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## TRANSFORMATION OF VATERITE TO CALCITE DURING GRINDING

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Calcium carbonate exists in three crystalline polymorphs with different symmetries structures, and densities, *viz.*, calcite, rhombohedral, density 2.71; aragonite, orthorhombic, density 2.93; and vaterite, hexagonal, density 2.56. Calcite and aragonite occur naturally in large quantities, but the existence of vaterite has rarely been reported (McConnell, 1960).

Vaterite has been subjected to a hydrostatic pressure of 24,000 bars without any transformation to calcite (Jamieson, 1957), but readily transforms to calcite on grinding at room temperature (Gammage and Glasson 1963) It was our opinion that this difference in behaviour was due to the shear strains which are generated during grinding. Since a mere inspection of many geological specimens which have come from the depth of the earth is sufficient to disclose the universality of flow under those conditions and therefore to suggest the importance of shear strains, it was thought that these shear strains could account for the rare occurrence of vaterite in nature.

A mill was therefore constructed for use over a range of temperatures and the changes produced in the powder were examined using X-ray techniques.

## EXPERIMENTAL DETAILS

The deformation of the powder was carried out in a ball-mill that was designed to operate at temperatures over the range  $-79^{\circ}\text{C}$  to  $200^{\circ}\text{C}$ ; details of this mill will be published elsewhere.

The vaterite used was kindly supplied by Mr. R. A. Furniss of J. and E. Sturge Limited. It was manufactured by the carbonation of a very pure calcium hydroxide slurry, under carefully controlled conditions. The vaterite slurry thus formed was further purified, concentrated and dried. A typical analysis of impurity content of the powder is shown in Table 1. It was found to contain 2-3 percent calcite.

The powder was first dried in a hot air oven at about  $100^{\circ}\text{C}$ . For each milling run, 2 gm samples were accurately weighed out into the grinding cylinder. After the grinding runs, the powder was allowed to attain room temperature.

The samples were examined on a Philips powder diffractometer. The percentage of calcite formed was determined by calibrating the intensity ratio (10 $\bar{1}$ 4) calcite/(11 $\bar{2}$ 1) vaterite with standard samples prepared from

TABLE 1. ANALYSIS OF VATERITE POWDER PRODUCED BY CARBONATION OF CALCIUM HYDROXIDE

Impurity	Concentration	Impurity	Concentration
Fe	1 ppm	Na	0.02%
Cu	1 ppm	Cl	0.03%
Pb	1 ppm	SO <sub>4</sub>	0.01%
Ni	1 ppm	NH <sub>3</sub>	0.05%
Mn	<1 ppm	SiO <sub>2</sub>	<0.02%
Sb	<1 ppm		

vaterite and natural calcite (Iceland spar variety). X-ray line broadening studies were also carried out in order to determine how the microstrains induced in the powder affected the transformation. The integral breadth method of Wagner (1966) was used to analyze the diffraction profiles. The instrumental broadening was found by using a well annealed calcite sample, since the strain could not be annealed out of the vaterite without causing its transformation to calcite.

#### RESULTS

Some of the results obtained are summarized in Figures 1 and 2. Figure 1 shows the effect of the milling temperature on the rate of the

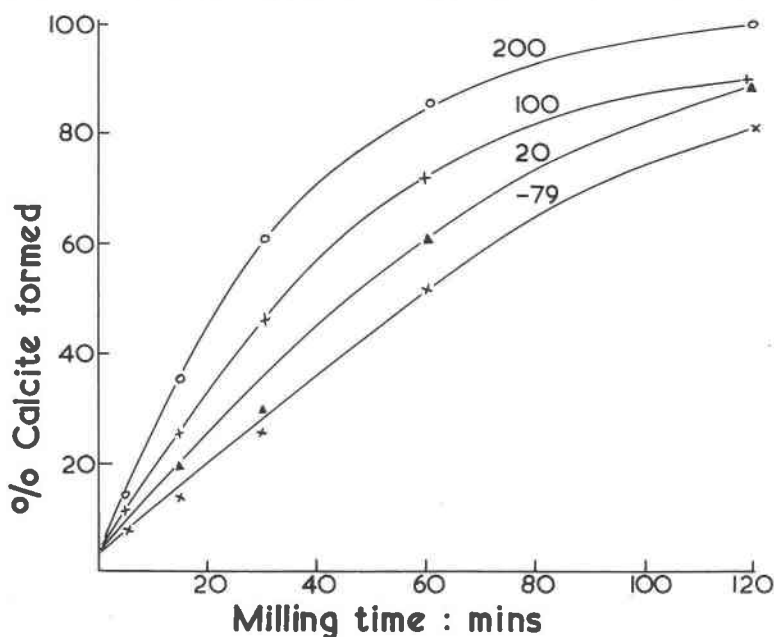


FIG. 1. Effect of milling temperature on the rate of transformation.

