

POLYHEDRAL THERMAL EXPANSION IN THE TiO_2 POLYMORPHS: REFINEMENT OF THE CRYSTAL STRUCTURES OF RUTILE AND BROOKITE AT HIGH TEMPERATURE

E. P. MEAGHER

*Department of Geological Sciences, University of British Columbia,
Vancouver, British Columbia V6T 1W5*

GEORGE A. LAGER

*Department of Geosciences, Rider College,
Lawrenceville, New Jersey 08648, U.S.A.*

ABSTRACT

Crystal-structure refinements, with anisotropic temperature factors, of single-crystal X-ray intensity data collected at 25°, 300°, 600° and 900°C for rutile and 25°, 280°, 425° and 625°C for brookite resulted in final weighted residuals ranging from 0.037 to 0.058. Oxygen positional parameters in both structures are temperature-independent. The non-equivalent Ti-O interatomic distances in rutile increase at about the same rate with increasing temperature. At room temperature the Ti atom in brookite is displaced by 0.181 Å from the centroid of the octahedron. With increasing temperature the Ti moves toward the centroid, and a wide range of thermal expansions in Ti-O distances result. Comparison of high-temperature structures of rutile, brookite and anatase reveals that the variation of mean Ti-O distance with temperature is linear. The coefficients α are: $8.4 \times 10^{-6}/^\circ\text{C}$ (rutile), $8.6 \times 10^{-6}/^\circ\text{C}$ (anatase), $6.4 \times 10^{-6}/^\circ\text{C}$ (brookite). Response of octahedral bond-angle variance to increasing temperature is different for each polymorph because of differences in polyhedral linkage.

SOMMAIRE

Les intensités X diffractées ont été obtenues: pour le rutile, à 25, 300, 600 et 900°; pour la brookite, à 25, 280, 425 et 625°C. L'affinement des structures, à facteur de température anisotrope, a donné des résidus pondérés s'échelonnant de 0.037 à 0.058. Les coordonnées des atomes d'oxygène sont indépendantes de la température dans chacune des deux structures. Les distances interatomiques Ti-O non-équivalentes du rutile croissent à peu près également avec la température. A basse température, Ti dans la brookite est à 0.181 Å du centroïde de l'octaèdre; il s'en rapproche quand la température s'élève, provoquant dans les distances Ti-O toute une série d'expansions thermiques. La comparaison des structures de haute température des trois polymorphes montre que la distance Ti-O moyenne en fonction de la

température est linéaire. Les coefficients α sont $8.4 \times 10^{-6}/^\circ\text{C}$ (rutile), $8.6 \times 10^{-6}/^\circ\text{C}$ (anatase), $6.4 \times 10^{-6}/^\circ\text{C}$ (brookite). L'effet d'un accroissement de température sur l'angle des liaisons octaédriques est différent pour chaque polymorphe, ce qui est dû à des différences dans l'enchaînement des polyèdres.

(Traduit par la Rédaction)

INTRODUCTION

Rutile and brookite, along with anatase, represent the naturally occurring polymorphs of TiO_2 . Kinetic and thermodynamic studies (Dachille *et al.* 1968, Rao *et al.* 1961) of the TiO_2 system have shown that rutile is the stable form at high temperature and pressure. Dachille *et al.* (1968) were unable to crystallize brookite, but converted natural crystals of brookite to rutile at $\sim 720^\circ\text{C}$, 1 atm. The crystal structure of rutile was determined by Vegard (1916) and refinements of the structure have since been carried out by Cromer & Herrington (1955), Baur (1956), Baur & Kahn (1971) and Abrahams & Bernstein (1971). Pauling & Sturdivant (1928) first determined the crystal structure of brookite, with subsequent refinements undertaken by Weyl (1959) and Baur (1961). To date, there have been no high-temperature crystal-structure refinements of brookite or rutile. The crystal structure of anatase at high temperatures has been investigated by Horn *et al.* (1972).

The polymorphs of TiO_2 are an ideal mineral group in which to study the effect of linkage on polyhedral thermal expansion without the complication of chemical variations. Structurally, all three polymorphs are similar in that the Ti atom is octahedrally coordinated, but differ in the way the TiO_6 octahedra are linked. The octahedral linkage is through corners and

EXPERIMENTAL

TABLE 1. CRYSTAL DATA FOR RUTILE AND BROOKITE

RUTILE		25°C	300°C	600°C	900°C
Cell dimensions:	a	4.593(2)*	4.603(2)	4.616(3)	4.623(4)
	c	2.959(2)	2.966(2)	2.977(2)	2.986(2)
Number observed reflections:		61	59	56	61
BROOKITE		25°C	280°C	425°C	625°C
Cell dimensions:	a	9.174(2)	9.175(4)	9.191(4)	9.211(4)
	b	5.449(2)	5.459(4)	5.463(4)	5.472(4)
	c	5.138(2)	5.149(2)	5.157(4)	5.171(4)
Number observed reflections:		272	252	256	252
Space Group:		RUTILE		BROOKITE	
Unit cell content:		P4 ₂ /mm		Pbca	
Calculated density (25°C)		2[TiO ₂]		8[TiO ₂]	
Crystal Size		4.250g/cm ³		4.133g/cm ³	
		0.09x0.11x0.13mm		0.08x0.10x0.13mm	

* Number in parentheses refers to one estimated standard error in the last decimal place reported.

edges such that in rutile two edges of each octahedron are shared, whereas three are shared in brookite and four in anatase. The details of the rutile and brookite structures are well documented in the above references. For a discussion of the anatase structure the reader is referred to Vegard (1916) or Cromer & Herrington (1955).

