Inverted High-Temperature Quartz

Unit Cell Parameters and Properties of the α−β Inversion

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Abstract. Fifty-two samples of inverted high-temperature quartz from volcanic rocks were investigated by Guinier-Jago powder diffractometry and differential scanning calorimetry (DSC). Quartz megacrysts from Clear Lake and Cinder Cone, California show a variability of $\simeq 2.5°$ K in their $\alpha-\beta$ transition temperature $(T_{\alpha-\beta})$. Quartz phenocrysts and quartz from crystalline rocks give a range of $0.5°$ K in $T_{\alpha-\beta}$. Neutron activation analysis of single crystals demonstrates that Al is the principal impurity (17–380 ppm). Its concentration is inversely correlated with $T_{\alpha-\beta}$. A very small variation was found in the a and c lattice parameters among the specimens of volcanic quartz studied. This variation does not correlate with Al content or transition temperature. Mean values at $22°$ C $(a = 4.1934 \pm 0.0004$ Å, $c = 5.4046 \pm 0.0006$ Å) are similar to those of quartz grown at low temperatures. Enthalpy of the $\alpha-\beta$ transition $(\Delta H_{\alpha-\beta})$, obtained over $9.0°$ from DSC runs, is dependent upon sample grain size and for a crushed powder with zero hysteresis $(T_{\alpha-\beta}$ on heating $= T_{\alpha-\beta}$ on cooling) is 92.0 ± 1.4 cal/mol. In contrast, a single piece of quartz requires $\Delta H_{\alpha-\beta}$ be 107.7 ± 1.4 cal/mol and has a $T_{\alpha-\beta}$ hysteresis of $1.1°$ K.

Regression of published data provides equations for the variation of the molar volume (cc/mol) of quartz with temperature:

23 to 848° K

$$V = 22.6965 + 5.94456 \times 10^{-4}(T-273.15) + 2.41848 \times 10^{-9}(T-273.15)^3$$

848 to 1323° K

$$V = 23.9341 - 6.64862 \times 10^{-4}(T-273.15) + 4.56642 \times 10^{-7}(T-273.15)^2.$$

These equations imply a $\Delta V_{\alpha-\beta}$ of 0.205 ± 0.031 cc/mol. Expressions are also provided for the temperature dependence of the thermal coefficient of expansion, α, the compressibility, β, and $(\partial\beta/\partial T)_P$ (which is identically $-(\partial\alpha/\partial P)_T$).

DSC heat capacity measurements over the range 400 to 900° K were fitted to extended Maier-Kelley type expressions to give:

$$C_P = 10.31 + 9.116 \times 10^{-3} T - \frac{1.812 \times 10^5}{T^2} - 5.630 \times 10^{-2} \frac{T}{(T-848)} - 0.3553 \frac{T}{(T-848)^2} - 0.9011 \frac{T}{(T-848)^3}$$

(400 to 842° K), and

$$C_P = -318.8 + 0.2532 T + \frac{8.687 \times 10^7}{T^2} + 0.1603 \frac{T}{(T-848)^4}$$

(851 to 900° K), which together with the values of $\Delta H_{\alpha-\beta}$ measured over the range 842–851° K give 7875.3 cal/mol for $H_{900}-H_{400}$.

The behavior of α, β, and C_P as a function of T emphasizes that structural changes which occur at the $\alpha-\beta$ transition do so over a broad temperature interval.

Introduction

Considering all the common rock-forming minerals the physical and chemical properties of quartz have probably been the most extensively investigated. This is undoubtedly due to the ready availibility of optically clear single crystals of considerable size. Almost without exception, however, large crystals of quartz have grown below 848° K, the α (low) to β (high)-

quartz transition temperature. This paper is particularly concerned with the composition, and its effect on the various thermodynamic and structural properties of quartz that occurs as phenocrysts in lavas, and therefore precipitated or equilibrated, in the β-quartz stability field. Although the $\alpha - \beta$ transformation is unquenchable, for the purposes of this discussion we shall refer to all quartz grown or equilibrated above 848° K as *high-temperature* quartz, though it is in the α-form at room temperature.

Quartz phenocrysts in silicic lavas often co-exist with plagioclase, and as these two minerals have similar densities, pure quartz can only be obtained by hand-picking individual grains under a microscope. It is not surprising, therefore, that studies of high-temperature quartz have been relatively limited. We would expect that as solid solution generally increases with temperature, samples of high-temperature quartz would be ideal for investigating potential variations in physical parameters with composition. Furthermore, if the temperatures at which the quartz precipitated were known, correlations involving both chemical and physical properties with temperature of crystallization or equilibration could be made. With these intents in mind, and before the experimental data are discussed, it is appropriate to briefly review some of the relevant and voluminous literature on the properties of quartz.

Previous Work

As a consequence of the fact that the $\alpha - \beta$-quartz transition occurs at a moderate, experimentally assessable temperature, the changes in properties that accompany this transformation have been studied for almost a hundred years. The sharp discontinuities in volume, thermal coefficient of expansion, dispersion of light, birefringence, and rotary polarization that take place at the transition were first observed in ceramic experiments in the late 1880's (Le Chatelier, 1890a and b; Mallard and Le Chatelier, 1890). A peculiar optical phenomena (lack of total extinction) at the inversion point was noted by Wright and Larsen (1909) and later substantiated by von Steinwehr (1938).

Subsequent determinations of the structure of the α and β-forms by Bragg and Gibbs (1925), Gibbs (1926), Wyckoff (1926) and most recently by Hanic and Sumichrast (1974), suggest a possible mechanism for this transition. The α-quartz structure belongs to one of two enantiomorphic space groups $P3_121$ or $P3_221$ (trigonal symmetry). Similarly, the β-form occurs in $P6_422$ or $P6_222$ (hexagonal symmetry). This enantiomorphism leads to Brazil twinning. One-hundred and eighty degree rotation about the c axis in α-quartz is not a symmetry operation; the junction of two lattices, related by such a rotation defines a Dauphiné twin (Fig. 1). Translation of the Si and O atoms from their positions in the α-structure to those in the β-form can be thought of in terms of averaging the atomic positions of the two Dauphiné twin domains associated with each of the two space groups $P3_121$ and $P3_221$, whereby superposition of the two fold symmetry axis in the c direction yields the structures $P6_422$ and $P6_222$.
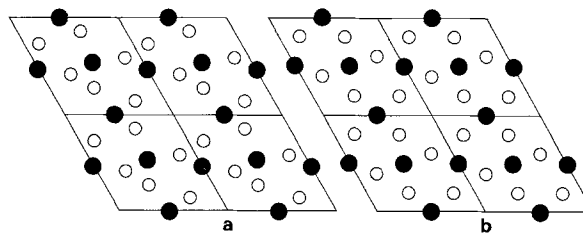

Fig. 1a and b. Comparison of the lattices of α- and β-quartz. **a** Basal projection of four unit cells of α-quartz. Note the three-fold c axis and large c axis channel. **b** Basal projection of four unit cells of β-quartz. Note the six-fold c axis, the relatively large shifts in the positions of the oxygen atoms and the movement of silicon into symmetric positions. In both **a** and **b** there are six oxygen *(open circles)* and three silicon *(dark circles)* atoms per unit cell

Recent transmission electron microscope (TEM) studies utilizing a heating stage (van Tendeloo et al., 1975, 1976; Goethem et al., 1977) support this suggestion. On heating close to the inversion temperature, $T_{\alpha-\beta}$, α-quartz develops a microdomain structure delineated by Dauphiné twinning (Fig. 2). As the temperature closely approaches $T_{\alpha-\beta}$ these domains begin to vibrate while continuously decomposing and reforming. They are triangular in shape, several hundred angstroms in width, and greatly elongated parallel to the c axis. At the transition point the twinning vanishes but reforms again on cooling below $T_{\alpha-\beta}$.

