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PRESSURE-TEMPERATURE STUDIES OF ANATASE, BROOKITE, RUTILE AND TiO_2-II

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ABSTRACT

Anatase and brookite have been converted in opposed-anvil high pressure apparatus to a new phase, TiO_2-II, which has the αPbO_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 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 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 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 αPbO_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 α-PbO_2 model and present the X-ray data.

Bendeliany, Popova and Vereschagin (1966) reported that rutile was converted to a high pressure phase of the α-PbO_2 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_2 polymorphs and gel in a broad pressure-temperature field. Henceforth, the high-pressure phase will be referred to as TiO_2II, or simply II, in keeping with the same designation for the analogous PbO_2 and MnF_2 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_2 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 μ 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_2-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 ±5°C and load pressures were regulated to ±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 in an early experimental study of the olivine–spinel transition (Dachille and Roy, 1960), and in a paper concerning calibration in opposed anvils systems (Myers, Dachille and Roy, 1963).

RESULTS

Opposed-anvil high-pressure experiments. In Figures 1 and 2 are summarized representative runs (plotted as circles) indicating quench

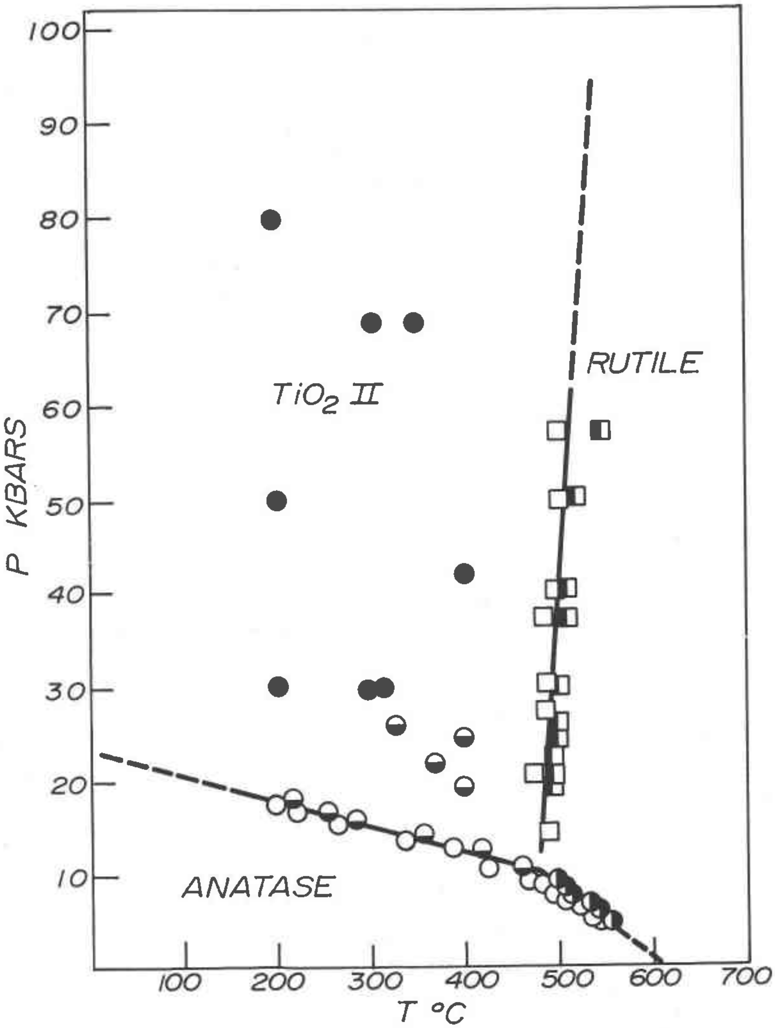

FIG. 1. The *p-T* reaction boundaries along which anatase was converted to II or rutile are marked by open or filled circles. The third boundary, marked by open or filled squares is for the II to rutile conversion.