TABLE 2. ATOMIC COORDINATES, ISOTROPIC TEMPERATURE FACTORS, AND WEIGHTED R-INDICES FOR BROOKITE AND RUTILE

		Brookite			
		25°C	280°C	425°C	625°C
Ti	x	0.1289(1)*	0.1290(1)	0.1289(1)	0.1290(2)
	y	0.0972(1)	0.0985(1)	0.0992(1)	0.0999(2)
	z	0.8628(1)	0.8627(1)	0.8628(1)	0.8628(2)
	B**	0.37(3)	0.75(3)	0.93(3)	1.22(3)
O _I	x	0.0095(4)	0.0096(4)	0.0098(4)	0.0098(6)
	y	0.1491(5)	0.1490(5)	0.1490(5)	0.1484(7)
	z	0.1835(5)	0.1832(5)	0.1838(5)	0.1831(7)
	B	0.46(6)	0.84(7)	1.08(7)	1.33(10)
O _{II}	x	0.2314(4)	0.2312(4)	0.2312(4)	0.2322(6)
	y	0.1110(4)	0.1118(5)	0.1116(6)	0.1117(8)
	z	0.5366(6)	0.5358(5)	0.5362(5)	0.5366(7)
	B	0.53(7)	0.88(7)	1.13(8)	1.43(11)
	R† = 0.039	R = 0.041	R = 0.037	R = 0.050	
		Rutile			
		25°C	300°C	600°C	900°C
Ti	B	0.42(6)	0.86(9)	1.31(9)	1.59(8)
	O	x	0.3051(7)	0.3045(9)	0.3045(9)
	B	0.60(6)	0.81(7)	1.29(7)	1.50(7)
	R = 0.047	R = 0.056	R = 0.058	R = 0.052	

* The number in parentheses represents one estimated standard deviation and refers to the last decimal place

** Isotropic equivalent of the anisotropic temperature factor (Hamilton, 1959)

† $R = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$

The rutile used in this study is a fragment of a synthetic crystal. The brookite crystal was chosen from a sample collected at Bin-natal, Switzerland. Electron microprobe analysis indicated less than 1% total iron occurs as impurities. Zero-through second-level Weissenberg photographs confirmed the space groups $P4_2/mnm$ and $Pbca$ for rutile and brookite, respectively. The 25°C cell parameters (Table 1) were obtained from least-squares refinements of back-reflection data and are statistically identical to a number of recent studies.

The high-temperature cell parameters (Table 1) were determined using a modified version of a furnace designed by Foit & Peacor (1967). The furnace, which requires flat-cone geometry, has been adapted to a Weissenberg camera for space-group and cell-dimension work and to a Supper Weissenberg diffractometer for single-crystal intensity data collection. Furnace temperatures, thought to be accurate to $\pm 15^\circ\text{C}$,

TABLE 3. ANISOTROPIC TEMPERATURE FACTORS FOR BROOKITE AND RUTILE*

		Brookite			
		25°C	280°C	425°C	625°C
Ti	β_{11}	1.27(22)	2.91(26)	3.56(20)	3.98(28)
	β_{22}	3.76(28)	6.50(30)	8.06(28)	10.97(40)
	β_{33}	2.23(31)	4.82(32)	6.01(32)	9.31(43)
	β_{12}	-0.05(11)	-0.21(12)	-0.23(13)	-0.08(19)
	β_{13}	0.09(10)	0.10(12)	0.41(12)	0.04(17)
	β_{23}	-0.19(16)	-0.03(15)	0.06(18)	0.09(26)
O _I	β_{11}	1.71(46)	2.45(54)	3.41(53)	3.40(73)
	β_{22}	4.46(82)	8.71(84)	10.56(90)	14.30(132)
	β_{33}	2.65(89)	6.22(90)	7.85(90)	10.37(127)
	β_{12}	-0.41(42)	-0.79(47)	-1.15(52)	-2.53(73)
	β_{13}	0.73(47)	0.72(47)	1.07(51)	0.35(70)
	β_{23}	-0.77(64)	-1.40(67)	-1.59(72)	-1.53(104)
O _{II}	β_{11}	0.66(48)	2.97(57)	3.61(57)	3.92(79)
	β_{22}	7.59(94)	8.77(88)	11.93(98)	15.55(148)
	β_{33}	4.39(94)	5.53(95)	6.98(91)	10.37(129)
	β_{12}	0.57(45)	0.78(49)	1.49(56)	2.32(85)
	β_{13}	0.52(45)	0.43(50)	0.98(50)	0.83(71)
	β_{23}	1.29(72)	0.83(67)	1.46(78)	1.04(114)
		Rutile			
		25°C	300°C	600°C	900°C
Ti	β_{11}	6.52(152)	12.75(219)	18.35(215)	21.12(201)
	β_{33}	4.56(180)	11.66(227)	22.39(223)	32.16(225)
	β_{12}	-0.13(83)	-0.11(83)	-0.65(77)	-1.14(73)
O	β_{11}	7.69(195)	11.89(179)	17.70(170)	19.02(161)
	β_{33}	9.83(379)	11.91(380)	24.34(381)	35.09(400)
	β_{12}	-1.39(150)	-3.04(245)	-2.87(254)	-6.99(192)

* Values reported are $\times 10^3$. The coefficients are of the form $(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)$.

