

The crystallization of anatase and rutile from amorphous titanium dioxide under hydrothermal conditions

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Abstract

The hydrothermal crystallization of amorphous titanium dioxide at 300–600°C, 1 kbar pressure, follows the reaction path: amorphous reactant → anatase → rutile. The transformation is accelerated by increasing temperature and decreasing solution pH. Two mechanism stages can be envisaged: (1) the formation of anatase by the dehydration and gradual structural rearrangement of the reactant titanium-oxygen lattice, and (2) solution of the anatase intermediate and direct precipitation of rutile. The metastable development of anatase is in accordance with a modern formulation of the Ostwald Step Rule.

Introduction

The kinetics and mechanisms of the solid state transformation anatase → rutile have been well studied (Czanderna *et al.*, 1958; Rao, 1961; Shannon and Pask, 1965; Heald and Weiss, 1972). However, less attention has been paid to the relationships existing between the two polymorphs in hydrothermal aqueous conditions. Osborn (1953) found that high temperature, and to a lesser extent pressure increase, favor the conversion of anatase into rutile. Dacheville *et al.* (1968) hydrothermally crystallized titanium dioxide gel, obtaining anatase at lower temperatures and rutile at higher temperatures. Mineralizing agents, such as alkali metal fluorides, catalyze the formation of rutile from gel or anatase (Osborn, 1953; Anikin and Romyantseva, 1964). Jamieson and Olinger (1969) showed that anatase is thermodynamically always unstable with respect to rutile. Thus the persistence or formation of anatase under hydrothermal conditions should be regarded as a consequence of sluggish reaction kinetics or metastable crystallization. Correspondingly, the formation of rutile from gels or anatase is catalyzed by increasing temperature, pressure, and the presence of mineralizing agents. The purpose of this paper is to investigate the conditions and mechanisms of anatase and rutile formation during the hydrothermal crystallization of amorphous titanium dioxide.

Experimental methods

Amorphous titanium dioxide was prepared by the addition of 0.88 sp gr ammonia to titanium tetrachlo-

ride until the pH of the solution was in the range 1–4. The resulting dense white precipitate was washed thoroughly and dried under infrared heat. X-ray diffraction indicated the material to be completely amorphous. Experiments were performed at 1 kbar pressure in cold seal hydrothermal bombs, with reactants sealed inside silver capsules. Charges consisted of 50 mg solid and 500–600 mg solution. Products were examined by X-ray diffraction, and where possible (at 600°C only) anatase-rutile proportions were estimated by the method of Spurr and Myers (1957). Solutions used were sodium carbonate, water, and hydrochloric acid. Tests with pHydration papers showed that the solutions underwent a slight increase in alkalinity during reaction. This presumably arises from the release during crystallization of ammonia trapped in the amorphous reactant during its preparation. No evidence could be seen of reaction between the silver capsules and the acid solutions. The solution conditions given in Table I detail both initial concentrations and final pH values.

Experimental results

The results of crystallization experiments are given in Table I. It can be seen that neutral, alkaline, and mildly acidic conditions favor anatase formation, whereas more strongly acid environments favor rutile. This is clearly indicated by the results of long experiments performed at 500°C. In sodium carbonate, water, and 0.01 M HCl, anatase is formed, whereas in 0.1 M and 0.5 M HCl the product is rutile. Increasing temperature also enhances rutile forma-

TABLE 1. Results of crystallization experiments

Solutions		T°C**	t.hrs*	Products
Initial	Final pH			
1.0 M.HCl	0.0	304	68	Rutile
		406	0.4	Rutile
0.5 M.HCl	0.4	500	0.4	Rutile,small anatase
		502	204	Rutile
0.1 M.HCl	1.0	305	0.3	Anatase developing
		295	1.5	Anatase developing
		295	3	Rutile,poor anatase
		295	14	Rutile,small anatase?
		304	68	Rutile
		404	0.3	Poor anatase,small rutile
		398	72	Rutile
		500	0.4	Rutile,small anatase
		501	216	Rutile
		597	264	Rutile
0.01 M.HCl	2.8	404	168	Anatase
		505	235	Anatase
		597	264	Anatase(75%),rutile(25%)
Water	8.8	302	0.2	Anatase developing
		295	3	Anatase developing
		304	68	Anatase
		410	0.3	Anatase developing
		401	188	Anatase
		502	0.4	Anatase
		501	216	Anatase
		597	264	Anatase(90%),rutile(10%)
0.1 M.Na ₂ CO ₃		500	0.4	Anatase
		505	235	Anatase

