GEOLOGICAL NOTES

EFFECTIVENESS OF SHEARING STRESSES IN ACCELERATING SOLID PHASE REACTIONS AT LOW TEMPERATURES AND HIGH PRESSURES[1]

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ABSTRACT

The use of displacive-shearing stresses in the study of phase equilibriums in opposed-anvil high-pressure apparatus has been of value in resolving the relationship of the anomalous polymorphic thorite-huttonite phases of $ThSiO_4$ and in achieving the first reversibility of the high-low–temperature forms of Nb_2O_5. Such stresses do not alter noticeably equilibrium, as shown previously by the examples of the calcite-aragonite and quartz-coesite transitions, among others, but do contribute markedly to increasing reaction rates at low temperatures. This is further illustrated in a kinetic study of the PbO_2-I$\rightarrow$II transition at 40 kb. from 25 to 400° C.

INTRODUCTION

The attainment of equilibrium is difficult in systems of the oxides of high-valency ions, and it is understandable that results obtained in laboratory studies or observed in mineral assemblages may occasionally be misinterpreted. To a degree, it may be possible to consider that one of the older concepts in petrology—that shearing stresses either are essential in the formation of particular minerals or actually alter stability relations among minerals—owes its origin to the fact that temperatures of some metamorphic processes were too low to establish equilibrium phase assemblages and that the phases actually observed were related to the presence or absence of the obvious stresses of orogenic activity.

The concept of specific equilibria for stress minerals (Harker, 1956) has been losing favor in the past two decades mainly because in this period of extensive laboratory investigation of petrologic problems, no evidence was found for the necessity of shearing stresses in preparing a particular

phase. This has been especially so since 1948 when the use of high-pressure water as a catalyst proved to be one of the most important aids in subsolidus oxide chemistry. Effective as they are, however, hydrothermal techniques have failed in the study of a number of oxide systems ($ThSiO_4$, Nb_2O_5, Sb_2O_3, SiO_2). More recently, new experimental data have been reported on the effect of very high pressures on accelerating subsolidus reactions, especially with the addition of displacive-shearing stresses (Hoffer, Dachille, and Roy, 1960; Dachille and Roy, 1961). It is interesting to note that the accelerating effect of shearing stresses was recognized clearly by Harker (1956) in the results of early work by Brewster, by Spring, and by Lea.

However, it was a note by Burns and Bredig (1956) that first recorded the apparently anomalous formation of aragonite from calcite merely by grinding in a mortar. Jamieson and Goldsmith (1960) studied a number of carbonates more extensively. Among their results they found that the MgO content of natural calcites controlled the transition to aragonite, suggesting a pressure maximum in the mortar. They also found evidence of the formation of solid solutions on grinding $MgCO_3$ and $MnCO_3$

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While this work was unknown to us, we had noted that it was indeed possible to make the dense orthorhombic form of PbO_2 in an ordinary automatic mortar. What was remarkable about this was that our own earlier equilibrium study showed that it required about 10 kilobars pressure (White, Dachille, and Roy, 1961) to enter the stability region of the orthorhombic PbO_2. A general study of such "grinding" operations was made and in a subsequent paper (Dachille and Roy, 1960) it was shown that in ordinary mortars and even in Wig-L-Bug–type mixers[2] it was possible to synthesize a wide variety of high-pressure phases, including those of PbO, PbO_2, $CaCO_3$, MnF_2, Sb_2O_3 and BeF_2. The question that was still unsolved was the cause of this unexpected ability to synthesize high-pressure phases in these simple devices. Was it due to the fact that the grains were actually subjected to pressures of the order of 15 kilobars, or was it due to an alteration of the relative free energies and hence of the equilibrium curve? Moreover, it was easily shown that merely generating pressures above the equilibrium curve is not enough to cause any of these reactions to proceed with a measurable velocity at room temperature. In order to separate the effects of pressure alone from the combined effect of shearing stresses applied at high pressures, series of reactions were studied in a rather simple adaptation of Bridgman-type opposed-anvil apparatus (Dachille and Roy, 1959, 1961). In this apparatus one can apply essentially hydrostatic pressures of 120–150 kilobars at a few hundred degrees centigrade for periods of several hours to days; in addition one can superimpose *at this pressure* under the same time and temperature conditions a "displacive-shearing" action continuously but alternating through a maximum amplitude of two degrees of arc every 15 seconds.