$\beta_{11} = \beta_{22}$ and $\beta_{13} = \beta_{23} = 0$ for Ti and O in rutile.

have been calibrated with minerals of known melting points and with a thermocouple in place of the sample. Flat-cone Weissenberg photographs obtained at the temperatures of the refinements are consistent with the room-temperature space-group assignments.

For intensity measurements, each crystal was placed in a tapered silica capillary which was then cemented to a platinum rod for insertion into the furnace. Three-dimensional intensity data were collected with flat-cone geometry on a manual Weissenberg diffractometer utilizing Zr-filtered Mo radiation and a pulse-height discriminator. Intensity data were collected at 25°, 300°, 600° and 900° for rutile, and 25°, 280°, 425° and 625°C for brookite. Symmetry-independent reflections of $\sin \theta \leq 0.5$ were scanned, traced on a strip-chart recorder and their relative intensities determined with an integrating planimeter.

The resulting intensities were corrected for Lorentz and polarization effects and an absorption correction was applied to the brookite data using a linear absorption coefficient of $\mu = 57.5 \text{ cm}^{-1}$. Symmetry-equivalent reflections in rutile revealed an average deviation in intensity of seven percent; this is marginally higher than the experimental error of the overall system and no absorption correction was applied.

TABLE 4. INTERATOMIC DISTANCES AND ANGLES IN RUTILE

	Ti-O Distance			
	25°C	300°C	600°C	900°C
Ti-O _{Ia} [4]*	1.947(2)**	1.954(2)	1.961(2)	1.962(2)
Ti-O _{Ib} [2]	1.982(3)	1.983(3)	1.988(3)	1.995(3)
<Ti-O>	1.959	1.964	1.970	1.973
O-O Distance				
O _{Ia} -O _{Ia} (s)† [2]	2.532(5)	2.544(6)	2.552(6)	2.547(5)
O _{Ib} -O _{Ia} [8]	2.778(2)	2.784(2)	2.792(2)	2.799(2)
O _{Ia} -O _{Ia} (u)† [2]	2.959(2)	2.966(2)	2.977(2)	2.986(2)
<O-O>	2.767	2.774	2.783	2.788
Ti-Ti Distance				
Ti-Ti	2.959(2)	2.966(2)	2.977(2)	2.986(2)
O-Ti-O Angle				
O _{Ia} -Ti-O _{Ia} (s)	81.12(12)	81.23(14)	81.22(14)	80.93(12)
Ti-O-Ti Angle				
Ti-O _{Ia} -Ti	130.56(6)	130.62(7)	130.61(7)	130.47(6)

* Multiplicity of interatomic distance

** Number in parentheses refers to one estimated standard deviation

† Shared edge (s), unshared edge (u)

Structure refinements were carried out using a modified version of the program ORFLS (Busing *et al.* 1962) and the atomic coordinates of Cromer & Herrington (1955) and Baur (1961) as starting parameters. Scattering factors for titanium and oxygen were taken from the International Tables (1962) and Suzuki (1960), respectively, assuming fully ionized atoms. A weighting scheme similar to that proposed by Cruickshank (1965) was used and adjusted for each refinement in order to yield constant values of $\langle w_i(F_o - ScF_c) \rangle$ in equally populated groups of increasing F_o , where w_i is the weight, F_o is the observed structure factor, F_c the calculated structure factor and Sc the scale factor. In the initial refinements for both rutile and brookite, a comparison of observed and calculated structure factors showed that $F_o < F_c$ for large F_o , indicating the effect of secondary extinction. An extinction correction therefore was applied

TABLE 5. INTERATOMIC DISTANCES IN BROOKITE

	Ti-O			
	25°C	280°C	425°C	625°C
Ti-O _{Ia}	1.990(3)*	1.989(3)	1.985(3)	1.991(5)
Ti-O _{Ib}	1.863(3)	1.870(4)	1.877(4)	1.881(5)
Ti-O _{Ic}	1.999(3)	2.000(3)	2.003(3)	2.005(5)
Ti-O _{IIa}	2.052(3)	2.043(3)	2.045(3)	2.050(5)
Ti-O _{IIb}	1.930(3)	1.938(3)	1.944(4)	1.945(5)
Ti-O _{IIc}	1.923(3)	1.928(3)	1.930(3)	1.937(4)
<Ti-O>	1.960	1.961	1.964	1.968
O-O				
O _{Ia} -O _{IIa}	2.734(4)	2.733(5)	2.736(5)	2.752(7)
O _{IIa} -O _{Ic} **	2.534(5)	2.533(5)	2.536(5)	2.548(7)
O _{Ic} -O _{IIb}	2.869(5)	2.874(5)	2.876(5)	2.872(7)
O _{IIb} -O _{Ib}	2.799(5)	2.800(5)	2.809(5)	2.806(7)
O _{Ib} -O _{IIc}	2.993(4)	3.000(5)	3.003(5)	3.016(7)
O _{IIc} -O _{IIb}	2.746(4)	2.751(2)	2.753(2)	2.756(2)
O _{IIb} -O _{IIc}	2.860(3)	2.870(3)	2.873(3)	2.879(4)
O _{IIc} -O _{IIa}	2.982(3)	2.984(3)	2.989(4)	2.996(5)
O _{Ia} -O _{Ic}	2.794(2)	2.801(3)	2.805(3)	2.814(4)
O _{Ic} -O _{Ib} **	2.495(6)	2.496(6)	2.505(6)	2.509(8)
O _{Ib} -O _{Ia}	2.814(2)	2.820(2)	2.821(2)	2.827(3)
O _{Ia} -O _{IIc} **	2.534(5)	2.533(5)	2.536(5)	2.548(7)
<O-O>	2.763	2.766	2.770	2.777
Ti-Ti				
Ti-Ti	2.951(2)	2.960(2)	2.965(2)	2.976(3)
Ti-Ti	3.062(2)	3.060(2)	3.060(2)	3.063(2)

* Number in parentheses refers to one estimated standard error.