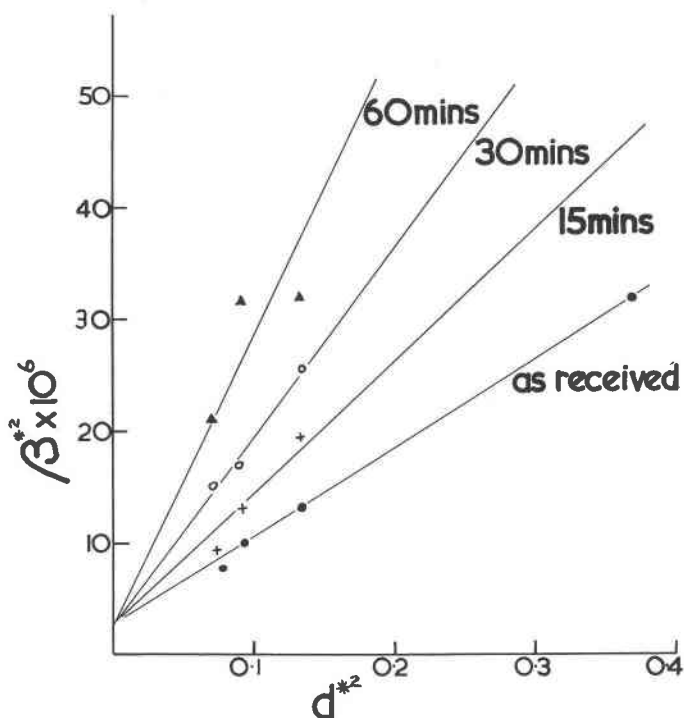


FIG. 2. Typical plot of  $\beta^{*2}(\beta^2 \cos^2 \theta_0 / \lambda^2)$  against  $d^{*2}(4 \sin^2 \theta_0 / \lambda^2)$  for various milling times.

transformation. Note that decreasing the temperature decreases the rate of the transformation. However, the transformation could not be suppressed at any of the temperatures investigated.

Figure 2 shows a typical plot of  $\beta^{*2} (\beta^2 \cos^2 \theta_0 / \lambda^2)$  against  $d^{*2} (4 \sin^2 \theta_0 / \lambda^2)$  for various milling times. The intercept at  $d^{*2}=0$  yields directly  $(1/D^{PF})^2$  and the slope is equal to  $4\epsilon^2$ , where  $D^{PF}$  is the effective crystallite size and  $\epsilon$  is the microstrain, *i.e.* random displacements from a perfect structure. The interesting fact shown by this plot is that the vaterite is in a highly strained state as received as shown by the large values of the slopes of the lines. The graph indicates a crystallite size of  $\sim 600 \text{ \AA}$ . It is usually thought that the X-ray line broadening always present in vaterite is due to a small crystallite size, but our results indicate that, although this factor accounts for part of the broadening, the main cause is microstrain broadening.

#### CONCLUSIONS

The vaterite transformed to calcite at all four temperatures investigated; the rate of transformation was greater at higher tem-

peratures. It is interesting to note that vaterite precipitates at a lower temperature than either calcite or aragonite (Wray and Daniels, 1957).

H. Mondage-Dufy (1960) has stated that vaterite is less pure than either calcite or aragonite and has suggested that the impurity atoms are associated with crystal defects. These crystal defects would produce the microstrains shown to be present by our X-ray line broadening studies.

As thermodynamic data do not indicate any stability range relative to calcite for pure well crystallized vaterite, we may conclude that the impurities, even though they are only 0.1 percent by weight, are necessary for the formation of the complex and strained vaterite structure, rather like the role of carbon in the martensite structure. The structure is relatively unstable and any further distortion of the lattice, such as is produced by grinding, is sufficient to bring about the transformation to calcite at all temperatures.

Since the conditions in the mill, a combination of hydrostatic and shear strains, approximate to those found in the earth's crust, our results would suggest that, even if vaterite were formed, these strains would quickly bring about its transformation to calcite.

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#### THE PROBLEM OF QUARTZ-CORUNDUM STABILITY

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#### INTRODUCTION

From their results of mineral synthesis using mainly amorphous reactants of high purity in a  $p$ - $T$  region centred at 600°C and 4 kbar, Aramaki and Roy (1963) claim the assemblage quartz-corundum may