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THE PROPERTIES OF ANATASE PSEUDOMORPHS AFTER TITANITE

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ABSTRACT

Two polycrystalline natural anatase pseudomorphs after titanite were studied by scanning electron microscopy, X-ray diffraction and differential thermal and thermogravimetric analyses. Millimeter-sized natural crystals of titanite, leached for 30 days in 0.3 or 1 mol/L HCl in water at 100°C, produced relatively porous pseudomorphs, many of which contain siliceous material and rutile in addition to anatase.

Keywords: anatase, titanite, pseudomorphs, leaching.

SOMMAIRE

Deux échantillons polycristallins d'anatase naturel produit par le remplacement de titanite ont été étudiés en utilisant la microscopie électronique à balayage, la diffraction X et des analyses différentielles thermique et thermogravimétrique. Des cristaux naturels de titanite de taille millimétrique ont été lessivés pendant 30 jours dans une solution aqueuse de 0.3 ou 1 mol/L de HCl à 100°C. Il y a eu remplacement, mais le produit contient un matériau siliceux et du rutile en plus de l'anatase.

(Traduit par la Rédaction)

Mots-clés: anatase, titanite, remplacement, lessivage.

INTRODUCTION

Anatase, a tetragonal form of TiO_2, can form by the alteration in water of titanite ($CaTiSiO_5$); rutile and brookite; other polymorphs of TiO_2 also can form. Recent studies have shown that the exposure of titanite to aqueous media at 90°C produces a Ti-rich surface layer (Nesbitt *et al.* 1981, Metson *et al.* 1982, Vance 1987) according to the reaction:

$$CaTiSiO_5 + 2\,H^+ + 2H_2O \rightleftharpoons Ca^{2+} + H_4SiO_4 + TiO_2 \qquad (1)$$

Such layers were found after reaction of titanite with aqueous HCl and NaCl solutions and low-Ca simulated groundwaters, but not with high-Ca waters, in which the reaction is driven back to the left.

The object of the present work was to investigate whether a Ti-rich surface layer tends to protect the titanite against further alteration. This information is of interest in connection with both the rates of formation of an anatase pseudomorph after titanite, and the long-term leaching of titanite glass-ceramics (Hayward & Cecchetto 1982, Hayward 1986) designed for the immobilization of radioactive waste. The Ti-rich layer produced in titanite leached in near-neutral media at ~90°C is only a few micrometers thick, even after several months of leaching in the laboratory (Vance 1987). A thicker layer would facilitate the study of protection against leaching, so that anatase pseudomorphs after both natural titanite and titanite crystals leached in HCl solutions were examined.

EXPERIMENTAL

Two samples of anatase pseudomorphs after titanite were investigated; also, natural and synthetic (Crowe *et al.* 1986) titanite crystals were used in the HCl leaching experiments. Properties of these samples are given in Table 1.

Sample densities and open porosities were obtained by ASTM test C20 (ASTM 1980). Chemical analysis of sample #2 (Table 2) was performed by X-ray fluorescence, using an ARC model 8420 sequential ARF spectrometer, after fusing part of the sample with 20 times its weight of $Li_2B_4O_7$ to make a glass disc.

Scanning electron microscopy (SEM) was performed with an ISI DS–130 instrument, operated at 15 kV, and equipped with a Tracor Northern TN-2000 energy-dispersion X-ray (EDX) analyzer. X-ray-diffraction (XRD) data were obtained using Cu$K\alpha$ radiation with (a) a Rigaku diffractometer fitted with a graphite monochromator, and (b) a 114.6-mm diameter Debye–Scherrer camera. Infrared absorption spectroscopy, using a Biorad Digilab FTS–60 instrument, was carried out in the transmission mode with pressed KBr pellets containing 2 wt.% of very finely powdered sample. Simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed with a Stanton Redcroft STA–781 apparatus, in which samples weighing 10 to 60 mg were heated at 10°C/min under flowing argon, using α-Al_2O_3 as the inert reference material.