** Shared edge

TABLE 6. INTERATOMIC ANGLES IN BROOKITE

		O-Ti-O			
		25°C	280°C	425°C	625°C
O _{Ia} -Ti-O _{IIa}	85.14(13)°	85.36(14)	85.50(14)	85.87(19)	
O _{IIa} -Ti-O _{Ic} *	77.43(12)	77.57(13)	77.58(13)	77.88(18)	
O _{Ic} -Ti-O _{IIb}	93.76(13)	93.71(14)	93.52(14)	93.27(20)	
O _{IIb} -Ti-O _{Ib}	95.07(13)	94.60(15)	94.61(15)	94.30(21)	
O _{Ib} -Ti-O _{IIc}	104.49(13)	104.33(14)	104.14(14)	104.33(20)	
O _{IIc} -Ti-O _{Ia} *	80.70(12)	80.56(13)	80.72(14)	80.87(19)	
O _{IIa} -Ti-O _{IIb}	87.13(8)	87.37(9)	87.26(9)	87.19(12)	
O _{IIb} -Ti-O _{IIc}	95.85(7)	95.85(8)	95.72(9)	95.71(12)	
O _{IIc} -Ti-O _{IIa}	97.20(13)	97.38(14)	97.50(14)	97.38(20)	
O _{Ia} -Ti-O _{Ic}	88.94(12)	98.21(14)	89.39(15)	89.54(20)	
O _{Ic} -Ti-O _{IIb} *	80.41(13)	80.29(13)	80.38(13)	80.08(18)	
O _{Ib} -Ti-O _{Ia}	93.78(5)	93.78(7)	93.82(7)	93.77(8)	
Ti-O-Ti					
Ti-O _{Ib} -Ti	99.59(13)	99.71(13)	99.62(13)	99.92(18)	
Ti-O _{Ic} -Ti	100.26(16)	100.21(16)	100.20(17)	100.08(23)	
Ti-O _{Ia} -Ti	159.20(16)	159.07(17)	159.17(17)	158.97(23)	
Ti-O _{IIa} -Ti	123.92(15)	124.16(15)	124.11(15)	124.10(21)	
Ti-O _{IIb} -Ti	134.80(16)	134.50(16)	134.67(17)	134.83(23)	
Ti-O _{IIc} -Ti	100.72(14)	100.76(15)	100.63(16)	100.35(22)	

* Angles opposite shared edges

to the data by minimizing the function $\sum w_i [F_{o,i} - ScF_{c,i}(1 + \alpha \cdot I_i)]^2$ where I_i are the uncorrected intensities and α is the extinction coefficient to be adjusted in the refinement. Refinements with anisotropic temperature factors at four temperatures yielded final weighted residuals between 0.047 and 0.058 for rutile, and between 0.037 and 0.049 for brookite. The atomic coordinates and anisotropic temperature factors are listed in Tables 2 and 3, respectively. The bond lengths and angles, uncorrected for thermal vibration, and their associated e.s.d., computed using the function and error program of Busing *et al.* (1964), are given in Tables 4 through 6. The observed structure amplitudes and the calculated structure factors are presented in Table 7, available at a nominal charge from Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa.

DISCUSSION

Parts of the structures of rutile and brookite are shown in Figures 1 and 2, respectively. In both minerals the dominant structural feature

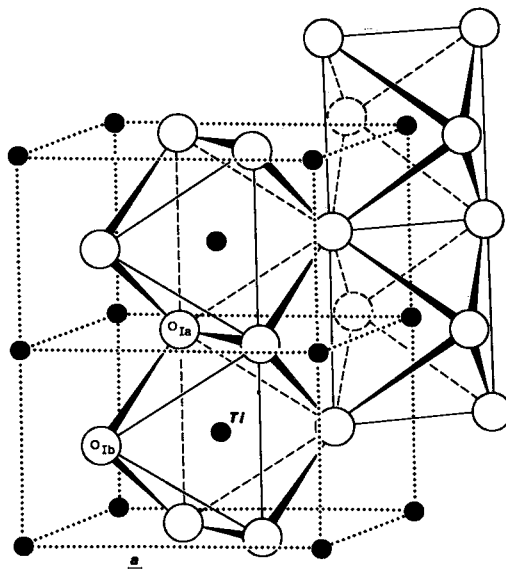


FIG. 1. Crystal structure of rutile.

is the chain of edge-sharing TiO₆ octahedra which run parallel to *c*. The octahedra in rutile

