datchille and Roy (*op. cit.*)—massicot remained unchanged for days at 262° C and 10,000 psi, well within the litharge field. The addition of a small amount of mechanical action during similar runs served to “nucleate” the litharge.)

*CaCO<sub>3</sub>*. Static pressure experiments on calcite at room temperature failed to form aragonite at 10,000 bars, very definitely in the aragonite field, after 24 hours. Even at this high pressure only 10–15 % of aragonite is formed at 150° C after 72 hours. The displacive shear experiments at room temperature and 4–5000 bars show plainly the formation of over 50 % aragonite in only 16 hours. The reverse reaction apparently is a more difficult one. Numerous shearing experiments in the calcite field to form calcite from well-crystallized natural aragonite failed at room temperature but were successful at 200° C and above. This reaction is usually accomplished only at 450–500° C at atmospheric pressure, and it remains very sluggish at static pressure near the equilibrium curve even at 400° C.

*SiO<sub>2</sub>*. Our general experience has been that coesite forms very slowly at 325–375° C close to the equilibrium pressure. At 150° C and 17,000 bars no coesite was formed after 24 hours, but the addition of displacive shear at these conditions produced nearly 40 % conversion in various runs.

#### QUANTITATIVE STUDIES

Several quantitative studies on the rates of these reactions are now in progress. Some of the data on the *PbO<sub>2</sub>* system only will be presented here. In Fig. 3 is presented the percentage conversion *versus* time plot for three temperatures with static pressure held constant at 40,000 bars. Part of the conversion noticed at room temperature is no doubt due to the unavoidable shearing stresses applied in starting a “static” run. In Fig. 4 we present a plot of percentage conversion *versus* time for runs made at room temperature at three different pressures, but with the addition of displacive shear. In Fig. 5 percentage conversion in 10 minutes *versus* static pressure is shown for two temperatures. Fig. 6 compares the percentage conversion in 10 minutes for different pressures under shear conditions at room temperature and 300° C. In Fig. 7 we present some results of a rate study (Hoffer, Datchille and Roy)<sup>10</sup> on a reaction in a ternary system: 2 jadeite ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ )  $\rightleftharpoons$  nepheline ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) + albite ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ). An example of the influence of shear is evident in the 60 % conversion to jadeite at 350° C and about 14,000 bars, conditions for which static runs produce less than 10 % jadeite. The typical activation energy “wall”,

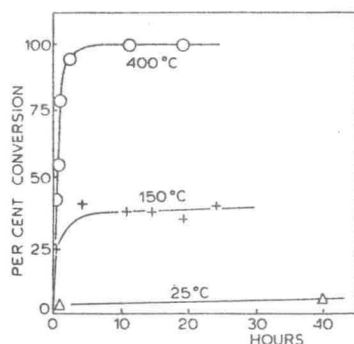


Fig. 3. Comparison of the extent of conversion effected at a constant pressure of 40,000 bars in the  $\text{PbO}_2$  I  $\rightarrow$  II transition at 25, 150, and 400°C under static uniaxial pressure conditions. In this and subsequent diagrams reproducibility of X-ray method and from run to run is  $\pm 10$  percent.

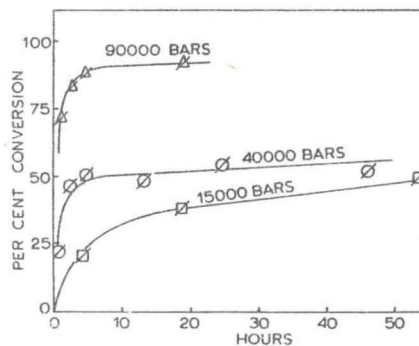


Fig. 4. Comparison of the extent of conversion of  $\text{PbO}_2$  I  $\rightarrow$  II at a constant temperature of 25°C at 15,000, 40,000 and 90,000 bars under displacing shear + uniaxial pressure conditions. Note that the effect of shearing on conversion at 40,000 bars may be estimated to be at least equal to that of 200°C. Points at 40,000 bars for two and four hours are averages of several runs.

and the influence of temperature at any one pressure or pressure at constant temperature are illustrated here also.