On the atomic scale displacement of the silicate tetrahedra during the transition (essentially a rotation about a 2-fold axis of each tetrahedra by approximately 2°) involves an energy change which is of the same order of magnitude as that of atomic thermal vibration at the inversion temperature (van Tendeloo et al., 1976). Young (1964) indicates that just below the transition temperature the atomic vibrational amplitude of the oxygen atoms in α-quartz becomes anharmonic to the extent of a 50% increase in the direction of the β-quartz oxygen position. The accompanying discontinuities in the optical and physical parameters are probably due to this anharmonicity (Young, 1964). Silverman (1956, 1970) calculated the activation energy of the $\alpha \rightarrow \beta$ transformation to be in the vicinity of 32.2 and 24 kcal/mol. In general, β-quartz can be thought of as the time-averaged structure of the vibrational mode between α-quartz Dauphiné twins, or as α-quartz possessing a very large number of Dauphiné twin domains of infinitesimal thickness (van Tendeloo et al., 1975, 1976; Goethem et al., 1977).

Subsequent to the work of Le Chatelier many authors (Wright and Larsen, 1909; Tuttle, 1949; Keith and Tuttle, 1952) studied the variation in the $\alpha - \beta$ inversion temperature (as much as 37° in natural samples, 536–573.8° C, op. cit., 1952, and 160° in synthetic quartz) and attributed it to structural changes arising from solid solution effects. Lattice defects have been found to affect $T_{\alpha-\beta}$ (Smykatz-Kloss, 1970) while the affect of fluid inclusions is uncertain. Panov et al. (1967) attach importance to the positive hysteresis ($T_{\alpha-\beta}$ heating $> T_{\alpha-\beta}$ cooling) of 1° to 8° C in quartz obtained from granites, and explained its occurrence in terms of fluid inclusions and impurities. Coe and Paterson (1969) found a hysteresis of $1.6 \pm 0.9°$ C for optically clear single crystals.

Virtually every element in the periodic table has been found, in some degree in naturally occuring quartz (Yoder, 1950; Walenczak, 1969; Frondel, 1962). The most commonly reported impurity is Al which can occur both interstitially (Frondel, 1962), as is probably the case in volcanic quartz (e.g. Konno, 1969; Kartenko, et al., 1967), and also as a substitutional replacement for silicon accompanied by cation occupation of interstitial positions (c axis channels), thus giving rise to stuffed derivative structures (Buerger, 1954). The stability of these stuffed derivatives is manifested in the
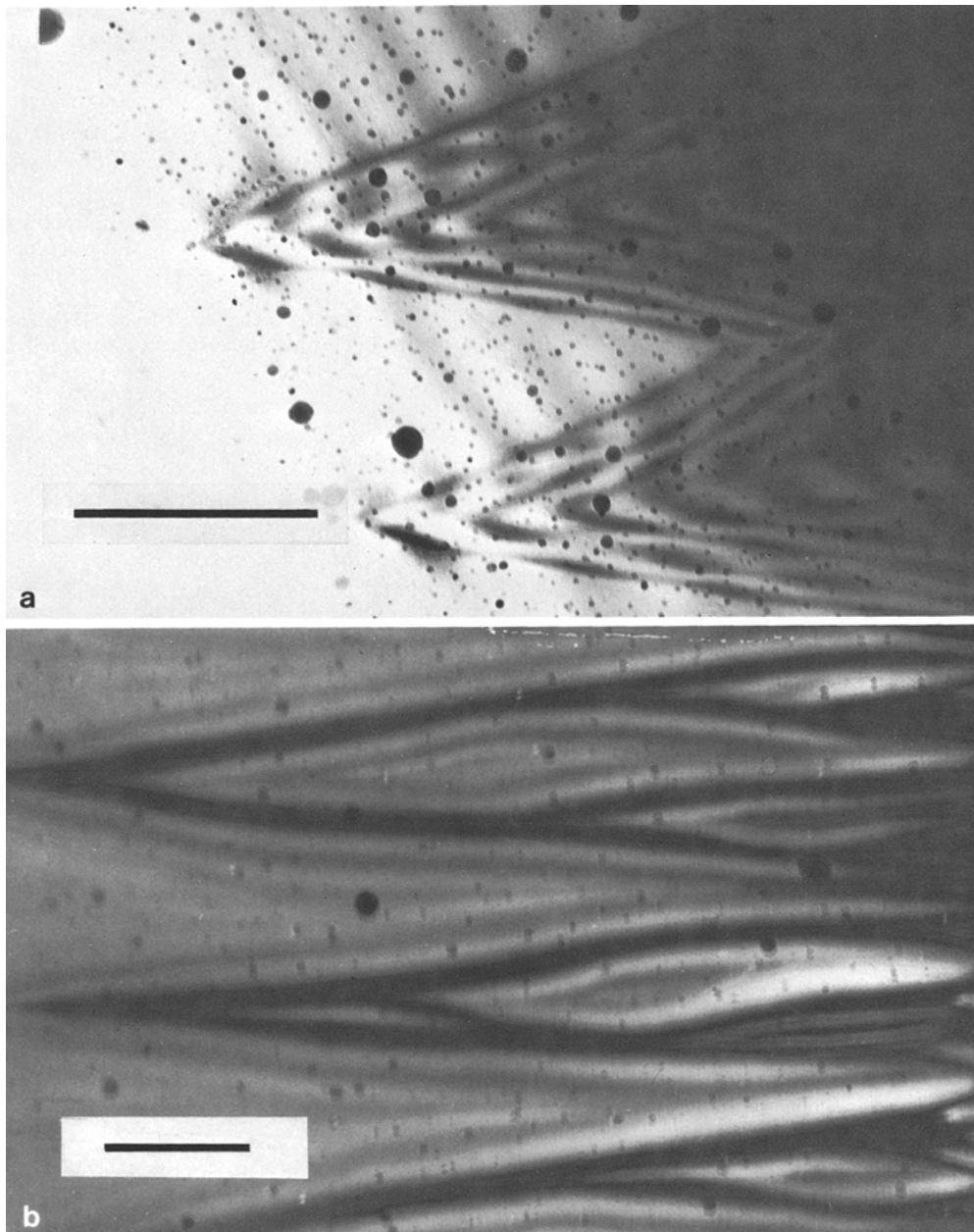
Fig. 2a and b. Transmission electron micrographs of Clear Lake quartz sample CL2, oriented with a^* and c^* in the plane of projection, showing heat induced Dauphiné twins near the inversion temperature. Dauphiné twin domains are usually 1 to 2 μ in size. On basal sections the twinning appears as triangular domains and bright field images are absent. Contrast occurs in dark field provided reflections not belonging to a zone which produces a center of symmetry in projection are excited. Two beam conditions yield alpha fringes. **a** Dauphiné twin domains, $T = 500°$ C, bright field. Dark line is 10,000 Å in length (1 μ). Note behavior of Bragg contours. **b** Dauphiné twin domains, $T = 570°$ C, dark field ($10\bar{1}3$) reflection). Dark line is 3,000 Å in length. Note fuzziness due to vibration of the crystal during exposure. This was the best beam condition found for the study of Dauphiné twins in this orientation