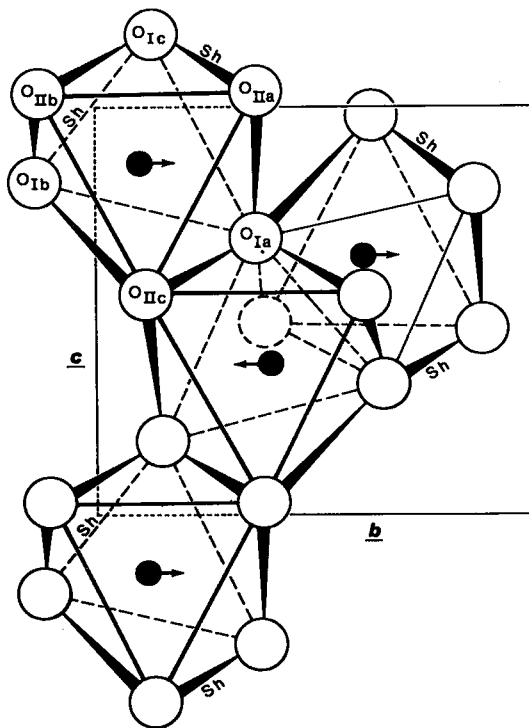


FIG. 2. Projection on the (100) plane of part of the brookite structure. Shared edges are labeled Sh. Arrows indicate the direction of Ti movement with increasing temperature.

share two opposite edges to form straight chains that are, in turn, linked by corners to complete the framework. In brookite, where three edges are shared, the octahedra are arranged in zig-zag chains with each octahedron sharing one edge with an octahedron of the neighboring chain. Oxygen atoms in both structures are coordinated to three titanium atoms in a near-planar configuration.

Rutile structure

Titanium in the rutile structure occupies the Wyckoff position *2a* at the origin, and oxygen occupies position *4f* at *x,x,0*. The *x* positional parameter at room temperature was most recently determined by Abrahams & Bernstein (1971) to be 0.3048(1), which compares favorably with 0.3051(7) determined in this study. No change occurs in the *x* positional parameter of oxygen with heating to 900°C (Table 2).

Because the oxygen parameter *x* is temperature-independent, the changes in interatomic distances and angles are dependent on lattice expansion. In rutile there are two non-equivalent nearest-neighbor Ti–O distances; two longer Ti–O_{Ia} bonds parallel (001) planes and four shorter Ti–O_{Ib} bonds parallel the (110) planes (Fig. 1). Both Ti–O interatomic distances increase at almost the same rate with temperature. Of the three octahedral edges, the shared edge O_{Ia}–O_{Ia}(s) increases at a lower rate than the two unshared edges.

The isotropic equivalents of the anisotropic temperature factors given in Table 2 for Ti and O suggest a slightly greater increase in *B*_{Ti} with temperature. Thermal vibration data (Table 8) show that the Ti ellipsoid has the shape of an oblate spheroid with the short axis in the direction of the shared octahedral edge. The direction of maximum thermal vibration for oxygen is perpendicular to the plane of coordinating Ti atoms. The degree of anisotropic thermal vibration out of this plane increases with increasing temperature.

Brookite structure

The titanium and two non-equivalent oxygens in brookite occupy general positions in space group *Pbca* (Fig. 2). The positional parameters determined at 25°C in this study are statistically identical to those determined by Baur (1961). Except for an increase in the *y* coordinate of titanium, atomic coordinates undergo no statistically significant change with

TABLE 8. ROOT-MEAN-SQUARE OF THERMAL DISPLACEMENTS ALONG THE PRINCIPAL AXES IN RUTILE

Atom	Axis	rms displacement $\bar{k}(\sigma)$	Angle, in degrees, with respect to		
			+a	+b	+c
25°C					
Ti	1	0.045(9)	90	90	0
	2	0.083(7)	45	45	90
	3	0.084(7)	45	135	90
O	1	0.066(13)	90	90	0
	2	0.082(11)	45	45	90
	3	0.098(9)	45	135	90
300°C					
Ti	1	0.072(7)	90	90	0
	2	0.117(6)	45	45	90
	3	0.118(6)	45	135	90
O	1	0.073(12)	90	90	0
	2	0.098(14)	45	45	90
	3	0.1266(11)	45	135	90
600°C					
Ti	1	0.100(5)	90	90	0
	2	0.138(5)	45	45	90
	3	0.143(5)	45	135	90
O	1	0.104(8)	90	90	0
	2	0.126(11)	45	45	90
	3	0.149(10)	45	135	90
900°C					
Ti	1	0.120(4)	90	90	0
	2	0.147(5)	45	45	90
	3	0.155(4)	45	135	90
O	1	0.114(9)	45	45	90
	2	0.126(7)	90	90	180
	3	0.168(7)	45	135	90

increase. As a result, the O_{Ia}–Ti–O_{Ia} octahedral angle undergoes a significant increase, and the O_{Ib}–Ti–O_{Ib} angle decreases with increasing temperature. The octahedral distortion, as measured by the octahedral bond-angle variance (Robinson *et al.* 1971), decreases from 65.42° at 25°C to 62.69° at 625°C.

At room temperature, as a result of the Ti displacement, there are three short Ti–O interatomic distances and three longer distances. The thermal displacement of Ti toward the octahedron centre results in significant increases in the shorter Ti–O distances and little or no change in the longer distances.

Changes in the relative lengths of the octahedral edges are also related to the Ti shift along *b*. For example, the edge O_{Ia}–O_{Ia}, which is in the direction of Ti displacement, increases significantly with temperature, whereas the opposite edge O_{Ib}–O_{Ib} experiences no significant increase. As a result, the O_{Ia}–Ti–O_{Ia} octahedral angle undergoes a significant increase, and the O_{Ib}–Ti–O_{Ib} angle decreases with increasing temperature. The octahedral distortion, as measured by the octahedral bond-angle variance (Robin-

son *et al.* 1971), decreases from 65.42° at 25°C to 62.69° at 625°C.