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TABLE 1. SAMPLES USED FOR THE LEACHING STUDIES

Sample No.	Form	Locality	Size$^+$ (cm)	Open Porosity (%)	Density (g/cm^3)	Reference
1	Pseudomorph after titanite	Roanoke Co, Va., USA	~ 1	40	1.6	Mitchell 1964
2*	Pseudomorph after titanite	Jones zircon mine, Henderson Co., North Carolina USA	~ 1	40	1.6	
	Natural titanite crystals	North Crosby, Ontario; Lake Clear, Ontario	~0.1	-	3.5	Vance & Metson 1985
	Synthetic titanite crystals		~0.1	-	3.5	Crowe et al. 1986

* Royal Ontario Museum sample M16497. $^+$ Samples are approximately equidimensional.

TABLE 2. CHEMICAL COMPOSITION OF SAMPLE #2

Oxide	wt.%	Oxide	wt.%	Oxide	wt.%
Na_2O	<0.1	V_2O_5	0.23±0.03	La_2O_3	0.08±0.01
MgO	<0.04	MnO	<0.02	CeO_2	0.46±0.03
Al_2O_3	7.56±0.15	Fe_2O_3	6.29±0.31	Pr_6O_{11}	0.09±0.01
SiO_2	1.76±0.09	ZnO	<0.03	Nd_2O_3	0.30±0.02
P_2O_5	5.94±0.30	Rb_2O	<0.01	PbO	0.02±0.01
K_2O	<0.1	SrO	0.06±0.01	ThO_2	0.05±0.01
CaO	<0.05	Y_2O_3	0.07±0.01	UO_2	0.03±0.01
TiO_2	66.2 ±1.3	ZrO_2	1.23±0.06	LOI	10.9 ±0.4

LOI, the loss on ignition, was determined by heating at 1000°C. Chemical analysis by X-ray fluorescence.

RESULTS

Natural anatase pseudomorphs

A SEM analysis of a fracture surface of a mm-sized piece of sample #1 showed it to have a grain size of <2 μm; the individual grains are not large enough to obtain chemical identification from EDX measurements. The overall composition from EDX showed mainly Ti, with some Si present.

From XRD measurements, sample #1 consists mainly of anatase, and some quartz. Additional weak diffraction peaks at *d* values of 7.31, 4.43, 3.98, 3.84, 3.19 and 2.52 Å are attributed to a clay mineral, *e.g.*, kaolinite, as suggested by Mitchell (1964). The integrated intensity of these additional peaks are all less than 5% of those of the strongest reflections of anatase. Stationary-sample photographs taken with the Debye–Scherrer camera do not show any evidence of preferred orientation of the anatase crystallites. The peaks due to anatase are broad (0.6–0.8° halfwidth for $25° < 2\theta < 80°$). Assuming particle-size effects to be responsible for the broadening, application of the Scherrer equation (Klug & Alexander 1954) yielded a particle size of ~20 nm.

DTA/TGA data obtained up to 700°C in an Ar atmosphere are shown in Figure 1. The amount of quartz in sample #1 evidently was insufficient to detect the $\alpha \rightleftharpoons \beta$ transformation at 573°C. The weight losses and associated endothermic DTA peaks are ascribed to the escape of water or hydroxyl: an infrared absorption spectrum of sample #1 shows the presence of absorption bands at about 1600 cm^{-1} due to the bending mode of H_2O, together with bands near 3400 cm^{-1} due to OH^- stretching modes. No other absorptions due to potentially volatile species such as CO_3^{2-} or hydrocarbons were observed. Examination of the piece of sample #1 heated to 500°C by IR showed that the bands due to H_2O and OH^- had almost disappeared. If the 12 wt.% loss upon heating sample #1 to 700°C is all due to loss of adsorbed H_2O, one can easily calculate that such H_2O could readily have been accommodated by the 40% of the sample occupied by open pore spaces (Table 1). After heating to 700°C, the X-ray reflections of anatase are unaffected, but the weak peaks assigned to clay were found to have disappeared. This disappearance may be due to decomposition to an X-ray amorphous (glassy) phase.

