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## GEOLOGICAL NOTES

### EFFECTIVENESS OF SHEARING STRESSES IN ACCELERATING SOLID PHASE REACTIONS AT LOW TEMPERATURES AND HIGH PRESSURES<sup>1</sup>

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#### ABSTRACT

The use of displacive-shearing stresses in the study of phase equilibria in opposed-anvil high-pressure apparatus has been of value in resolving the relationship of the anomalous polymorphic thorite-huttonite phases of ThSiO<sub>4</sub>, and in achieving the first reversibility of the high-low-temperature forms of Nb<sub>2</sub>O<sub>6</sub>. 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<sub>2</sub>-I→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<sub>4</sub>, Nb<sub>2</sub>O<sub>6</sub>, Sb<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>). 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<sub>3</sub> and MnCO<sub>3</sub>.

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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  $\text{PbO}_2$  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, Dacheille, and Roy, 1961) to enter the stability region of the orthorhombic  $\text{PbO}_2$ . A general study of such "grinding" operations was made and in a subsequent paper (Dacheille and Roy, 1960) it was shown that in ordinary mortars and even in Wig-L-Bug-type mixers<sup>2</sup> it was possible to synthesize a wide variety of high-pressure phases, including those of  $\text{PbO}$ ,  $\text{PbO}_2$ ,  $\text{CaCO}_3$ ,  $\text{MnF}_2$ ,  $\text{Sb}_2\text{O}_3$  and  $\text{BeF}_2$ . 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 (Dacheille 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

##### $\text{CaCO}_3$ ; $\text{SiO}_2$ ; JADEITE

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

<sup>2</sup> Crescent Dental Mfg. Co., Chicago, Illinois.

$\text{CaCO}_3$  calcite-aragonite,  $\text{SiO}_2$  quartz-coesite and the albite + nepheline-jadeite reactions reported in 1960 at the Fourth International Symposium on the Reactivity of Solids (Dacheille 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.

##### $\text{ThSiO}_4$

The stability relations of the  $\text{ThSiO}_4$  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  $1,200^\circ\text{C}$ .), 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  $220^\circ\text{C}$ . 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  $218^\circ\text{C}$ . 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  $52 \pm 3$  bars/ $^\circ\text{C}$  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],  $\gamma$ - $\alpha$   $\text{Ca}_2\text{SiO}_4$  [Roy, 1958], and only a few other reconstructively related poly-