The isotropic equivalents of the anisotropic temperature factors (Table 2) increase linearly with temperature at approximately the same rates for Ti, O_I and O_{II}. The thermal vibration of O_I and O_{II} is anisotropic (Table 9) with the maximum thermal vibration for both oxygens directed out of the plane of coordinating titaniums. The vibration ellipsoid of the Ti has the shape of an oblate spheroid with the short axis parallel to *a*. With increasing temperature, the vibration ellipsoids increase in size but maintain a similar shape.

Comparison of the TiO₂ polymorphs at room temperature

As mentioned, the three polymorphs differ in their octahedral linkage such that two, three and four octahedral edges are shared in rutile, brookite and anatase, respectively. The shared

octahedral edges are the shorter edges in each of the polymorphs, presumably the result of cation-cation antibonding interactions.

The density of the polymorphs decreases as the number of edges shared in the structure increases. The apparent reason for this density decrease is the increase in Ti-Ti interatomic distances. The mean nearest-neighbor Ti-Ti distance is 2.959Å in rutile, 3.024Å in brookite and 3.039Å in anatase; this and all other data quoted for anatase are taken from Horn *et al.* (1972). If one considers the mean of all Ti-Ti interatomic distances within a radius of 5.0Å, the same trend exists. Accordingly, the molar volumes (25°C) follow the trend: rutile (18.79 cm³/mole) < brookite (19.33) < anatase (20.51), with a concomitant decrease in density.

In rutile and anatase, each Ti octahedron has a symmetric disposition of shared edges about its centroid position which is occupied by the Ti atom (point symmetry *D_{2h}* and *D_{2d}*, respectively). In brookite the distribution of three shared edges is asymmetric and the Ti atom is displaced from the centroid position. Weyl (1959) suggested that displacement of Ti from the octahedron centre in brookite is a result of cation-cation repulsive forces. His argument is based upon the fact that the resultant of the repulsive-force vectors for titanium atoms out to a distance of 4.5Å is in the direction of displacement of the Ti atom.

The TiO₆ octahedral volumes differ for the three polymorphs such that an increase in the number of shared edges correlates with a decreasing volume (Fig. 3). Note, however, that the mean Ti-O distances at 25°C for rutile (1.959Å), brookite (1.960Å) and anatase (1.949Å) do not reflect the trend of the octahedral volumes because of the off-centring of Ti in brookite. For a given octahedral volume the shortest mean Ti-O distance is obtained where the cation occupies the centroid of coordinating oxygens. The calculated mean centroid-oxygen distance for brookite at 25°C is 1.951Å, intermediate to rutile and anatase, and is consistent with the octahedral volumes.

One measure of relative distortions in polyhedra is the quadratic elongation (Robinson *et al.* 1971). Calculated elongations of the TiO₆ octahedra reveal increased distortion with increased number of shared edges in rutile (1.008), brookite (1.019) and anatase (1.031), respectively. Another measure of polyhedral distortion is the variance of oxygen-metal-oxygen angles from those of an ideal polyhedron. The octahedral bond-angle variance (Robinson *et al.* 1971) for rutile (28.67°),

TABLE 9. ROOT-MEAN-SQUARE OF THERMAL DISPLACEMENTS ALONG THE PRINCIPAL AXES IN BROOKITE

Atom	Axis	rms displacement Å(σ)	Angle, in degrees, with respect to:		
			+a(σ)	+b(σ)	+c(σ)
25°C					
Ti	1	.054(4)	6(6)	92(5)	85(6)
	2	.073(6)	86(9)	114(68)	155(66)
	3	.076(3)	86(6)	25(67)	114(68)
O _I	1	.053(12)	21(11)	100(15)	71(15)
	2	.077(9)	88(20)	145(23)	125(23)
	3	.094(8)	111(10)	123(24)	41(23)
O _{II}	1	.048(20)	74(20)	95(9)	17(17)
	2	.074(9)	155(16)	110(9)	76(20)
	3	.111(7)	108(8)	21(9)	79(7)
280°C					
Ti	1	.080(3)	2(3)	90(4)	88(3)
	2	.098(2)	90(4)	169(7)	101(7)
	3	.112(5)	88(3)	79(7)	169(7)
O _I	1	.085(7)	25(19)	100(17)	68(27)
	2	.097(9)	77(30)	124(13)	143(19)
	3	.123(6)	111(8)	144(12)	62(13)
O _{II}	1	.084(8)	11(8)	82(11)	82(14)
	2	.105(9)	90(17)	49(20)	139(20)
	3	.124(7)	101(8)	43(20)	50(20)
425°C					
Ti	1	.089(2)	8(3)	88(3)	82(2)
	2	.110(2)	86(4)	170(6)	100(6)
	3	.124(3)	83(2)	80(6)	68(5)
O _I	1	.096(7)	23(12)	99(14)	69(18)
	2	.111(8)	81(21)	133(11)	135(13)
	3	.140(6)	111(6)	136(11)	53(11)
O _{II}	1	.092(7)	17(10)	84(10)	74(13)
	2	.113(8)	81(16)	52(10)	140(10)
	3	.147(6)	104(5)	39(10)	55(10)
625°C					
Ti	1	.112(3)	2(5)	92(5)	89(5)
	2	.129(3)	91(6)	159(53)	111(53)
	3	.131(4)	92(5)	111(53)	21(53)
O _I	1	.104(12)	82(31)	122(9)	147(15)
	2	.117(8)	14(19)	95(19)	78(27)
	3	.161(7)	101(8)	148(7)	60(8)
O _{II}	1	.112(10)	49(52)	107(25)	45(39)
	2	.121(9)	42(52)	63(21)	120(42)
	3	.166(9)	100(7)	32(9)	60(9)