tendency for stoichiometric substitution of cation pairs (Al, Ti^{+4}, Fe^{+3} with H^+, Li, Na, Ca, Fe^{2+}, Mn) for Si in natural quartz, which has been demonstrated by Bambauer (1961) and Dennen (1966). Na—Al and Li—Al coupled substitution is a possible source for color center formation (Dennen et al., 1970). Li—Al coupled substitution is extensive in quartz from Li-bearing pegmatites (Stavrov, 1961) where the formation of the stuffed de-

rivative structure eucryptite ($LiAlSiO_4$, Schulz and Tscherry, 1972a and b) is thought to occur to the extent of 0.047 wt % Li. French et al. (1978) have identified Virgilite, a naturally occuring stuffed derivative with the structure of β-quartz and composition ($LiAlSi_2O_6)_{61}Qtz_{39}$ in the Macusani peraluminous volvanic glass. Synthetic Mg—Al stuffed derivatives of β-quartz were prepared and studied by Schreyer and Schairer (1961). They found that

stable solid solutions between Mg-eucryptite and β-quartz could be quenched to the α-quartz structure at room temperature which exhibited smaller c/a axial ratios, anomalously low $\alpha-\beta$ inversion temperatures, and very small thermal coefficients of expansion. $MgAl_2O_4-SiO_2$ solid solutions with 73 wt% SiO_2 were quenched to a β-structural form at room temperature by Bradley and Grimm (1951).

Walenczak (1969) indicates that while the majority of contaminants in quartz occupy the 2 Å c axis channels, anion impurities (OH^-, F^-, Cl^-, S^-) may reside in voids (O^- vacancies). Ge^{+4} will substantially replace Si (Tuttle, 1949) and its concentration in hydrothermal, granitic, and pegmatitic quartz varies by a factor of 90 (0.08–7.3 ppm, Walenczak, 1969). The Al content of quartz is linked to temperature of growth (Kamentsev, 1965), and Dennen et al. (1970) have indicated that the total Al content is independent of pressure (at the time of growth) forming a useful geothermometer for quartz grown in the α-field (below 848° K). Scotford (1975) in applying the Dennen et al. (1970) geothermometer to high Al (513 ppm) pegmatitic quartz finds conflicting results, and its applicability to volcanic samples is unknown. From experiments on synthetically grown quartz Keith and Tuttle (1952) showed that the addition of Al+Li tends to lower the $\alpha-\beta$ transition temperature, whereas addition of Ge tends to increase $T_{\alpha-\beta}$. The behavior of $T_{\alpha-\beta}$ upon the addition of Al+Li is consistent with the studies on solid solution mentioned above and has been verified on natural plutonic specimens by Smykatz-Kloss (1970). Keith and Tuttle (1952) also indicate a pronounced variation in the d_{234}-spacing with inversion temperature. Sabatier and Wyart (1954) have shown that $T_{\alpha-\beta}$ varies as a function of Na content as does the a lattice parameter, shortening as more Na enters the structure. Further work by Bambauer (1961) and Cohen and Sumner (1958) has demonstrated that lattice dimensions tend to reflect impurity contents, though not in any precisely definable manner. Afanas'eva et al. (1958) studied plutonic and vein quartz finding large variations in lattice dimensions and an inverse correlation between volume and the sum of all impurities in the structure.

Samples of High-Temperature Quartz

Phenocrysts of quartz are found in many silicic lavas, in pumice or ash flows, and more rarely as partially resorbed "phenocrysts" in basaltic-andesites. For the purposes of this study samples were separated from a pumice suite of the Bishop Tuff (Hildreth, 1976), from rhyolites of Yellowstone, and from the 1922 Katmai, Alaska pumice (Hildreth, 1978). Quartz phenocrysts were obtained from the Recent rhyolites at Mono Craters in eastern California (Carmichael, 1967) and at Coso Hot Springs (Bacon and Duffield, 1976), as well as several other samples listed in Table 1. In addition, a small collection was made of Clear Lake "diamonds" (Anderson, 1936), optically clear quartz crystals weathering out from underlying lavas, as well as "phenocrysts" of quartz in the 1851 basaltic-andesite of Cinder Cone, Lassen Volcanic National Park (Finch and Anderson, 1930; Smith and Carmichael, 1968). The localities of all the remaining quartz samples are given in Tables 1 and 5, which include some low-temperature synthetic and natural quartz for comparison purposes.

Transmission electron microscopy (TEM) of sample 120–2a from Cinder Cone revealed an extraordinarily perfect crystal with no primary Brazil or Dauphiné twinning, few dislocations (two were found along the entire thinned edge of the sample) or other structural defects, and an absence of fluid inclusions. TEM studies on a single crystal from Clear Lake showed a similar absence of twinning and dislocations. Such a small number of structural defects suggest that these quartz crystals were not subjected to stresses during their most recent cooling episode.

Composition of High-Temperature Quartz Samples

Samples of single crystals from Clear Lake and Cinder Cone were carefully cleaned and 100 mgms of each were analysed by neutron activation techniques. Some multi-crystal aggregates and a few samples of low temperature synthetic quartz were also analysed. The results are given in Tables 2 and 3.

The predominant impurity is clearly Al. In view of the large uncertainty in the reported neutron activation values, however, Al was also determined colorimetrically using Aluminon (Sandell, 1959). Estimated errors are $\pm5\%$ above and $\pm10\%$ below 100 ppm for the colorimetric determinations. The second most abundant impurity is Na. The ratio Na/Al shows wide variation, with Na and K particularly concentrated in quartz from the Cinder Cone basaltic-andesites.

The chemical composition of quartz "phenocrysts" that are found in the Clear Lake and Cinder Cone lavas should be governed by an equilibrium distribution coefficient which relates the activities of each chemical component in the quartz to that in the lava. One would therefore not expect large variations within a given suite in the absolute concentration of each element present nor the atomic ratios of elements contained in quartz from different lavas (i.e. different equilibrium temperatures) to be constant. The existence of phenocryst-melt equilibrium is the basis for the quartz geothermometer proposed by Dennen et al. (1970). For Al to vary between 17 and 380 ppm among crystals from Clear Lake suggests either a very large temperature interval of equilibration, which seems implausible, or a nonequilibrium "composition" controlled by diffusion. Small variations in the activity of water may have a marked effect on the rates of diffusion in quartz.