In air, an additional exothermic DTA peak near 300°C was observed, but the curve was otherwise similar to that observed in the Ar atmosphere. This peak is very probably due to the combustion of traces of organic matter.

Results for sample #2 were, broadly speaking, similar to those obtained on sample #1, especially with respect to density, open porosity (Table 1) and widths of XRD peaks from the major anatase phase. XRD also showed very weak peaks (integrated intensity <5% of those of the strongest reflections of anatase) due to phases other than anatase; the corresponding *d* values are 3.34 (quartz), 5.72, 2.95, 2.21 and 2.09 Å. As with sample #1, an SEM scan showed the sample to be very fine grained; no EDX chemical identification could be obtained for single grains, though again Ti is the major cation, with some Si present. However, chemical analysis (Table 2) showed that Al, P and Fe are more abundant impurities than Si.

The chemical analysis of sample #2 agrees fairly well with values given by Eakins (1888) for anatase from the same locality, except that values of Al_2O_3 (7.6 wt.%) are considerably lower than those reported previously (17.6 wt.%). The XRD impurity peaks at 5.72, 2.95 and 2.21 Å could correspond to goyazite, $SrAl_3(PO_4)_2(OH)_5{\cdot}H_2O$; although the Sr in the sample is inadequate to explain the Al and P impurities on this basis, some of the divalent Fe^{2+} may have substituted in the (Ca, Sr, Pb) site to form one of the crandallite-type minerals.

DTA–TGA data for sample #2 up to 700°C in the Ar atmosphere are shown in Figure 1. The weight losses are slightly less than those for sample #1 and again are ascribed to the escape of water and hydroxyl ions. Although the origin of the endothermic DTA peak at 460°C is not known, it is clearly associated with the escape of a volatile species, as shown by the corresponding TGA curve. Unfortunately, no sample was left to conduct infrared absorption measurements. The DTA curve is fairly similar to that reported by Goñi (1957) over the 25–700°C range for a natural anatase formed by alteration of titanite. An XRD scan shows that structural effects on the anatase from the heating to 700°C in the DTA–TGA apparatus are negligible. However, the very weak diffraction peaks from the impurity phase(s) have disappeared by 700°C, and no new peaks are formed. Thus the impurity phase may have melted or decomposed into a glassy phase, and this may have enhanced the endothermic DTA peak at 460°C, assuming that such melting or decomposition occurs in the vicinity of 460°C.

Acid leaching of titanite crystals

From leaching results on synthetic titanite crystals grown by the Czochralski method (Crowe *et al.* 1986) and leached in dilute HCl (Vance 1987), it seemed likely that the complete dissolution of millimeter-sized samples would occur in 30 days at 100°C, at a pH of 1. However, this was not achieved with the skull-melted crystals (Crowe *et al.* 1986), even with 1 mol/L HCl, so that further experiments, with 0.3 and 1 mol/L HCl solutions, involved natural crystals, which are more reactive, presumably because of a greater concentration of imperfections. The reaction products had the same size and shape as the starting crystals in each case. However, several small pieces ($\leq$ 1 vol.% of the total) were observed to have separated from the samples, which are very fragile after the reactions, and a small amount of anatase (again ~1% of the total) was usually found on the bottom of the container. Consequently, the similarities in the shape and size of the products to those of the starting samples are based only on visual observations and measurements to the nearest 0.1 mm.

From XRD and SEM–EDX studies, many of the reacted samples consist of amorphous Si-rich material and rutile, in addition to anatase. In such samples, which were broken for SEM examination, the anatase and rutile are concentrated in the outer regions, and the Si-rich material occurs in the central areas. Stationary-sample XRD showed the anatase and the rutile to be randomly oriented. In two cases, where 0.3 mol/L HCl is used, the pseudomorphs consist almost entirely of anatase.