* Time at temperature, ie. after completion of run up

** Temperature $\pm 5^\circ\text{C}$

tion; crystallization of the amorphous reactant in water and 0.01 M HCl at 400°C and 500°C yields anatase only, but at 600°C rutile appears in the products. A third naturally occurring polymorph, brookite, is not found in any experimental products.

The mechanism of reaction is illustrated by X-ray diffraction patterns obtained from the products of reactions at 300°C using 0.1 M HCl (Fig. 1). After 1½ hours reaction anatase only is developing (Fig. 1a), but after 3 hours reaction the poorly developed anatase has diminished and rutile is forming (Fig. 1b). Fourteen hours reaction yields rutile, with perhaps a small amount of anatase remaining (Fig. 1c), and 68 hours reaction gives rutile only. Similarly, other short experiments at 400°C and 500°C using 0.1 M and 0.5 M HCl indicate that anatase precedes the formation of rutile. Reactions in water at 300°C, 400°C, and 500°C, in which anatase is the only product, also show anatase developing in short experi-

ments. These observations are consistent with the transformation:



The data given in Table 1 indicate that the rate of the transformation is accelerated by increasing temperature and decreasing solution pH.

The proposed reaction mechanism is analogous to that observed for the hydrothermal crystallization of amorphous silica, in which the polymorphs cristobalite and occasionally silica K precede the formation of the thermodynamically stable phase, quartz. It is found that the rate of quartz formation is accelerated by increasing temperature and pressure (Carr and Fyfe, 1958), but in contrast to the above observations the reaction is catalyzed by alkaline solution species (Campbell and Fyfe, 1960; Fyfe and McKay, 1962; Matthews, 1972). Campbell and Fyfe related the alkali catalysis to the nature of the silicate solution species, and presumably the differences noted reflect

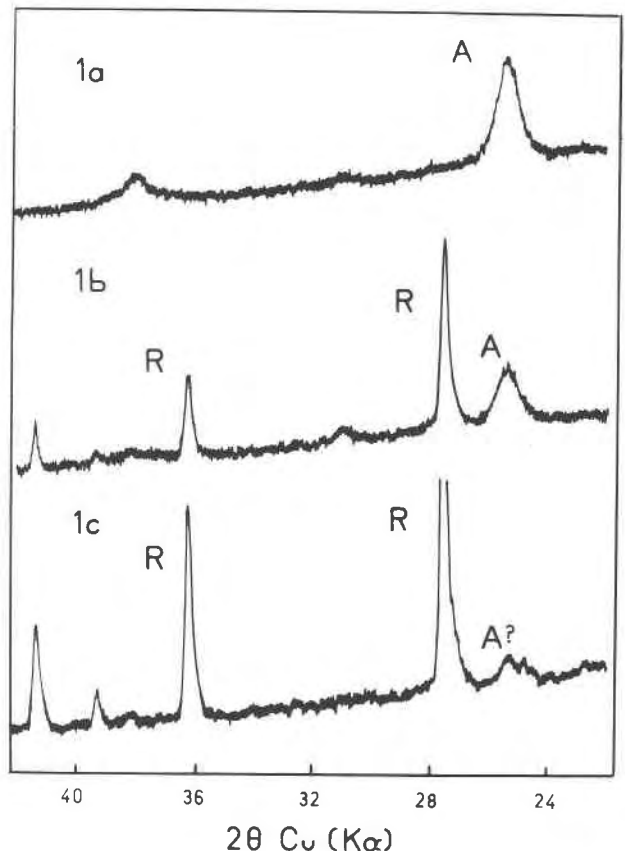


FIG. 1 X-ray diffraction patterns of products from crystallization experiments at 300°C using 0.1 M HCl. (a) 1.5 hours reaction. (b) 3 hours reaction. (c) 14 hours reaction. Legend: A=Anatase, R=Rutile.

that titanium-oxygen species are acid- rather than alkali- stabilized.