Lattice Constants

Lattice constants of the quartz samples investigated in this study are reported in Tables 1, 2, and 3. Twenty-four hour exposures on a Guinier (Jago) powder camera at room temperature (22 $\pm$2° C) were made using monochromated K_{α_1} radiation produced

Table 1. Data for inverted high temperature quartz

	$a(\text{Å})$	$c(\text{Å})$	$V(\text{Å})^3$	$T_{\alpha-\beta}$ heating	$T_{\alpha-\beta}$ cooling	T_{equil} °C	Method	Reference
Quartz phenocrysts in Bishop Tuff rhyolites, California								
B-73	4.9132	5.4045	112.98	847.8	847.0	770	1	a
B-77	4.9130	5.4053	112.99	848.0	847.0	790	1	a
B-78	4.9132	5.4041	112.97	847.8	847.0	785	1	a
B-79	4.9139	5.4040	113.00	847.9	847.0	763	1	a
B-83	4.9136	5.4047	113.01	848.0	847.4	722	1	a
B-94	4.9133	5.4053	113.00	848.0	847.0	725	1	a
B-96	4.9125	5.4057	112.98	848.0	847.5	755	1	a
B-107	4.9128	5.4060	113.00	847.9	847.2	756	1	a
B-108	4.9128	5.4055	112.98	848.0	847.5	749	1	a
B-109	4.9126	5.4048	112.96	848.1	847.6	727	1	a
B-136	4.9131	5.4048	112.98	847.9	847.1	749	1	a
B-143	4.9137	5.4059	113.04	847.9	847.0	772	1	a
Quartz phenocrysts in Coso Hot Springs rhyolites, California								
CD7	4.9135	5.4055	113.02	847.9	847.5			b
CD8	4.9130	5.4042	112.97	848.0	847.7			b
CD12	4.9141	5.4043	113.02	–	–			b
CD24	4.9130	5.4045	112.97	847.8	847.6			b
CD25	4.9135	5.4029	112.96	848.0	847.6			b
CD37	4.9134	5.4048	113.00	848.0	847.6			b
CD38	4.9141	5.4051	113.04	847.9	847.3			b
Quartz phenocrysts in peralkaline rhyolites								
NZC-1	4.9121	5.4045	112.93	848.2	847.3			c
	4.9134	5.4052	113.01	848.3	847.4			
5750	4.9138	5.4049	113.01					d
Quartz phenocrysts in silicic lavas (biotite absent)								
YT-1	4.9140	5.4037	113.00	847.8	847.1	~925	1	e
YT-2	4.9134	5.4045	112.99	847.7	847.2	~925	1	e
YT-3	4.9134	5.4025	112.95	847.8	847.3	~925	1	e
K-122a	4.9134	5.4039	112.98	847.6	847.2	~875	1	e, f
Cam 73	4.9131	5.4046	112.98	847.7	847.1	810	1	g
Cam 93	4.9145	5.4053	113.06	847.9	847.1	790	1	g
AC-7	4.9138	5.4048	113.02	847.5	846.9	900	1	h
992-37	4.9135	5.4051	113.01	847.9	847.5	–		i
Quartz phenocrysts in silicic lavas (biotite present)								
Cam 86	4.9140	5.4049	113.09	847.8	847.1	~940	1	g
Cam 93	4.9133	5.4048	113.00	847.8	847.5	~960	1	g
Low temperature quartz								
N-51A-68	–	–	–	848.0	847.5	230	2	j
X-507-15	4.9131	5.4046	112.98	848.3	847.2	337	2	j
C-109	–	–	–	848.0	847.9	525	2	j
Kaw 377	4.9134	5.4047	113.00	848.2	847.8	450	2	j
75 mm-1	4.9135	5.4058	113.03	848.2	847.8	265	2	j
61C-68	4.9139	5.4054	113.03	848.1	847.9	190	2	j
X-0-kirby	4.9135	5.4053	113.01	848.1	847.6	400	2	j
Anomalous quartz								
TMW	4.9175	5.4057	113.21	824.0	830.2			j
N51C-68	4.9127	5.4055	112.98	846.8	848.8	250	2	j
N-14-68	4.9158	5.4034	113.08	815–830				j
J-7	4.9132	5.4047	113.03	846.3 } 847.0 }	846.7 } 846.4 } 2 peaks	~975	1	e

Method of equilibration temperature estimation
1 Iron-titanium oxide temperatures
2 Oxygen isotope temperatures

References: a Hildreth (1976)   f Clocchiatti and Bassett (1978)
   b Bacon and Duffield (1976)   g Carmichael (1967)
   c Nicholls and Carmichael (1969)   h Carmichael (1962b)
   d Carmichael (1962a)   i Mahood (1978)
   e Hildreth (1978)   j O'Neil (1978)

Table 2. Data for quartz from basaltic-andesite of Cinder Cone, Lassen Volcanic National Park, California

	Cal 24	Cal 43	120-2a	120-cc6	120-cc2	120-2A[a]	120-2B[a]	120-2A[b] heated
a (Å)	4.9142	4.9134	4.9136	4.9130	4.9136	–	–	–
c (Å)	5.4047	5.4035	5.4042	5.4042	5.4048	–	–	–
V (Å)^3	113.03	112.97	113.00	112.97	113.01	–	–	–
$T_{\alpha-\beta}$ heating	847.2	847.4	846.2	847.2	846.9	845.7	846.0	846.0
$T_{\alpha-\beta}$ cooling	846.6	846.7	845.4	846.6	846.0	845.5	845.4	845.2
Δ (heating-cooling)	0.7	0.7	0.8	0.6	1.0	0.3	0.6	0.8
$\Delta H_{\alpha-\beta}$	–	–	107.2±0.8	103.8±0.8	106.2±0.6	106.2±0.8	106.8±0.2	106.5±0.6
Al[c]	–	–	264	290	–	284	241	
Al			670±290	371±250	583±260			
Ba			13.0±0.7	2.7±0.6	4.6±0.7			
Dy			0.009±0.002	0.018±0.004	0.022±0.004			
K			48±9	106±11	78±11			
Mn			1.74±0.06	3.67±0.12	6.55±0.2			
Na			80.3±2.7	140±4	145±5			

[a] Single crystals, crushed to <150 mesh (ASTM)

[b] Heated at 900° C for $4^1/_2$ days

[c] Colorimetrically determined. All concentrations in ppm

Al, Ba, Dy, K, Mn, Na determined by neutron activation

$\Delta H_{\alpha-\beta}$ in cal/mol. Cal 24 and Cal 43 were contaminated with small amounts of plagioclase

$\pm$ represent one standard deviation

References: Finch and Anderson (1930); Smith and Carmichael (1968)