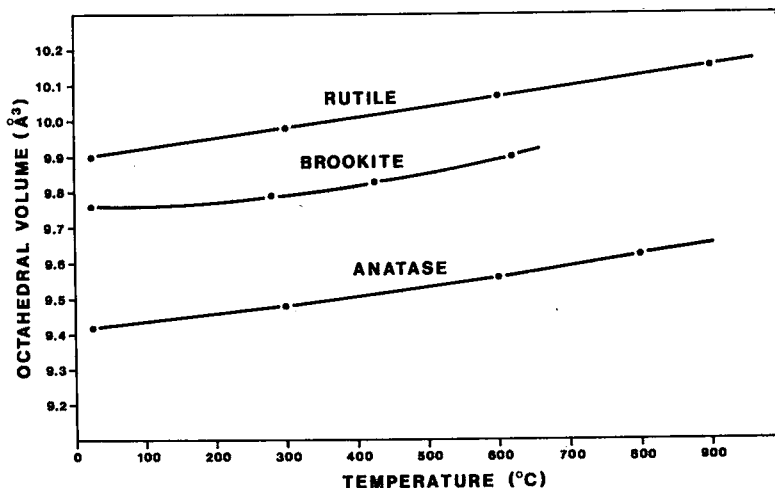


FIG. 3. Octahedral volumes *versus* temperature for the TiO₂ polymorphs.

brookite (65.42°) and anatase (105.15°) further illustrates the fact that distortion increases with the number of shared edges.

Comparison of TiO₂ polymorphs at high temperatures

Of the three polymorphs, brookite exhibits the greatest range of thermal expansion in individual Ti-O bond lengths. No significant change occurs in the Ti-O_{Ia} and Ti-O_{IIa} bond lengths over the temperature range 25°-620°C, whereas the largest expansion occurs in the Ti-O_{Ib} distance ($\alpha = 1.7 \times 10^{-5} / ^\circ\text{C}$, where $\alpha = \frac{1}{l_{25}^\circ} \left(\frac{l_T - l_{25}^\circ}{T - 25^\circ} \right)$; dl/dT is determined by simple linear regression). These extremes are a result of the Ti shift away from O_{Ib}, O_{IIb} towards O_{Ia}, O_{IIa}. In rutile and anatase, where Ti is constrained to the centroid position of the oxygens, the individual $\alpha(\text{Ti-O})$ values are similar.

A comparison of the thermal expansion coefficients for the mean Ti-O distances, $\alpha(\overline{\text{Ti-O}})$, reveals that rutile and anatase have similar values, 8.4×10^{-6} and $8.6 \times 10^{-6} / ^\circ\text{C}$, respectively. The brookite coefficient of $6.4 \times 10^{-6} / ^\circ\text{C}$ is approximately two estimated standard errors below the values of rutile and anatase and cannot be considered significantly different. Hazen & Prewitt (1977) have proposed an empirical relationship between the linear expansion coefficient of mean cation-oxygen bonds and Pauling's bond strength. Using their relation, $\alpha(\overline{\text{Ti-O}})$

is predicted to be $2.7 \times 10^{-6} / ^\circ\text{C}$, considerably lower than observed values.

The rate of change of octahedral volume with increasing temperature is illustrated in Figure 3. For rutile and anatase a constant rate of increase is apparent but the relationship for brookite is not as clear. Accordingly, a stepwise polynomial regression of octahedral volume *versus* temperature for brookite was undertaken; it yielded a second degree coefficient with an F probability ratio of 0.10. This ratio, along with the fact that one is working with so few data points, leads us to believe that we cannot reject the possi-

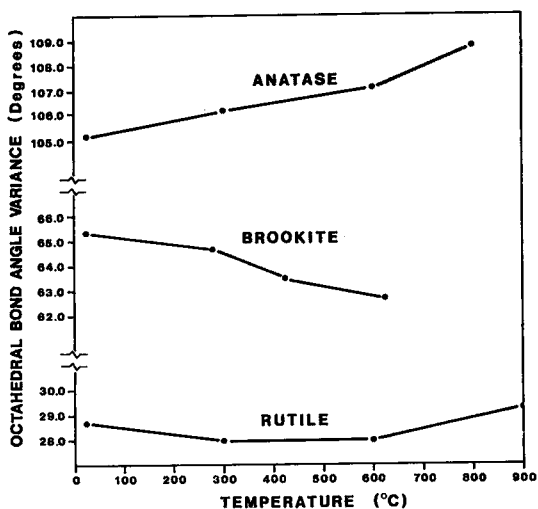


FIG. 4. Octahedral bond-angle variance *versus* temperature for the TiO₂ polymorphs.

bility of a quadratic relationship with a high degree of certainty. In rutile and anatase, expansion of the oxygen-oxygen distances about the octahedron is similar in that unshared edges expand at a greater rate than shared edges. No clear trend is observed in brookite.