EXPERIMENTAL RESULTS
$CaCO_3$; SiO_2; JADEITE

Typical studies made with the modified opposed-anvil apparatus are those of the

[2] Crescent Dental Mfg. Co., Chicago, Illinois.

$CaCO_3$ calcite-aragonite, SiO_2 quartz-coesite and the albite + nepheline–jadeite reactions reported in 1960 at the Fourth International Symposium on the Reactivity of Solids (Dachille and Roy, 1961). The results showed that it has been possible to separate effects due to "grinding" and due to pressure, and further, that the P-T relations of the reactions are not affected by the "grinding" stresses, at least within experimental error.

$ThSiO_4$

The stability relations of the $ThSiO_4$ thorite-huttonite polymorphs are not unambiguously resolved. Mumpton and Roy (1961) give evidence that the *denser* huttonite is the phase stable at higher temperatures (certainly above 1,200° C.), and perhaps at all temperatures and pressures. They suggest, in a footnote, that crystallization from gels could result in a metastable phase, in this case thorite, which is by far the one most commonly found in nature. However, in the present work it was found that gels could react at 220° C. to yield either thorite or huttonite depending on the pressure, provided the crystallization was accelerated with the use of displacive shearing. Thus it is shown in figure 1 that when the gel is subjected to a static pressure of about 40 kilobars for 40 hours at 218° C. the product remains amorphous, but at pressures in this region the addition of displacive-shearing stresses for 20–40 hours produces either the thorite or huttonite phases, the huttonite forming at a higher pressure. Along with runs at other pressures and higher temperatures, with or without shear, it appears reasonable to deduce a univariant P-T equilibrium line with a negative slope equal to 52 ± 3 bars/C° as shown in figure 1. The negative slope agrees with the apparently anomalous condition of the less dense thorite being the low-temperature phase. (This relation also has been observed with the boehmite-diaspore [Erwin and Osborn, 1951], litharge-massicot [White *et al.*, 1961], γ-α Ca_2SiO_4 [Roy, 1958], and only a few other reconstructively related poly-

morphs.) Applying the Clapeyron equation with the usual assumptions of negligible differences of compressibilities (and thermal expansion), a first estimate of the enthalpy of the transition is calculated as 5.6 ± 0.3 kcal. per mole at room temperature. This value is of the same numerical range as those for the graphite-diamond (Rossini and Jessup, 1938) or the olivine-spinel (Dachille and Roy, 1960) reconstructive transitions.

havior of the two polymorphs. A geological connotation is that the very rare occurrence of huttonite might be related to its instability in the more accessible portions of the earth's crust where pressures and temperatures would be those of the thorite stability field.

Nb_2O_5

It was found that the shearing modification was useful to bring about the first and complete reversal of the Nb_2O_5-I (high-tem-
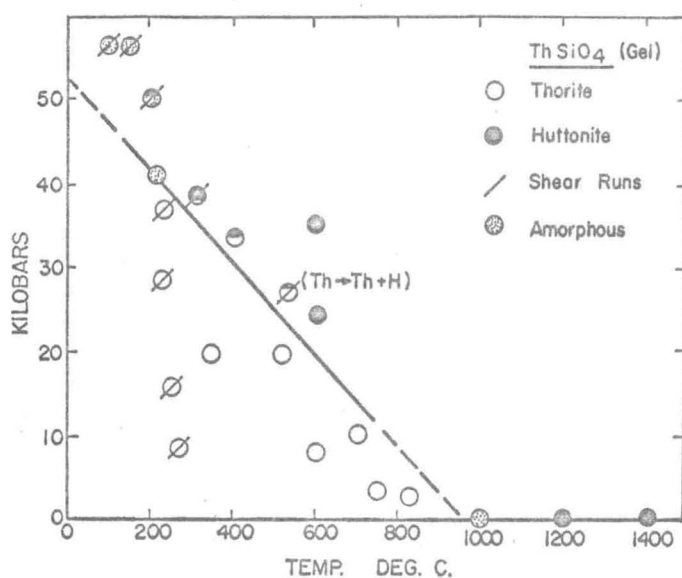

Fig. 1.—P-T diagram based on static and shear runs using $ThSiO_4$ "gel" starting material