Table 3. Data for single crystals from Clear Lake, California (samples crushed to <40, >100 ASTM mesh size)

	a (Å)	c (Å)	V (Å)^3	$T_{\alpha-\beta}$ °K heating	$T_{\alpha-\beta}$ °K cooling	Δ (heating-cooling)	$\Delta H_{\alpha-\beta}$	Al[b]	Al	Ba	Mn	Na
CL1	4.9135	5.4037	112.98	847.1	846.8	0.3	109.0±0.7	–	211±216	11.5±2.0	0.81 ±0.05	62.4 ±2.3
CL2	4.9137	5.4045	113.00	848.0	847.2	0.9	108.9±1.0	78.6	–	–	–	–
CL2A	4.9131	5.4050	112.99	848.4	847.5	0.9	109.6±0.6	16.9	16±300	<3.2	0.017	1.84±0.3
CL2B	4.9131	5.4050	112.98	847.8	846.8	1.0	109.2±1.3	106	440±270	<2.8	0.079	1.81±0.3
CL2C	4.9133	5.4053	113.00	847.8	846.8	1.0	108.2±1.3	90.4	72±290	<3.2	0.063 ±0.006	8.60±0.4
CL3A	4.9131	5.4040	112.97	848.4	847.6	0.8	107.8±0.9	60.0	–	<3.0	0.102	3.16±0.2
CL3B	4.9137	5.4047	113.01	848.0	847.1	0.9	105.7±0.4	105	65±217	<1.9	0.063	7.38±0.3
CL3C	4.9132	5.4049	112.99	848.6	847.7	0.9	108.7±0.8	27.6	–	4.1±0.9	0.028±0.01	–
CL6A	4.9140	5.4042	113.01	846.4	845.6	0.8	107.9±0.6	381	–	–	–	–
CL6B	4.9139	5.4044	113.01	847.8	847.1	0.7	108.1±1.0	84.3	275±250	2.2±0.6	0.063	12.8 ±0.5
CL6C	4.9139	5.4049	113.02	847.6	846.8	0.8	108.4±0.7	–	–	–	–	–
11053[a]	4.9128	5.4044	112.96	847.8	846.9	1.0	108.6±0.6	–	120±280	1.8±0.5	0.18 ±0.03	12.4 ±0.4

[a] Multiple crystals

[b] Determined colormetrically. $\Delta H_{\alpha-\beta}$ in cals/mole. All concentrations are in ppm

$\pm$ represents the standard deviation

Al, Ba, Mn, Na analysed by neutron activation

References: Anderson (1936); Hearn et al. (1976); Donnelly and Hearn (1978)

by an Fe tube operating at 40 kv and 20 mamps (λ = 1.93597 Å).

The films were read on a standard measurement device, equipped with a travelling microscope, with a precision of $\pm 3\,\mu$ (1 mm = 1° 4θ). Each sample was ground in an agate mortar to less than 200 mesh and mixed with Si powder as an internal standard (a_0 = 5.43054 Å). To increase the precision only central

chamber photographs were taken. The first twelve quartz and first five Si low angle reflections were measured (to five significant figures in degrees 4θ).

This data was processed in two steps. The measured Si peaks were compared to calculated values from the unit cell dimensions. The error (in degrees 2θ) at each of the five points was fitted with a second degree polynomial and corrections based upon this

Table 4. Data for single crystal quartz standard

	A (i)	A (ii)	B	C	D
$T_{\alpha-\beta}$ heating	848.6	848.6	848.3	848.2	847.9
$T_{\alpha-\beta}$ cooling	847.5	847.5	847.7	847.9	848.1
Δ (Heating-cooling)	1.1	1.1	0.6	0.3	−0.2
T_{mean}	848.0	848.0	848.0	848.0	848.0
$\Delta H_{\alpha-\beta}$ cal/mol	107.7±0.8	107.7±1.2	104.5±1.4	99.5±1.5	85.6±1.1
Grain size	single piece	single piece	40–100 mesh	<250 mesh	about 1 μ
	28.316 mgms	20.010 mgms	0.42–0.15 mm	<0.06 mm	

All temperatures are in K
This quartz contains 65 ppm Al

polynomial were then made to the quartz observations. The error polynomial was always greatly dominated by the linear term and at most involved a correction of 0.015° 2θ.

The corrected quartz measurements were then refined against standard unit cell values ($a = 4.913$ Å, $c = 5.402$ Å) by least-squares. The average standard deviations obtained for the cell parameters are: $\hat\sigma(a) = 0.0002$ Å and $\hat\sigma(c) = 0.0003$ Å. The best refinements yielded $\hat\sigma(a) = 0.0001$ and $\hat\sigma(c) = 0.0002$ Å respectively, and the worst $\hat\sigma(a) = 0.0004$ and $\hat\sigma(c) = 0.0005$ Å. The unit cell volume, $V = a^2 c \sqrt{3}/2$, has an average $\hat\sigma(V) = 0.01$ Å³. The reproducibility of the technique was checked for numerous samples, particularly those from Clear Lake, California. The results agree to within two refinement standard deviations. These values ($\sigma(a) = 0.0004$ Å, $\sigma(c) = 0.0006$ Å, and $\sigma(V) = 0.02$ Å³) should be considered the precision of the reported lattice constants (Tables 1, 2, 3).

Consideration of the large thermal coefficient of expansion of quartz ($\alpha = 34 \times 10^{-6}$ °C^{-1} at 20° C, Skinner, 1966) indicates that temperature may have a significant effect on the measurement of lattice constants. Temperature fluctuations on the order of 6° C (i.e. 65° F to 75° F) will produce changes in lattice parameters of 0.00043 Å in a, 0.00028 Å in c, and 0.023 Å³ in V (values of α_V, α_a, and α_c from Skinner, 1966 and Jay, 1933).

The average lattice parameters for 52 quartz specimens from volcanic rocks are $a = 4.9134 \pm 0.0004$ Å, $c = 5.4046 \pm 0.0006$ Å, $V = 112.99 \pm 0.02$ Å³, with uncertainties that could potentially arise from a 6° C variation in temperature during the 24 h. exposure period. Within the error limits described above there appears to be no correlation between lattice constants and impurity content of the quartz analysed. The average lattice parameters are almost identical to those of low quartz (Robie et al., 1967). In view of the major effect of temperature on the cell parameters, some care should be taken to control

temperature if quartz is to be used as a standard in precise lattice constant determinations.

Measurement of the α − β Inversion Temperature

Using the technique of differential scanning calorimetry (DSC), measurements were made of the energetic properties of the α − β transition. Samples of pure quartz weighing approximately 30 mgms and sieved to 40–100 mesh (ASTM), were placed in gold capsules, sealed and flattened. An optically clear single crystal of quartz from a vein in an Arkansas Paleozoic sandstone, was chosen as an internal standard, and various crushed size fractions of this were used to determine the effect of grain size on inversion temperature. This standard was calibrated against the transition temperature of K_2SO_4 (858.2° K)[1] and melting point of Pb (600.62° K) on a weekly basis. Samples were scanned at 2.5° min^{-1}, and each scan was repeated four times with the gold capsule rotated 90° in the DSC platinum holder between each run.

The temperatures of the α − β inversion on heating and cooling were obtained from the DSC trace using the convention of Keith and Tuttle (1952). These measurements for the standard are given in Table 4. Inversion temperatures for the 40–100 mesh sample are 848.30 ± 0.09° K on heating and 847.66 ± 0.09° K on cooling, where the error is one standard deviation obtained from 52 determinations. The difference between the two temperatures is called here the temperature hysteresis, and in almost all samples it is positive, the inversion temperature on heating

