

PRESSURE-TEMPERATURE STUDIES OF ANATASE,  
BROOKITE, RUTILE AND  $\text{TiO}_2$ -II

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## ABSTRACT

Anatase and brookite have been converted in opposed-anvil high pressure apparatus to a new phase,  $\text{TiO}_2$ -II, which has the  $\alpha\text{PbO}_2$  structure. Starting with anatase and II, or brookite and II,  $p$ - $T$  reaction boundaries were obtained which yield apparent triple points among the polymorphs anatase-II-rutile and brookite-II-rutile in the region of 480°C and 9 kbars. Inasmuch as no reversal transitions were observed along these boundaries, the boundaries approximate equilibria on the high temperature side, in a stable or metastable relation. Further, because brookite may be a crystalline solution, it would fall out of the system  $\text{TiO}_2$ .

Other results using the polymorphs and a gel as starting materials in opposed-anvils and hydrothermal apparatuses suggest the critical importance of fluid composition in the various transitions to rutile.

## INTRODUCTION

Titanium dioxide is known to occur in nature as anatase, brookite, and rutile. Rutile is usually considered to be the high-temperature and high-pressure phase relative to anatase, whereas brookite is often considered to be of secondary origin.

Studies of the effect of pressure on the  $\text{TiO}_2$  polymorphs are few. Tu and Osborn (Osborn, 1953) studied the conversion of anatase to rutile in the presence of water from temperatures of 375° to 660°C and pressures of 1000–3000 atmospheres. They found that pressure lowered the temperature at which this took place. Dachille and Roy (1962a) did work in the super pressure region ( $>10$  kbars), and reported that a new high pressure phase of  $\text{TiO}_2$  was produced from anatase. The small number of X-ray reflections, some of which overlapped those of the starting phase, were not sufficient for an accurate indexing of the powder patterns. However, further efforts were successful in preparing the phase in a well crystallized condition. Data was being analyzed when Jamieson (private communication, 1965) revealed that he had shocked a rutile single crystal and found extra X-ray diffraction lines which could be indexed on the basis of the  $\alpha\text{PbO}_2$  structure. The diffraction pattern obtained from the high pressure phase of our static experiments was practically identical with that obtained by Jamieson. Simons and Dachille (1967) were therefore able to refine the structure

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of this phase on the basis of an  $\alpha$ -PbO<sub>2</sub> model and present the X-ray data.

Bendliany, Popova and Vereschagin (1966) reported that rutile was converted to a high pressure phase of the  $\alpha$ -PbO<sub>2</sub> structure, at pressures of 40–120 kbars and temperatures from 700°–1500°C. McQueen, Jamieson and Marsh (1967) studied the effect of shock waves on rutile and found the new phase after shocks of about 330 kbars. DeCarli and Linde (1967) find evidence of this high pressure phase after shocks of 150–250 kbars.

Using electrical resistance measurements, and quench techniques with 30-min runs in "belt" apparatus, Vahldiek (1966) found that anatase transformed to rutile from about 785°C and 3.8 kbars, but with the temperature decreasing with increasing pressure to about 420°C at 24 kbars. He did not observe a high pressure phase.

The present paper reports the results of experiments with TiO<sub>2</sub> polymorphs and gel in a broad pressure-temperature field. Henceforth, the high-pressure phase will be referred to as TiO<sub>2</sub>II, or simply II, in keeping with the same designation for the analogous PbO<sub>2</sub> and MnF<sub>2</sub> phases (White, Dachille and Roy 1961; Azzaria and Dachille, 1961).

#### EXPERIMENTAL PROCEDURES

Most of the work was done in the opposed anvil apparatus described by Dachille and Roy (1962b) and Myers, Dachille and Roy (1963). In the low pressure region under 4 kbars, cold seal hydrothermal units were used (Tuttle, 1949).

Starting materials were commercial reagent grade TiO<sub>2</sub> with the anatase structure (Fisher Scientific Co.), commercial anatase annealed at 525°C for 24 hours, crystals of anatase from Val Vals, Switzerland, crystals of brookite from Magnet Cove, Arkansas, and rutile synthesized from anatase by heating in air at 950°C for 10 days. The commercial anatase was composed of rounded crystals about 0.2  $\mu$  in diameter. It was spectroscopically "pure", but electron microprobe analysis showed an estimated 1 percent chlorine dispersed heterogeneously throughout the anatase. The annealed anatase was chlorine free. The anatase and brookite natural crystals were crushed under acetone to pass 100 mesh and cleaned by the usual methods. Other starting materials were TiO<sub>2</sub>-II prepared from brookite, and a gel.

In the opposed anvil apparatus dry runs, and wet runs in which the wafer samples were moistened, were made from temperatures of 25–800°C and at pressures up to 100 kbars. The unannealed anatase was used extensively but many comparative runs were made with annealed anatase and natural crystals, and the results were identical. The duration of the runs was from 1–5 days in most cases, with some lasting 30 days.

Quench products were identified by powder-X-ray diffraction techniques. The small grain size of the reaction products did not permit satisfactory phase identification under the petrographic microscope.

In the critical runs temperatures were accurate to  $\pm 5^\circ\text{C}$  and load pressures were regulated to  $\pm 0.1$  kbars in the anvil apparatus. The actual pressure on the sample is taken to be within 10 percent of the load pressure on the wafer assembly. We believe justification for this is to be found in the long experience of this laboratory in high pressure procedures using the opposed anvils and other types of apparatus. Pertinent facts are given