The development of phases as indicated by X-ray diffraction reveals a dissimilarity in the specific mechanisms of anatase and rutile formation. The development of anatase is first indicated by the appearance of a broad 'hump' in the 2θ region of the anatase 101 peak. For reactions in water (and presumably also 0.1 M Na_2CO_3 and 0.01 M HCl) this hump gradually develops and sharpens (see Fig. 1a) until fully crystalline anatase is indicated. For reactions in 0.1 M and 0.5 M HCl, rutile growth commences before full crystalline development of the anatase can occur (Fig. 1b). However, the rutile gives well defined X-ray peaks, even when present in small amounts; *i.e.* in the early stages of development (Figs. 1b and 1c). Similar observations can be made for the silicic acid crystallization (*cf.* Carr and Fyfe, 1958, Fig. 1). The appearance of well-ordered rutile is consistent with its formation occurring through a solution and precipitation mechanism. However, anatase formation may occur by the gradual structural rearrangement of the titanium-oxygen lattice of the amorphous reactant, with accompanying dehydration. Dehydration may precede the structural rearrangement. The isotopic studies of Clayton *et al.* (1972) on silicic acid crystallization showed that dehydration occurs before any loss of amorphous character can be detected in the reactant.

Scanning electron microscopy was used to in-

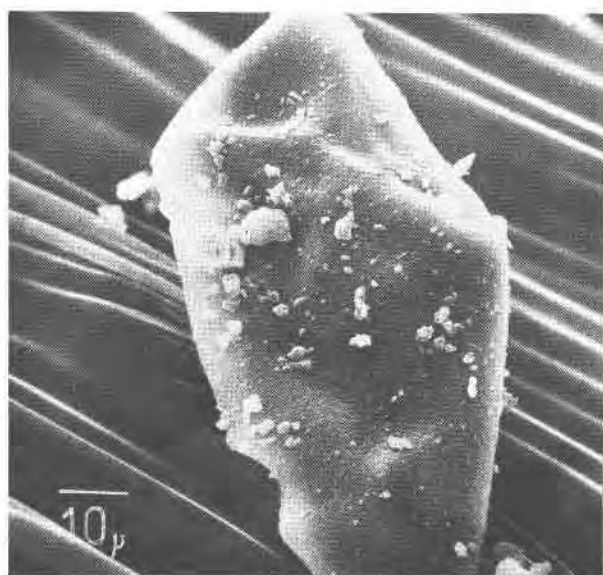


FIG. 2. SEM micrograph showing gross morphology of a reactant grain.

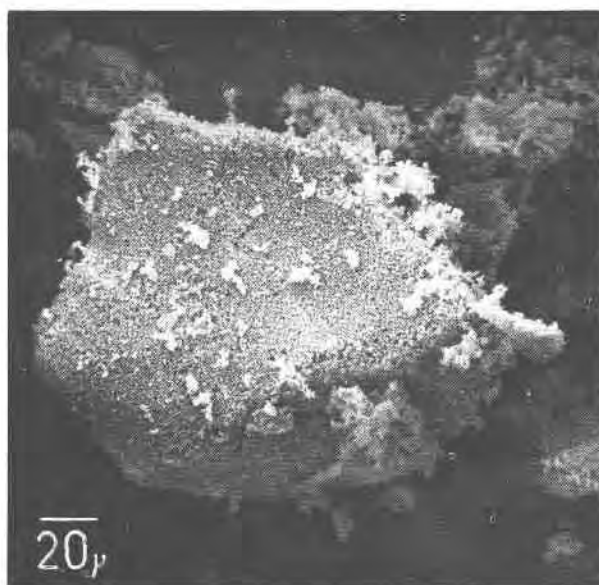


FIG. 3. SEM micrograph showing gross morphology of an anatase grain. Product from 235 hours reaction at 505°C using 0.01 M HCl.

vestigate these mechanism proposals. Representative micrographs are given in Figs. 2-6, and the following observations can be made:

(1) The gross morphologies of the reactant grains are preserved in the product anatase (Figs. 2 and 3).

(2) The large, fully crystalline, anatase grains consist of a mass of reasonably equidimensional small crystals (Fig. 4).