[1] This value is taken from Roberts (Phys. Rev. 23, 386, 1924) and has an uncertainty of ±1° K. Alternatively a transition temperature of 855° K could be adopted (NBS Special Publication 260-40, 1972; K_2SO_4 standard reference material 759). This situation imposes large errors on the accuracy of the α − β quartz transition temperatures reported below but has no effect on the relative precision
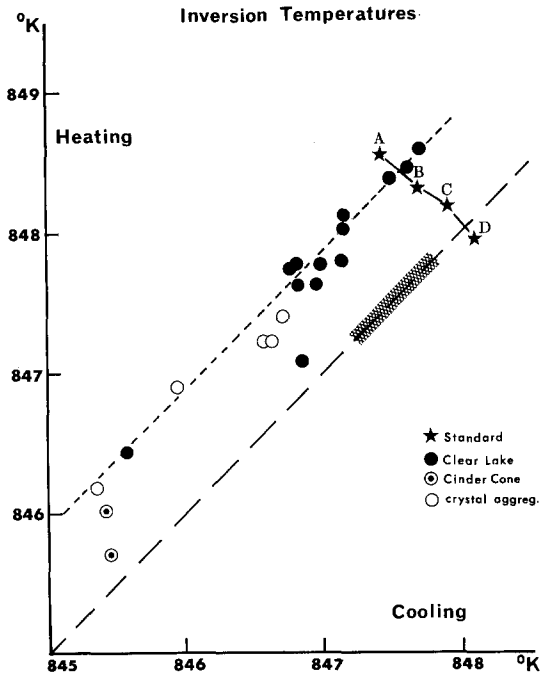
Fig. 3. Inversion temperature on heating plotted against inversion temperature on cooling. ABCD refer to the standard (Table 4), and the hatched area to the range of mean inversion temperatures of all measured high-temperature quartz samples (Tables 1, 2, 3, 5). Dashed lines are of unit slope
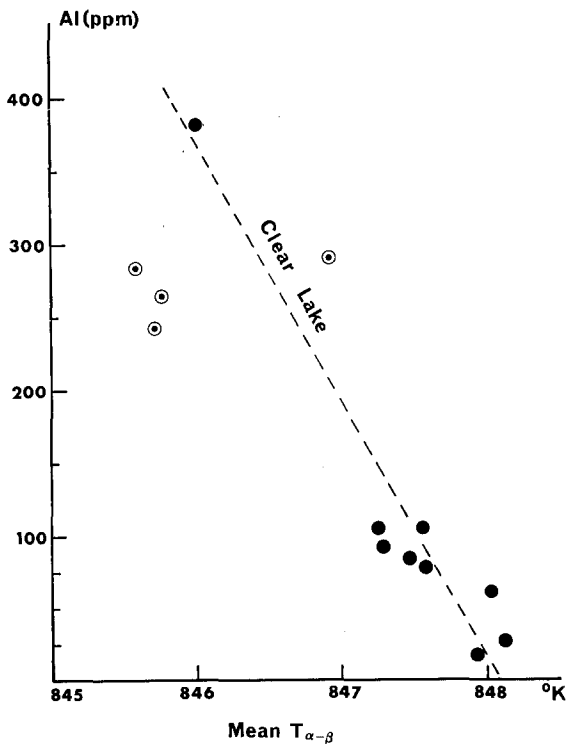

Fig. 4. The mean inversion temperature of chemically analysed quartz samples plotted against concentration of Al (ppm). Dashed line refers to linear least squares regression of Clear Lake data (solid circles). Semi-open circles indicate Cinder Cone quartz

being larger than the inversion temperature on cooling. The standard was run daily to correct for instrumental drift, and no evidence was found, within the limits of error, of an annealing effect despite the standard sample having been scanned over 400 times. One sample, 120-2a (Table 2) was heated at 900° C for $4^1/_2$ days and $T_{\alpha-\beta}$ on both heating and cooling decreased slightly, but the change is not significant within 2 standard deviations (95 % probability level).

The uncertainty represented by one standard deviation ($\pm 0.09°$ K) increases to $0.12°$ K if the same sample is scanned in different capsules, and all the data are combined. All in all, it may be assumed that a difference of $0.25°$ K is significant at the 95 % probability level.

The effect of grain size on the inversion temperature for the standard sample is illustrated by the data in Table 4, which are plotted in Fig. 3. A single piece of the quartz standard has a larger hysteresis than all other grain size fractions, and there is a progressive decrease in $T_{\alpha-\beta}$ on heating, and an increase in $T_{\alpha-\beta}$ on cooling, with diminishing grain size (Table 4). Thus the positive displacement of almost all the quartz samples from the zero hysteresis line (Fig.3) is taken to reflect the grain size of the samples. There are one or two exceptions to this; one example is Cl 1 (Table 3), which was sieved to the same size as the other Clear Lake samples, and yet has a smaller hysteresis.

The mean inversion temperature of the standard (Table 4) is sensibly constant for the four different size fractions, and the mean inversion temperature is used in all subsequent diagrams to show the effect of composition etc. on the inversion temperature.

Inversion Temperature and Composition

The concentration of Al (Tables 2, 3) is plotted against the mean inversion temperature in Fig. 4, and clearly there is a general correlation. For the Clear Lake samples a least squares fit shows that at zero Al, the mean inversion temperature is $848.1 \pm 0.1°$ K, and as no specimen measured by us significantly exceeds this value, this may be taken to represent the limit of pure high-temperature quartz. The Cinder Cone samples also display a dependency of $T_{\alpha-\beta}$ on Al, but in these, other elements (e.g. Na, K) are present in similar concentrations, and may contribute to the variation in $T_{\alpha-\beta}$. It would take substantially more data than is available to identify the extent to which each element contributes individually to affect $T_{\alpha-\beta}$.

In contrast to the wide range in the inversion temperature found in the Clear Lake and Cinder

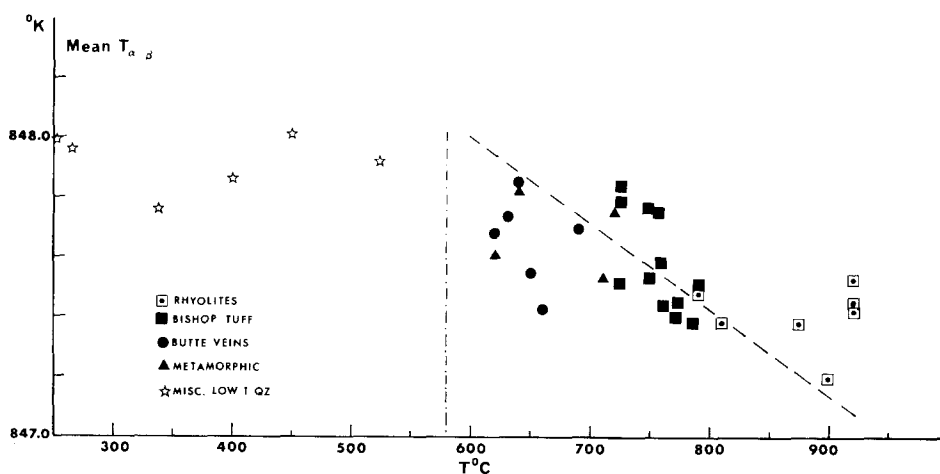**Table 5.** Inversion temperatures for inverted high temperature quartz

Sample No.	$T_{\alpha-\beta\,heating}\,°K$	$T_{\alpha-\beta\,cooling}\,°K$	$T_{equil}\,°C$	Equilibrium temperature estimation method
Quartz from high-temperature veins, Butte, Montana				
906-25	847.6	847.2	660	1
906-27	847.8	847.5	620	1
906-29	847.7	847.7	690	1
906-92	847.7	847.4	650	1
906-111	848.0	847.5	630	1
906-112	848.0	847.7	640	1

Source: Brimhall 1977, 1978

Quartz from metamorphic rocks				
FH-2-2	847.8	847.4	620	2
BT-7	848.0	847.6	640	2
TP-20-1	848.0	847.5	720	2
SP-2-3	847.7	847.4	710	2

Source: Valley 1978

1: Exchange equilibria among co-existing silicate phases
2: Oxygen isotopes

Cone samples, the inversion temperatures of all the other high-temperature quartz samples (Tables 1 and 5) show a relatively restricted range from 847.2 to 847.8° K (hatched area in Fig. 3). If this is solely related to the concentration of Al, then based on the Clear Lake correlation these quartz samples contain between 50 and 100 ppm aluminum. For quartz precipitated at high temperatures, this seems small (i.e. the Al-geothermometer of Dennen et al., 1970, would predict much more).