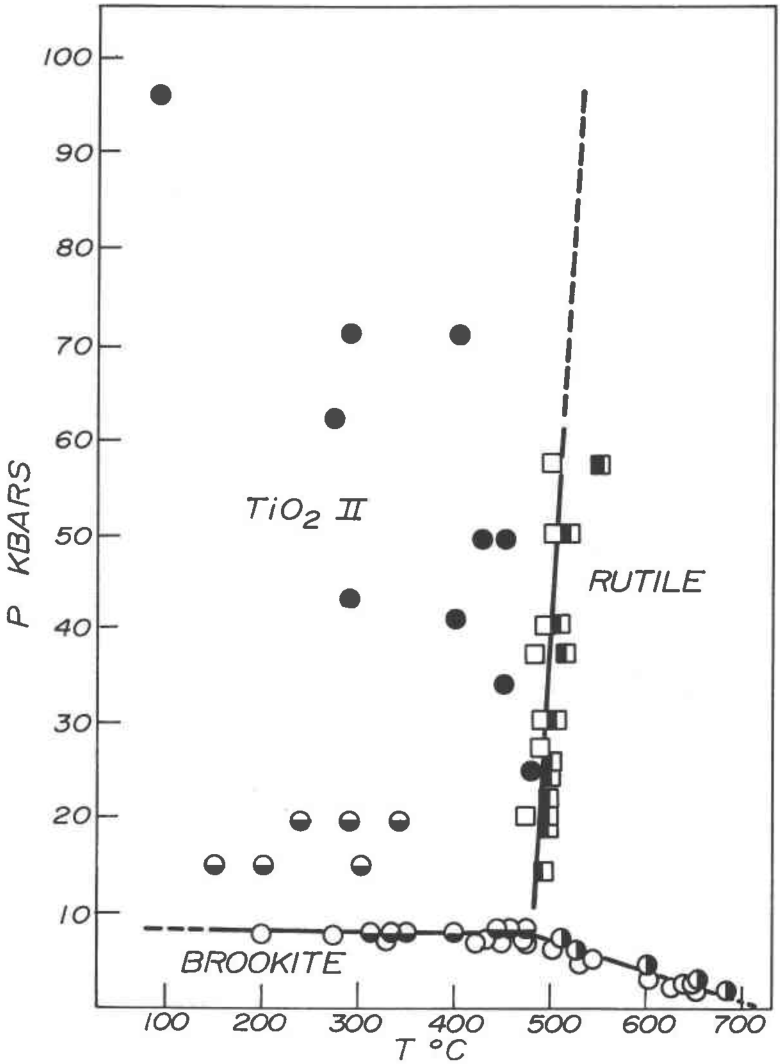

FIG. 2. The p-T reaction boundaries along which brookite was converted to II or rutile are marked by open or filled circles. The II to rutile boundary is the same as in Fig. 1.

products obtained using anatase and brookite, respectively, as starting materials. Most of the runs were for three days at pressure and temperature but several were much longer. In general, the runs were temperature-quenched while pressure was maintained.

Runs also were made using rutile as the starting material. However, despite the use of mineralizers, oscillating shearing stresses, and very long runs, no transitions of rutile to other phases were observed. Similarly, no conversion to brookite was observed when a prepared II was the starting material. Therefore, the boundaries separating the phase fields on the diagram do not represent equilibrium positions but probably approximate them on the higher temperature side. Furthermore, metastable relations may be involved with anatase and brookite, and perhaps even the II phase. What the boundaries definitely show are the conditions at which enough of the product of a "forward" reaction was observed after 1–5 day runs in a quenched charge by powder X-ray diffraction analysis.

The definition of the boundary between the II and rutile fields was poor in runs starting with anatase and brookite. There was a region about 75°C in width in which two product phases, II and rutile, appeared together with or without residual starting material. Of course, a residue of starting material is often observed in slow reactions. The presence of two product phases over a broad p-T range might be attributed to the metastable nucleation and growth of one or the other phase, and/or to transitory variations of pressure sufficient to sustain stable growth for finite intervals. Once formed, the slowness of reactions could allow a phase to remain in identifiable amounts in a metastable field.