These data need hardly any comment as to the general influence of shear, pressure and temperature on this reaction. It appears that the addition of displacive shear at room temperature and 40,000 bars is about equal to the effect of using 200°C under static conditions, a conclusion very similar to one made by Bridgman<sup>11</sup> many years ago, without perhaps as many data available, when he stated "... in general one can expect to find transitions by the shearing method 100° to 150° below the temperature at which they become suppressed by internal viscosity for the volume method." Increases in conversion of 50–200 times can be found under the various conditions of reaction. Quantitative treatment of the influence of pressure on activation energies of these reaction and influence of shear on these rates is deferred to later publications.

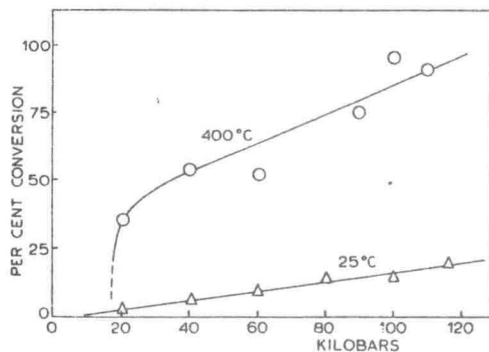


Fig. 5. Effect of temperature on the conversion  $\text{PbO}_2$  I  $\rightarrow$  II versus pressure for 25° and 400°C. Constant time of reaction is 10 minutes. Compare with the more rapid conversions due to the effect of shearing as shown in Fig. 6.

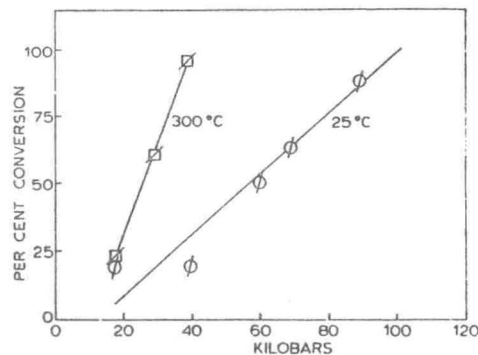


Fig. 6. Combined effect of temperature and shearing on the conversion of  $\text{PbO}_2$  I  $\rightarrow$  II versus pressure for 25° and 300°C. Constant time of reaction is 10 minutes.

The question of the mechanism for this increase in reaction rate with shear is still a moot one. One can conceive at least two explanations. The first is merely that when the shearing stress exceeds the ultimate strength of the material, bonds are broken, and in the reorganization of this matter the phase stable at the ambient

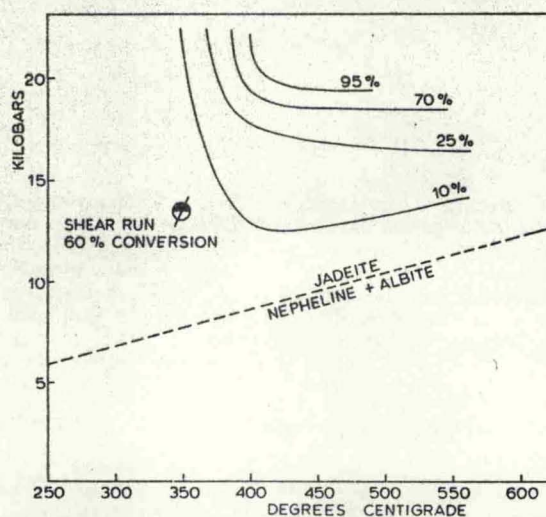


Fig. 7. Albite + Nepheline  $\rightarrow$  2Jadeite. This reaction has been studied at a large number of pressures and temperatures in the region above the extension of the  $p$ - $t$  equilibrium line of Robertson *et al.*<sup>12</sup>. The percent conversion in 40 hours of reaction is shown as contours for 10, 25, 70 and 95 percent conversion. Note that the addition of shearing increases the conversion to over 60% in a region of very low yield.