As mentioned, the octahedral bond-angle variance increases with the number of shared edges in the three polymorphs. Furthermore, the change in bond-angle variance with heating differs for each polymorph. As illustrated in Figure 4, the angle variance remains approximately constant across the temperature range for rutile. In brookite, as the Ti atom shifts toward the octahedron centroid, the angular distortion decreases; in anatase, the distortion increases with heating as a result of the shift of the oxygen atom along the *c* axis (Horn *et al.* 1972). The quadratic elongation shows no significant change with temperature in any of the polymorphs.

Anisotropic thermal vibration of the oxygen atom is apparent in all three minerals at all temperatures. In each polymorph the major axis of the thermal vibration ellipsoid for oxygen is out of the plane of three coordinating Ti atoms (Tables 8 and 9; Horn *et al.* 1972).

CONCLUSIONS

The TiO₆ octahedra in the three polymorphs of TiO₂ differ with respect to size and distortion at room temperature and pressure. The range in TiO₆ octahedral volume is approximately 0.4Å³ whereas the quadratic elongation and octahedral bond-angle variance have a range of 0.023Å and 76.5°, respectively. Accordingly, the response of the TiO₆ octahedron to increasing temperature would also be expected to reflect the differences in polyhedral environment.

Indeed, the change in distortion with heating, as measured by the octahedral bond-angle variance, does differ for the three polymorphs; the octahedron in brookite becomes less distorted, whereas that in anatase increases in distortion and rutile remains effectively unchanged. The thermal expansion coefficients of the mean Ti-O interatomic distance in the three polymorphs range from 8.6x10⁻⁶ to 6.4x10⁻⁶/°C, not significantly different at the level of precision of our analyses. The rate of increase of octahedral volume with temperature is constant

in rutile and anatase, whereas in brookite a curvilinear relation cannot be rejected with a high degree of certainty.

ACKNOWLEDGEMENTS

This study was supported by a National Research Council Operating Grant to EPM and Grant #EAR77-12905, Earth Science Section, NSF, to GAL. Thanks go to Krista Scott for her assistance in the laboratory and to Jan Ashdown for manuscript preparation.

REFERENCES

- ABRAHAMS, S. C. & BERNSTEIN, J. L. (1971): Rutile: normal probability plot analysis and accurate measurement of crystal structure. *J. Chem. Phys.* 55, 3206-3211.
- BAUR, W. H. (1956): Über die Verfeinerung der Kristallstrukturbestimmung einiger Vertreter des Rutiltyps: TiO₂, SnO₂, GeO₂ und MgF₂. *Acta Cryst.* 9, 515-520.
- (1961): Atomabstände und Bindungswinkel im Brookit, TiO₂. *Acta Cryst.* 14, 214-216.
- & KAHN, A. A. (1971): Rutile-type compounds. IV. SiO₂, GeO₂ and a comparison with other rutile-type structures. *Acta Cryst.* B27, 2133-2139.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962): ORFLS, a FORTRAN crystallographic least squares program. *Oak Ridge Nat. Lab., No. ORNL-TM-305.*
- , ——— & ——— (1964): ORFFE, a FORTRAN crystallographic function and error program. *Oak Ridge Nat. Lab., No. ORNL-TM-306.*
- CROMER, D. T. & HERRINGTON, K. (1955): The structures of anatase and rutile. *J. Amer. Chem. Soc.* 77, 4708-4709.
- CRUICKSHANK, D. W. J. (1965): Errors in least squares methods. In *Computing Methods in Crystallography* (J. S. Rollett, ed.). Pergamon Press, Oxford.
- DACHILLE, F., SIMONS, P. Y. & ROY, R. (1968): Pressure-temperature studies of anatase, brookite, rutile and TiO₂-II. *Amer. Mineral.* 53, 1929-1939.
- FOIT, F. F. & PEACOR, D. R. (1967): A high temperature furnace for a single crystal X-ray diffractometer. *J. Sci. Instr.* 44, 183-185.
- HAMILTON, W. C. (1959): On the isotropic temperature factor equivalent to a given anisotropic temperature factor. *Acta Cryst.* 12, 609-610.
- HAZEN, R. M. & PREWITT, C. T. (1977): Effects of temperature and pressure on interatomic distances in oxygen-based minerals. *Amer. Mineral.* 62, 309-315.

- HORN, M., SCHWERDTFEGER, C. F. & MEAGHER, E. P. (1972): Refinement of the structure of anatase at several temperatures. *Z. Krist.* **136**, 273-281.
- IBERS, J. A. & HAMILTON, W. C., (1962): *International Tables for X-Ray Crystallography. III. Physical and Chemical Tables*. Kynoch Press, Birmingham, England.
- PAULING, L. & STURDIVANT, J. H. (1928): The crystal structure of brookite. *Z. Krist.* **68**, 239-256.
- RAO, C. N. R., YOGANARASIMHAN, S. R. & FAETH, P. A. (1961): Studies on the brookite-rutile transformation. *Trans. Farad. Soc.* **57**, 504-510.
- ROBINSON, K., GIBBS, G. V. & RIBBE, P. H. (1971): Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. *Science* **172**, 567-570.
- SUZUKI, T. (1960): Atomic scattering factor for O²⁻. *Acta Cryst.* **13**, 279.
- VEGARD, L. (1916): Results of crystal analysis-III. *Phil. Mag.* **32**, 505-518.
- WEYL, R. (1959): Präzisionsbestimmung der Kristallstruktur des Brookites, TiO₂. *Z. Krist.* **111**, 401-420.

Received May 1978; revised manuscript accepted September 1978.