It was found that the boundary could be determined more accurately by removing one of the reaction steps. Brookite was converted completely to a well-crystallized II phase in the region of 40 kbars and 400–450°C in 48 hours or less. This product was recharged and used to determine points near the apparent II-rutile reaction boundary. However, a more convenient but equally effective procedure was to form the II phase from brookite with 2–3 days reaction in the "active" region and then to shift the conditions to the final temperature and pressure for an additional three or more days. Using this method the apparent reaction boundary from II to rutile shown in Figures 1 and 2 was determined. A graphical fit of this line to yield a triple point in both the "anatase" and "brookite" diagrams is possible. This may be fortuitous, but that it could have significance with regard to the existence of actual triple points in stable or metastable phase diagrams should not be dismissed. The positions of the apparent triple points are at 9.5 kbars, 484°C for the anatase, and 7.8 kbars, 475°C for the brookite series.

Hydrothermal experiments. Charges of approximately 10 mgms were sealed with or without water into 1.5 mm O.D. platinum tubing by welding with a carbon electrode. Table 1 lists a few runs made at 2.1 kbars.

The results showed that the annealed and "unannealed" anatase be-

TABLE 1. RUNS IN HYDROTHERMAL APPARATUS

St. Mat.	Temp. ±5°C	Time days	Results
Annealed An $+H_2O$	400	16.6	An
Annealed An, no H_2O	485	7.9	An
Annealed An $+H_2O$	485	7.9	Ru
Annealed An, no H_2O	640	7.9	An
Annealed An $+H_2O$	640	7.9	Ru
An $+II_B$	400	16.6	no change
An $+II_B$	462	6	Ru
II_A+H_2O	400	11	An
II_B+H_2O	400	11	no change
II_A+H_2O	400	11.9	no change
II_A+H_2O	450	9.8	50% Ru+50% II
II_B+H_2O	450	9.8	50% Ru+50% II
II_A+H_2O	515	9.8	Ru
II_B+H_2O	515	9.8	Ru
Ru$+H_2O$	400	11.9	Ru
Gel+brookite seeds[a]	255	6.0	An
Gel$+TiO_2$II seeds	250	6.0	An
Gel$+TiO_2$II seeds	373	6.0	An+Ru
Gel	373	6.0	An+Ru
Gel	440	9.0	Ru

[a] Seeds amounted to less than 6% by weight.
II_A=II prepared from anatase.
II_B=II prepared from brookite.

haved in the same manner and that the presence of excess water apparently lowered the temperature of conversion to rutile to a value less than 485°C. However, even doubling the time at 400°C failed to form any rutile under the same pressure. Under "dry" conditions the 1/1 anatase-brookite mixture was inert at 400°C but converted to rutile at 462°C and 2.1 kbars.

The II prepared from anatase and brookite in opposed anvils appeared to be quite resistant to alteration under water pressure at 450°C and below, although one of four runs at 400°C was converted to anatase.

Experiments with the gel starting material. The gel preparation is based on that of Czanderna *et al.* (1957), but using 30 percent hydrogen peroxide and concentrating the gel at 110°C. Spectrochemical analysis showed only trace concentrations of Si, Mg, Fe, Mn and Ca. The solids content of the gel was 52 percent. The high residual concentration of ammonia in the gel was not determined quantitatively. It was amorphous with respect to Debye-Scherrer X-ray diffraction.

Experiments were conducted in the hydrothermal units (with the charge sealed in platinum tubing) and in opposed anvil apparatus but the *p-T* range used was not as broad as for the main series. In the opposed anvil runs nickel rings 0.02-in. thick were used because it was found that the 0.01-in. rings had a tendency to blow out or become very thin on decomposition of the gel.