It still has not proven possible to convert the huttonite to thorite by hydrothermal or shearing treatment in the thorite stability field, and this fact might justify withholding acceptance of figure 1 as the true equilibrium diagram. However, in a number of mortar runs in air of 3–20 hours' duration the noticeable breakdown of huttonite to an amorphous material was observed, whereas thorite was reasonably more persistent. Mechanical mortars have been found to generate pressures of the order of 10–20 kilobars (Dachille and Roy, 1960) in addition to the very considerable shearing stresses so that the conditions of these runs at room temperature fit very definitely in the thorite-phase field and might explain the comparative be-

perature) form to the III (low) form, at a temperature of only 350° C. at 7 kilobars pressure. This reversal also could be achieved, but to much lesser extent, under static conditions at considerably higher pressures and temperatures, but it never could be realized under the most intense hydrothermal conditions (Shafer and Roy, 1958). This further establishes the existence of Nb_2O_5 III as the stable low-temperature phase contrary to the suggestion of Holtzberg, Reisman, Berry, and Berkenblit (1941).

PbO_2-I→II QUANTITATIVE RESULTS

A more than qualitative picture of the influence of shear on the rate of reaction may

be obtained from a study of figures 2 and 3 summarizing the results of a large number of runs on the conversion of PbO_2 I→II. In these runs the starting material was the I (rutile) form of PbO_2, without the addition of any form of "mineralizer." Its conversion with time to the II (orthorhombic) form at
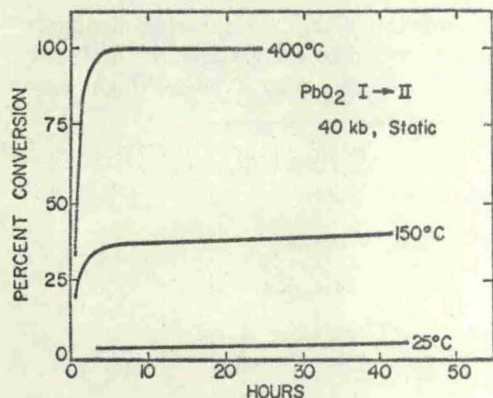

Fig. 2.—Isotherms at 40 kilobars for PbO_2 I→II transition showing the variation of conversion with time of run under static conditions.

different conditions of pressure and temperature was estimated by the use of integrated intensity ratios of selected X-ray diffraction lines of the two phases and an appropriate calibration curve obtained with the use of mixtures of the two phases. One set of runs was made at 40 kilobars under static conditions at three different temperatures—25°, 150°, and 400° C. Another set at the same temperatures and pressure but with the addition of displacive shearing shows very clearly the increase in conversion which results. (An intensification of shearing stresses under the application of higher pressures was shown by the increased conversion of a set of runs at 25° C., 90 kilobars. This might be expected as a consequence of the applied stresses having to overcome the gain in shear strength of material under pressure previously demonstrated by Bridgman [1935].)

From the data of figures 2 and 3, an approximate value of the activation energy of the reaction PbO_2 I→II both for the static and the shearing conditions may be calcu-

lated. This is done by assuming that the first-order reaction "constant" for each temperature (in each series) is directly proportional to the conversion to PbO_2 II in the same interval and, therefore, according to the Arrhenius relation, conversion is thus proportional to $e^{-A/KT}$. By calculating or by graphical means the activation energy, A, is found to be about 3.5 kcal/mole for the static runs and about 1.4 kcal for the displacive-shearing runs.[2] The reaction rates for the shearing runs therefore would be of the order of four to thirty times greater than for the equivalent static runs in the temperature range of 30°–500° C.

From the studies described above and in the references, it is seen that the presence or absence of shearing stresses is an important variable in determining the actual as-
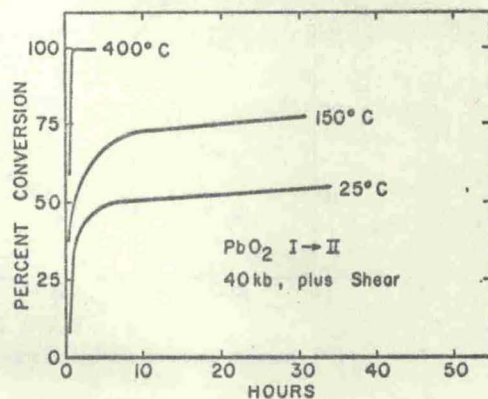

Fig. 3.—Isotherms as in fig. 2 but for shear conditions.

semblages in rocks or in experimental samples which may or may not have been brought to equilibrium.

[2] These values essentially give the magnitude and relative comparison of the activation energies. Greater precision cannot be attached to them because of the inherent difficulties of kinetic studies in solid-state reactions and the limitations of X-ray methods of quantitative analysis of phases.

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