(3) The gross morphologies of rutile grains do not possess the similarities to the reactant that are shown by anatase grains (Figs. 2, 3, and 5).

(4) The rutile grains consist of a mass of small crystals. However, these crystals are much more intergrown than anatase crystals (Figs. 4 and 6).

Observations (1) and (2) are consistent with the idea that anatase forms by the dehydration and gradual structural rearrangement of the reactant lattice. Small volumes of reactant appear to be forming into discrete fine anatase crystals, with the gross morphology of the reactant being preserved in the product. The loss of water from the reactant during dehydration potentially provides 'space' in which the lattice rearrangements can occur. The role of the aqueous solution may be to catalyze the rearrangement by aiding the disproportionation of Ti-O bonds; or alternatively small scale dissolution/precipitation processes are possible.

The observations for rutile are seemingly indicative of the greater role that solution processes are playing in its formation. They are consistent with the pro-

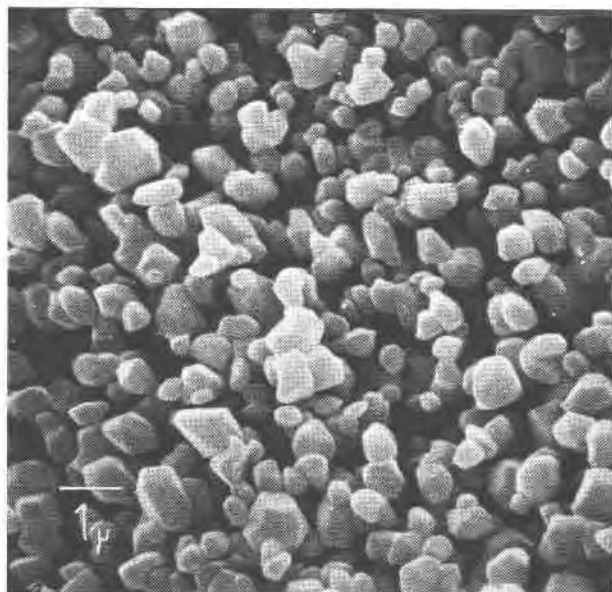


FIG. 4. SEM micrograph of anatase crystals. Detail from Fig. 3.

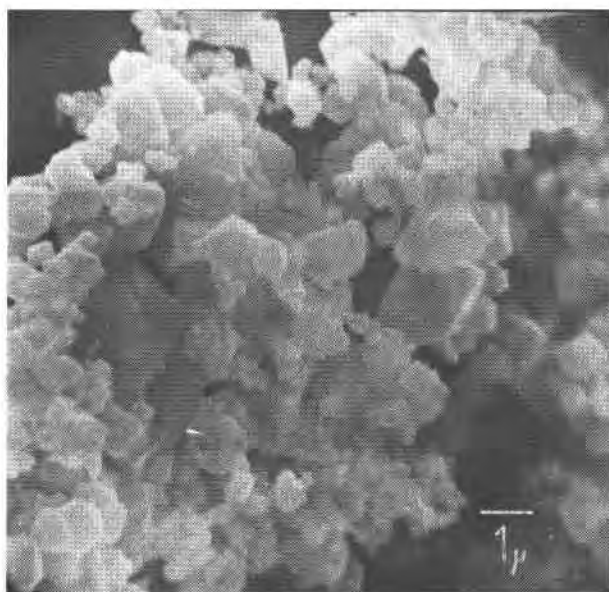


FIG. 6. SEM micrograph of rutile crystals. Detail from Fig. 5.

posal that rutile forms by solution of precursor anatase and subsequent nucleation and crystal growth of rutile from the solution.

Discussion

The SEM micrographs given in Figs. 2–4 emphasize that a close structural relationship exists between

the developing anatase and the amorphous reactant. This connection between amorphous reactant and product was noted by Carr and Fyfe (1958) for the amorphous silica crystallization (in this case cristobalite shows order related to that of the amorphous reactant). Carr and Fyfe proposed that the overall reaction mechanism is governed by a series of epitaxial controls, in which products only form when sufficient surfaces of a structurally related precursor phase are available for nucleation. In the crystallization of amorphous titanium dioxide this would mean that anatase nucleates first because it is structurally closer to the reactant, and rutile only forms later, when a sufficient surface of anatase is available for nucleation to commence.