Inversion Temperature and Temperature of Equilibration

Many of the quartz samples investigated by us came from rhyolitic flows or pumice deposits for which the temperatures of precipitation may be estimated from the equilibration temperatures of the co-existing iron-titanium oxide minerals (Table 1). In addition in Table 1, there are temperature estimates based on exchange equilibria in the coexisting silicate minerals, oxygen isotopes, and fluid inclusions. The temperature of growth was measured in the case of synthetic quartz. In Fig. 5, the mean inversion temperature of the quartz samples is plotted against their growth or equilibration temperature. One can see a general, but weak, inverse correlaion which has previously been discussed by Keith and Tuttle (1952). A least squares fit of these data gives $T°C = 2.946 \times 10^5 - 346.7\,T_{\alpha-\beta}$ with a coefficient of determination (r^2) of 0.38. The standard error of the residuals is $\pm 74°\,C$. From this correlation the equilibration temperatures of the Cinder Cone samples fall into two groups, one about 975° C and the other about 1400° C – the latter temperature is in general accord with the proposition that these quartz crystals represent high-pressure phenocrysts in basaltic-andesites (Marsh and Carmichael, 1974). Quartz is a poor geothermometer at best, and before it can be used with precision, the effect of water on the inversion temperature, and on the extent of interstitial solid solution will have to be investigated systematically. Insofar as the mean inversion temperature is a function of composition, the absence of a correlation to growth or equilibration temperature implies a kinetic control for the entrance of impurities into the β-quartz structure.

Fig. 5. Mean inversion temperature plotted against probable equilibration temperature (see tables and text). The dashed line represents the best linear least squares fit to the high-temperature quartz samples (equilibrated above 848° K)
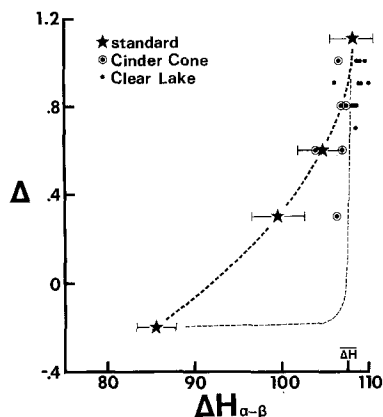
Fig. 6. $\Delta H_{\alpha-\beta}$ plotted against $T_{\alpha-\beta}$ hysteresis (H-C, °C) for Clear Lake *(solid circles)*, Cinder Cone *(open circles)* and the standard *(stars*, see Table 4). Bars denote ± 2 standard deviations. Light dashed line refers to enhalpy decrease associated with a surface energy of 682 ergs/cm^2

Among the low temperature quartz samples examined by us several show anomalous inversion behavior over a wide range of temperatures and these are identified in Table 1. They all have characteristics of being composite, in that the transition behavior is what would be expected if each sample was made up of individual grains, each with its own inversion temperature, with the whole covering a wide range. In these samples there is usually negative hysteresis, but in none is the characteristic sharp inversion peak found. One pumice sample, J-7, has quartz with two clear transition temperatures, and presumably this reflects a mixture of two compositions. None of the other high temperature quartz samples studied by us show this behavior.

Enthalpy ($\Delta H_{\alpha-\beta}$) of the $\alpha-\beta$ Transition

The enthalpy change involved in the $\alpha-\beta$ transformation is proportional to the integral of the DSC peak trace as a function of temperature, which is conveniently measured by digitizing and numerically integrating over a prescribed temperature interval. Values of $\Delta H_{\alpha-\beta}$ (DSC peak areas) were determined from $T_{\alpha-\beta} - 6.0$ to $T_{\alpha-\beta} + 3.0°$ K and were calibrated against the known enthalpy of fusion of Pb (5.51 cal/gm) and In (6.79 cal/gm).[2] Four peaks each, of five separate weights of In and Pb were used for this purpose and illustrate the reproducibility of the overall technique (a combination of instrumental and

handling error, $\sigma = \pm 0.32$ %). Averaging the results obtained on 8 runs (4 cooling peaks, 4 heating peaks) for quartz samples of high purity provide the $\Delta H_{\alpha-\beta}$ values given in Tables 2, 3, 4 and Fig. 6.

The parameter that correlates well with out values of $\Delta H_{\alpha-\beta}$ is sample grain size. Its effect is assessed in Fig. 6 where values of $\Delta H_{\alpha-\beta}$ for the standard are plotted against the $T_{\alpha-\beta}$ hysteresis ($\Delta T_{\alpha-\beta}$). It is clear, from the discussion above, that $\Delta T_{\alpha-\beta}$ is a reflection of grain size and that this quantity correlates positively with $\Delta H_{\alpha-\beta}$ (Fig. 6). This decrease in enthalpy associated with decreasing sample grain size could be due to a positive enthalpy term associated with disolcations (induced by crushing) or surface energy.

The 22 cal decrease from the $\Delta H_{\alpha-\beta}$ of the single crystal standard to that of the finely crushed sample (D, Table 4) can be accounted for by a surface energy of 682 ergs/cm^2 (assuming spheres 1 μ in diameter, or cubes 1 μ on edge). This value is typical of crystalline oxides. The enthalpy decrease associated with this surface energy as a function of grain size is shown by the light dotted line on Fig. 6. Sample C was sieved to <250 mesh, hence the abundance of finer particles may account for its displacement to the left of this line in Fig. 6.

Berger et al. (1965) noticed a similar dependence of $\Delta H_{\alpha-\beta}$ on sample grain size during their DSC experiments (see Table 6). Using DTA measurements, Young (1964) has shown that by varying the amount of Dauphiné twin associated strain energy ($\#$ of twin domains per sq. cm.) the heat required to induce the transition increased, or decreased, thus indicating that previous history/treatment should effect $\Delta H_{\alpha-\beta}$. The effects of composition on the inversion enthalpy have been utilized by Lameyre et al. (1968) and Giret et al. (1972). They were able to show empirically that DTA transition peak areas of uniformly cleaned crushed quartz, varied as a function of the chemical composition of the host rock. As the Clear Lake samples plotted on Fig. 6 have widely varying aluminum contents, yet statistically indistinguishable enthalpies of transition, it appears that grain size, or the process of sample preparation, has a far greater influence on $\Delta H_{\alpha-\beta}$ than composition.

