



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  $373^\circ C$ . Is this of greater importance than the persistence of anatase for almost 17 days at  $400^\circ C$  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<sub>2</sub> 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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#### REFERENCES

- AZZARIA, L., AND F. DACHILLE (1961) High pressure polymorphism of manganous fluoride. *J. Phys. Chem.*, **65**, 889-890.
- BENDELIANY, N. A., S. V. POPOVA AND L. F. VERESCHAGIN (1966) A new modification of titanium dioxide stable at high pressure. *Geokhimiya*, **1966**, 5, 499-502 [Transl. *Geochem. Internat.* **1966**, 387-390].
- CZANDERNA, A. W., A. F. CLIFFORD AND J. M. HONIG (1957) Preparation of highly pure TiO<sub>2</sub> (anatase). *J. Amer. Chem. Soc.*, **79**, 5407-5409.
- DACHILLE, F., AND R. ROY (1959) High pressure studies of the system Mg<sub>2</sub>GeO<sub>4</sub>-Mg<sub>2</sub>-SiO<sub>4</sub> with special reference to the olivine-spinel transition, *Amer. J. Sci.*, **258**, 235-246.
- (1962a) A new high pressure form of titanium dioxide (abstr.), *Amer. Ceram. Soc. Bull.*, **41**, 225.
- (1962b) Modification of opposed anvil devices. In *The Physics and Chemistry of High Pressure*. Society of Chemical Industry, London, 77-85.
- DECARLI, P. S., AND R. K. LINDE (1967) Residual effects of shock waves in rutile (abstr.). *Meteorit. Soc.*, **30th Ann. Meet.**, Moffett Field, Calif, October, 1967.
- KLUG, H. P., AND L. E. ALEXANDER (1954) *X-ray diffraction procedures*. John Wiley and Sons, Inc., 716 p.
- MCQUEEN, R. G., J. C. JAMIESON AND S. P. MARSH (1967) Shock wave compression and X-ray studies of titanium dioxide. *Science*, **155**, (3768) 1401-1404.
- MYERS, M. B., F. DACHILLE AND R. ROY (1963) Contributions to calibration of high pressure systems from studies in opposed anvil apparatus. In A. A. Giardini and E. C. Lloyd, eds.) *High Pressure Measurement*. Butterworths, Washington, 11-33.
- OSBORN, E. F. (1953) Subsolidus relations in oxide systems in presence of water at high pressures. *J. Amer. Ceram. Soc.*, **36**, 147-151.