It is also possible to view the reaction sequence in an alternative manner, in terms of the Ostwald Step Rule. One interpretation of this rule is that there is a tendency for reactions to occur in which there is a minimum ΔS , rather than reactions which yield the thermodynamically stable phase (Turner, 1968, p.77). In the crystallization reactions discussed there is an overall decrease in entropy, and the condition above would be satisfied if the first-formed phase possesses a higher entropy than subsequent phases. Such is the case for cristobalite and quartz, but not for anatase and rutile (Fig. 7). Anatase has a slightly lower entropy than rutile (~ 0.1 cal/deg/mole in the range 300–600°C.). The error limits for the anatase and rutile entropies overlap, and so it is possible that the entropy relationships given in Figure 7 can be re-

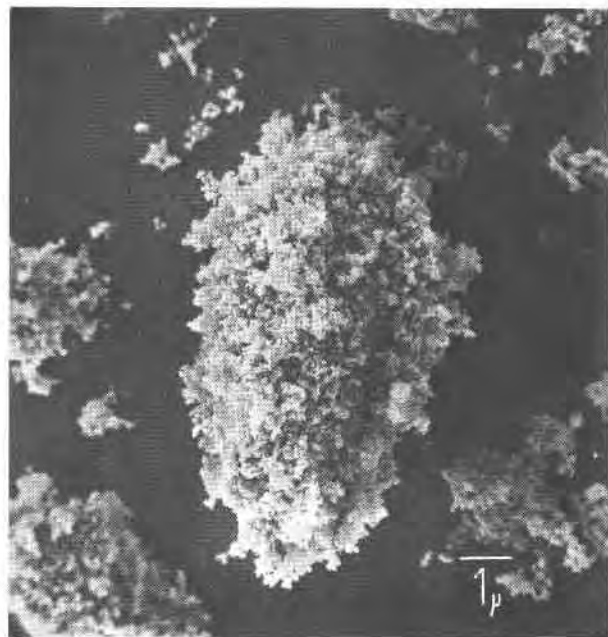


FIG. 5. SEM micrograph showing gross morphology of a rutile grain. Product from 72 hours reactions at 398°C using 0.1 M HCl. Scale Bar should read 10 μ .

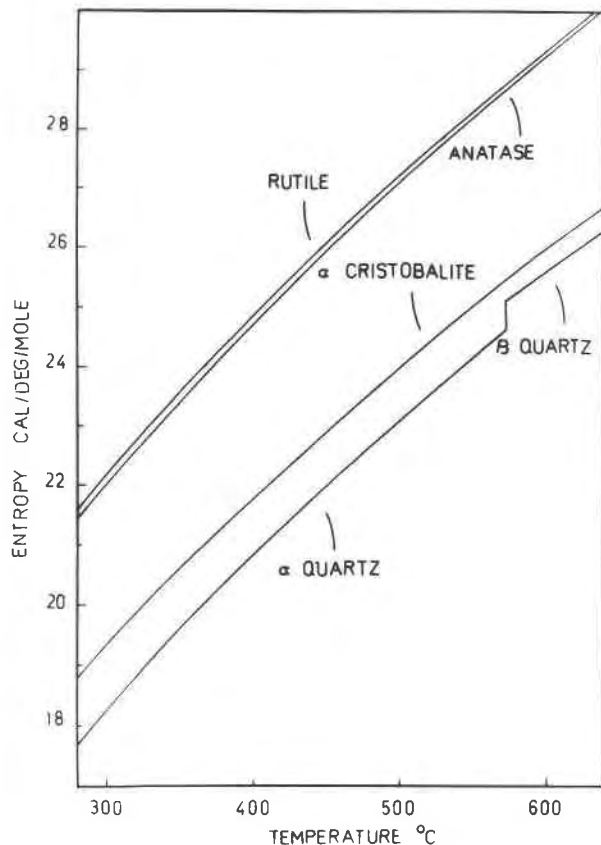


FIG. 7. Molar entropies at 1 kbar pressure. The curves were calculated from entropy data at 1 atm, using the relation $S_{T,1 \text{ kbar}} = S_T + \alpha V \Delta P$, in which α = thermal expansion coefficient, P = pressure in bars, and V = molar volume in cal/bar. Data sources: entropies and molar volumes, Robie and Waldbaum (1968); thermal expansion coefficients for rutile, quartz, and cristobalite, Skinner (1966), and for anatase, Clarke (1928).

versed. Nevertheless, entropy criteria do not provide a satisfactory interpretation for anatase formation.