high pressures is nucleated and then continues to grow because of the pressure. One may contend that the actual amount of bond breakage due to comminution is really not enough in the apparatus used. On the other hand, to virtually every piece some shearing stress or torque is applied. The crystals respond by being strained—mutual displacement of ions from their equilibrium position—and the amount of energy stored as strain energy in the sample may, therefore, be quite considerable, and this strain energy could serve as a chemical tunnel through the activation energy wall. In an attempt to check this, oriented sections of single crystals of quartz and calcite have been subjected to this shearing action. Very little reaction was noted, and what coesite or aragonite was present was found to have no structural relation to the original quartz or calcite. This would tend to speak against the strain theory except for the fact that the efficient transmission of the shear to even a very thin plate is impossible. Only the surfaces appear to convert at all.

If the bond breakage picture is correct, new devices employing this principle will be important in industrial high pressure syntheses.

#### ACKNOWLEDGEMENT

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## DISCUSSION

A. WEGENER SLEESWIJK, Amsterdam (The Netherlands): Referring to the remarks about the heat input due to the friction: the calculation of Prof. Bridgman refers only, I believe, to the *overall* heating of the material. On the other hand the researches of Prof. Bowden at Cambridge University have shown conclusively the *local* heating of the grains may easily take the material to temperatures near the melting point. In this connection it might be interesting to know what the estimated energy input due to friction was.

R. A. LAUDISE, Murray Hill, N.Y. (U.S.A.): (1) Have you considered the possibility that due to the manner in which your "displacive stress" is applied that local heating such as is known in ordinary grinding operations may be taking place?

(2) Have you studied the effect of the rate of rotation and the angle through which the rotation takes place on the kinetics of transformations?

*Author's reply:* In reply to the first question of Laudise, which is similar to that of Dr. Wegener Sleswijk, it should be said that we have, of course, considered the question of "heating by friction" very seriously. The calculations we have carried out—quite analogous to those of Bridgman's—show that the whole sample cannot be heated by more than 5° C, and in all probability it may be as low as fractions of a degree. It is quite true, as the latter discussant has pointed out, that this does refer to a "bulk" heating. The reasons we have not given much further thought to this matter are:

(1) Even our calculations are extremely crude; to make calculations about "local" heating would require very far-reaching assumptions about the one as involved, the coefficients of friction etc.

(2) We believe that our data here provide the very best evidence that in fact the effect is *not* due to local heating. It should be noted that in every case we go from the high temperature (low pressure) phase to the low temperature (high pressure) phase. If there was a heating effect this would both favor the retention of the low pressure form as well as resulting in a diminished effect of shear with temperature.

If the "local heating" concept is applied to the question of the activation energy under shear, then we may be dealing only with a question of semantics. What we have described as the introduction of lattice strain—the mean relative displacement of the ions in the lattice from their *equilibrium* sites for that pressure and temperature—can be conceived of also as a quenching in of thermal vibrations corresponding to a much higher temperature. Local "heating" at a freshly broken surface must then also be said to be intense.

In reply to the second question by Laudise we do not have available as yet a wide enough range of rates of shear, but within our range (only 4:1) there is no marked change. We expect to try much greater rates shortly.

CYRUS KLINGSBERG, Washington D.C., (U.S.A.): If displacive shear is unlike isotactic pressure as a parameter except towards equilibrium conditions, then should we not expect a more frequent appearance of new metastable phases than are found?

*Author's reply:* This is a question of which we have been made aware, in the hope of finding new phases. It is true that we have not found any as yet but we have studied perhaps only 50 phases. Also it may be added that the disordered ZnS which can be produced by grinding either sphalerite or wurtzite is an example of such a phase, though a poor one.