The main observations are (1) the gel is stable over an appreciable *p-T* range, (2) anatase crystallizes at lower *p-T* conditions than rutile, (3) the II phase crystallizes with some difficulty from the gel at higher pressures than anatase and rutile, (4) seeding is not effective and, (5) rutile crystallizes at lower temperatures than when other starting materials are used.

Discussion of Results

The first preparation of the II phase from anatase was not well-crystallized. Comparison of diffractometer traces with those of the II obtained from brookite emphasized this observation. The concentrations were determined by powder X-ray diffractometry (Klug and Alexander, 1948). TiO_2 not contributing to the X-ray diffraction maxima of the crystalline phases is estimated by difference and is designated SRO. A review of the structures of anatase, brookite, rutile and II showed that their oxygen layering schemes and distribution of titanium ions suggest a definite influence of structure on the relative difficulty of transitions. Results of this study are to be presented later. Pertinent here is that the complexity of atomic rearrangement for An-II is very much greater than for Br-II so that at temperatures which are low for this refractory oxide incomplete recrystallization from anatase could result, leaving a substantial amount of commingled residue of SRO. This is clearly demonstrated by the lower density of the II made from anatase and by the trend of concentration with time of reaction of anatase and II. The density, measured by the sink-float method, of II from anatase is 4.11 compared to 4.32 of II prepared from brookite. X-ray density is 4.330 and 4.329 respectively (Simons and Dachille, 1967). In Figure 3 are plotted the decrease in concentration of anatase with time of reaction at 42 kbars and 400°C, together with the increase of the II phase. The anatase was completely reacted after one day and the II phase increased slowly over a period of five days to about 50 percent of the sample. Measurements made for the Br-II reaction indicated a complete conversion to II in two days or less.

In view of the more precise results obtained with well-crystallized II in establishing the apparent boundary between the II and rutile fields (Figs. 1 and 2), it is believed that the SRO state which anatase, and, to

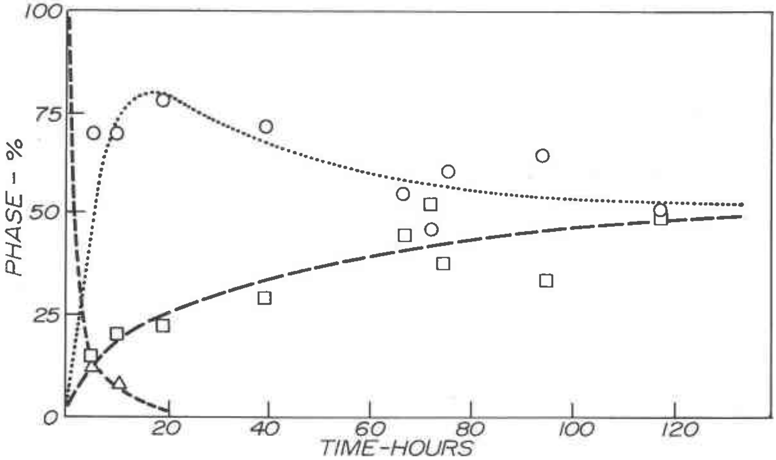

FIG. 3. The trend with time of the disappearance of anatase and of the slow crystallization of II. By difference, the amount of a short range order transition phase of TiO_2 is estimated. (△ = anatase; □ = II; ○ = SRO).

a lesser extent, brookite go through may be sensitive to local differences within the sample. The reactions then may follow metastable paths.

The essentially coincident triple points of Figures 1 and 2 favor the view that three TiO_2 phases coexist at such point either in a *stable or metastable* relation. Moreover, the extrapolations to atmospheric pressure of the An-Ru and Br-Ru boundaries determined in the opposed anvil experiments, intersecting the temperature axis at 605 and 720°C respectively, are in good agreement with the temperatures below which Rao *et al.* (1961) and Rao (1961) found effectively zero rates of conversion to rutile. It may be interpreted that below these temperatures rutile is not in its stability field or that reaction rates to rutile are immeasurably slow. However, the latter view requires such an abrupt decrease of the rate constants with a small decrease in temperature that there is question as to the validity of the kinetics argument. If the former view is taken, then the agreement of the An-Ru reaction boundary with that determined by Tu and Osborn (Osborn, 1953) gives support to the extrapolation and provides another example of the similarity of pressure effects of hydrothermal and opposed anvil systems (Fig. 4).