DISCUSSION AND CONCLUSIONS

For equation (1) to apply, free ingress of H_2O molecules into the titanite and the concomitant egress of Ca^{2+}, Si^{4+} and O^{2-} ions would be required. This situation is not feasible since H_2O molecules are too large to penetrate the titanite structure. Penetration of protons would be reasonable, however, and if the reaction proceeds by H^+ exchange with Ca^{2+} and Si^{4+}, the stoichiometric requirements of Equation (1) could be met. The titanite → TiO_2 transformation at the sample surface cannot, however, allow the formation of dense anatase because this would prevent the exit of Ca^{2+} and Si^{4+} from the underlying titanite. Thus, the anatase formed by crystallization must be porous or, in the absence of crystallization, a semirigid hydrated Ti oxide–hydroxide gel must form to allow passage of Ca^{2+} and Si^{4+} ions. The Si^{4+} ions in solution would presumably exist as $Si(OH)_4$ or a related species (Rimstidt & Barnes 1980). In the latter case, after conversion of the titanite to the gel, anatase could crystallize. Of course, a plausible alternative would be the quasicongruent dissolution of the titanite, followed by local precipitation of TiO_2, involving anatase crystallization.

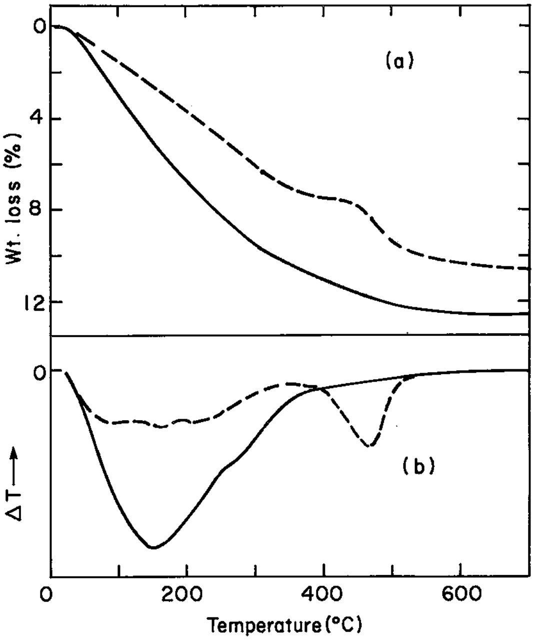

FIG. 1. DGA (a) and DTA (b) curves for natural pseudomorphs of anatase after titanite. Solid and dashed lines refer to samples #1 and #2, respectively.

There is a 63% contraction in molar volume attendant upon the titanite → anatase transformation (Vance 1987). Assuming no macroscopic contraction, anatase formed from solid titanite would have a calculated porosity of 63% and a density of ~1.5 g/cm^3. The density of the pseudomorph samples #1 and #2 (Table 1) is in good agreement with this value. The discrepancy between the experimentally determined porosities (40%) and the 63% calculated can be explained by proposing that the experimental values relate to open porosity only, not closed porosity. The presence of impurity phases would also tend to reduce porosity.

Complete dissolution of titanite according to Equation (1) would give rise to concentrations of dissolved silica well below the solubility limits of either quartz or amorphous silica (Rimstidt & Barnes 1980, Lenher & Merrill 1917). The appearance of siliceous material in addition to TiO_2 in the case of titanite altered in the 0.3 and especially the 1 mol/L HCl solutions thus would seem to represent a real deviation from the predictions of Equation (1), which is based on results obtained for pH values ≥ 1 (Vance 1987).

Finally, it is evident that anatase formed from titanite by leaching in groundwater has considerable porosity, so that the altered layers on the surface of the titanite will have little retarding effect on the alteration of the underlying titanite.

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