An alternative interpretation of the Ostwald Step Rule has that the first phase to form will be the one possessing the least surface energy with respect to the reactant (Fyfe *et al.*, 1958, p. 73). Surface energy is inversely related to molar volume (Fyfe *et al.*, 1958, p. 73), and thus the Step Rule may be alternatively formulated to state that a reaction is preferred which gives the product with the highest molar volume with respect to the reactant. In Figure 8, molar volumes have been plotted for the various phases under discussion. The molar volumes at 1 atm pressure have been plotted, since insufficient compressibility data is available for them to be computed at 1 kbar. However, the pressure corrections to 1 kbar are very small (~ 0.001 cc. for rutile) and will not affect the relationships depicted in Figure 8. It can be seen that both

cristobalite and anatase have considerably higher molar volumes than their respective polymorphs. Thus, this alternative formulation of the Ostwald Step Rule provides a satisfactory interpretation of the observed product sequences.

Anatase and rutile occur in a variety of natural hydrothermal environments; for example, in veins in granitic pegmatites. However, anatase formation is a metastable phenomenon, and it may be queried why anatase does not transform into rutile. It is possible that the anatase is removed from contact with the hydrothermal solution immediately after formation. The anatase-rutile transformation would then have to take place by solid state reactions, and these have been shown to be extremely slow below 600°C (Rao, 1961). Alternatively, the metastable persistence of anatase could reflect the temperature and pH conditions of hydrothermal deposition. Low temperature/high solution pH could result in the anatase-rutile transformation being inhibited. Temperature

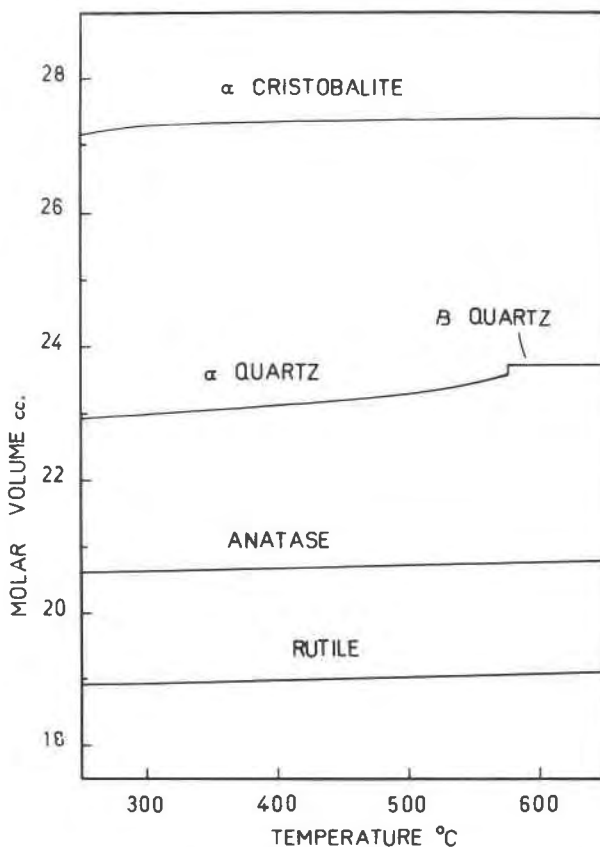


FIG. 8. Molar volumes at 1 atm pressure. The curves were calculated from molar volume data at 25°C (Robie and Waldbaum, 1968), and thermal expansion data taken from the sources referred to in Fig. 7.

determination of TiO₂-bearing assemblages is possible by oxygen isotope geothermometry (Addy and Garlick, 1974). Thus, accurate calibration of the solution pH and temperature conditions under which the anatase-rutile transformation takes place may provide a valuable high temperature pH indicator.

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