Our hydrothermal studies and those made with the gel starting material pose problems with respect to the significance of Figures 1, 2, and 4. If the results listed in Table 1 are referred to these diagrams it will be seen that rutile forms from oxides below 450–485°C at 2.1 kbars, well inside the respective anatase or brookite fields. Does this mean

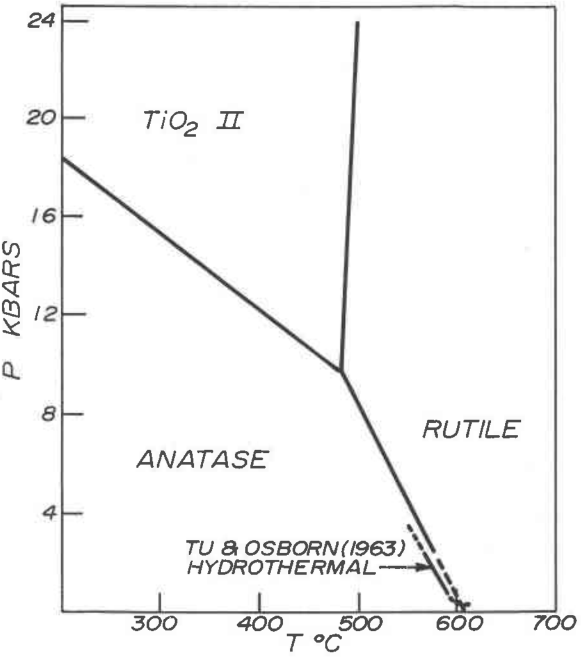

FIG. 4. Comparison of the anatase to rutile reaction boundary obtained in opposed anvils apparatus with that of hydrothermal results of Tu and Osborn.

that the An-Ru transition temperature for TiO_2 is as low as this or that anatase and brookite are everywhere metastable? In the hydrothermal runs using the ammonia-containing gel it is evident a portion of the charge crystallized to rutile at 373°C. Is this of greater importance than the persistence of anatase for almost 17 days at 400°C at the same water pressure in the same kind of sealed capsule?

This brings up the discrepancy between the results of Tu and Osborn and our *hydrothermal* work with anatase. It was found on examination that the main difference in procedures is the former used open envelopes so that the sample is in contact with the entire fluid contained in the stainless steel test tube "bomb", whereas we used samples *sealed* into platinum capsules with a limited amount of water and thus separated from the pressure fluid. In the "open" system the TiO_2 recrystallizes in a fluid in which the pO_2 is buffered by Fe, Ni and Cr oxides lining the cavity. In the sealed capsules the pO_2 is determined by the composition in the capsule and by diffusion of H through its wall.

It is significant that a buffering mechanism also is available in the wafer assembly used with the opposed anvils because of the nickel and

NiO in contact with the sample. Furthermore, fine cracks developed under pressure in the enclosing Pt-10% Rh foils expose the sample to buffering by Fe, Co and other oxides on the anvil faces. It is believed that closely related buffering mechanisms might account for the effective agreement on the An-Ru boundary as given by Tu and Osborn and our *opposed anvil* results.

To this point our findings support a phase diagram for TiO_2 approximated by Figure 1 in which fields of anatase, II and rutile coalesce at a triple point. Because of the inability to reverse reactions along the boundaries, the equilibrium positions must be at lower temperatures but not necessarily to the extent indicated by the sealed-tube hydrothermal and gel-type runs. Furthermore, the failure to crystallize brookite under any of the many conditions in which anatase or rutile were formed leads us to view it as a metastable phase which is also dependent on compositional variations.

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