To obtain an equilibrium value of $\Delta H_{\alpha-\beta}$ for the (reversible) reaction

α-quartz = β-quartz

at $T_{\alpha-\beta}$ we must extrapolate the reported values of $\Delta H_{\alpha-\beta}$ to zero temperature hysteresis. The value obtained from Fig. 6 is 92.0 ± 1.4 cal/mol which *could* be taken as the reversible transition enthalpy. However, even this value has been obtained over a temperature range of $9.0°$, when strictly it should be measured

[2] Richardson and Savill (1975, Thermochimica Acta **12**, 221) give a vaue of 6.97 cal/gm for the enthalpy of fusion of Indium. The value we accept, however, is consistent with our independently derived DSC calibration curve for the enthalpy of fusion of Pb
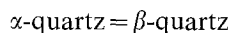
Table 6. Published measurements on $\Delta H_{\alpha-\beta}$ (cal/mol)

$\Delta H_{\alpha-\beta}$ (cal/mole)	Material	$T_{\alpha-\beta}$ hysteresis	Source
150	powder	—	Sosman (1927)
290		—	Kelley (1960) (compilation)
108[a]	single crystal	—	Mayer (1960)
80	single crystal	—	Young (1964)
86 ± 20	powder (?)	—	Majumdar et al. (1964)
198	single crystal	—	Leonidov et al. (1964, 1965)
174 ± 9[b] 155 ± 12[c]	Silica $L < 40$	2 ± 2.5	Berger et al. (1965)
160 ± 9[b] 132 ± 9[c]	Sable de Nemours >60, <450	2 ± 2	(same)
102 ± 10[b]	Quartz Sifraco <10	0.5 ± 1.5	(same)
193 ± 12[b]	quartz crystal Madagascar	7 ± 2	(same)
178 ± 10[b] 161 ± 5[c]	single crystal	8 ± 1.5	(same)
148 ± 6[b] 130 ± 6[c]	single crystal pulverized	9 ± 1.5	(same)
174		—	Stull and Prophet (1971) (compilation)
114		—	Robie et al. (1978) (compilation)
107.7 ± 1.4	single crystal	1.1	this paper
92.0 ± 1.4	powder, extrapolated to zero hysteresis (see Fig. 6 and text)	0.0	this paper

[a] $\Delta S_{\alpha-\beta}$ reported, $T_{\alpha-\beta}$ taken as 848°K
[b] DSC fast heating rate, 1°/min
[c] DSC slow heating rate, 0.5°/min

over an infintesimally small temperature range. The effect of sample preparation on $\Delta H_{\alpha-\beta}$ poses an intriguing problem in choosing standard state properties for quartz. Experimental limitations may prevent the measurement of reversible transition enthalpies for perfect crystals.

Calculation of $\Delta H_{\alpha-\beta}$ From the Clapeyron Slope

An alternative approach to direct measurement of $\Delta H_{\alpha-\beta}$ is to combine experimental data on the Clapeyron slope of the inversion (1 bar) with the measured volume of the $\alpha-\beta$ quartz transition:
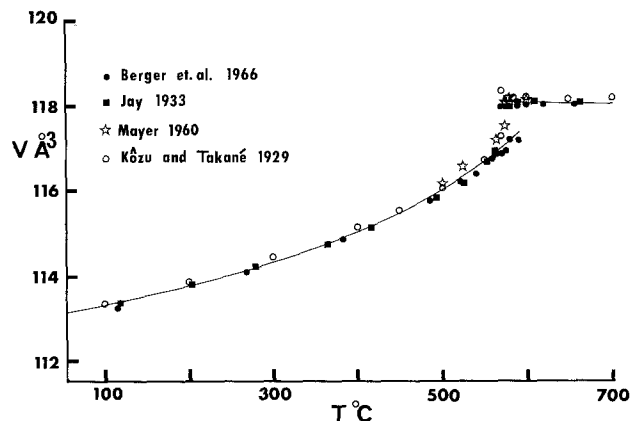
Fig. 7. Unit cell volume of quartz, determined by X-ray measurements, as a function of temperature. Smooth curves represent regression equations for the α and β fields given in the text

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T \Delta V}$$

at P and $T_{\alpha-\beta}$

$$\left(\frac{dP}{dT}\right)_{\alpha-\beta} T_{\alpha-\beta} \Delta V_{\alpha-\beta} = \Delta H_{\alpha-\beta}.$$

The quantity $(dP/dT)_{\alpha-\beta}$ has been extensively investigated (Table 8). It is noteworthy that the low pressure data of Cohen et al. (1974), obtained from fifty data points in the range 19–997 bars, are in conflict with those of Koster van Groos and ter Heege (1973), but the manner in which the thermocouple pressure correction was applied in the latter experiments is questionable (Cohen et al., 1974). Majumdar et al. (1964) utilized existing $\Delta V_{\alpha-\beta}$ data (see below) and their measured Clapeyron slope to obtain $\Delta H_{\alpha-\beta}$ of 78 ± 10 cal/mol.[3] Helgeson et al. (1978) argue that to achieve consistency between the measured volumetric properties of quartz (data on the volume and thermal coefficient of expansion as a function of temperature reported in Skinner, 1966), $\Delta V_{\alpha-\beta}$ of 0.12 cc/mol, and the Clapeyron slope (Cohen and Klement, 1967) of the $\alpha-\beta$ inversion implies a transition enthalpy of 94 cal/mol. Adopting the more recent value of $(dP/dT)_{\alpha-\beta}$ (Cohen et al., 1974) and $\Delta V_{\alpha-\beta} = 0.12$ cc/mol, results in a value of $\Delta H_{\alpha-\beta}$ of 86.2 cal/mol. It is apparent that the calculated transition enthalpy is critically dependent upon minor variations in $\Delta V_{\alpha-\beta}$.

The change in volume at the $\alpha-\beta$ transition has been studied most recently by Berger et al. (1966). Inspection of Fig. 7 reveals that their data for V as a

[3] DTA measurements of the same material gave 86 cal/mol (Majumdar et al., 1964)

function of temperature near the inversion point are considerably different than that of Jay (1933), Kôzu and Tukané (1929), and the work of Mayer (1960). The data in Fig. 7 for α-quartz, including the low temperature work of Lindemann ($-250°$ C to $25°$ C, see Mayer, 1960), was fitted by multiple regression techniques to a polynomial in temperature. Polynomial coefficients were tested for significance at the 5 % level and entered or removed in a stepwise manner during the regression. The best fit is a cubic polynomial (multiple $r^2 = 0.99148$, variance of residuals $= 0.15519$ Å^3, 0.031154 cc/mol):

$$V = 113.058 + 2.96117 \times 10^{-3}(T - 273.15)$$
$$+ 1.20472 \times 10^{-8}(T - 273.15)^3 \text{ Å}^3/\text{unit cell}$$

(T in °K)

or

$$V = 22.6965 + 5.94456 \times 10^{-4}(T - 273.15)$$
$$+ 2.41848 \times 10^{-9}(T - 273.15)^3 \text{ cc/mol}$$

(T in °K).

For β-quartz, again using the data in Fig. 7 and including the results of Kôzu and Tukané (1929) up to 1050° C, we obtain a second degree polynomial (multiple $r^2 = 0.84893$, variance of residuals $= 0.073504$Å^3/unit cell, 0.014756 cc/mol):

$$V = 119.223 - 3.31188 \times 10^{-3}(T - 273.15)$$
$$+ 2.27467 \times 10^{-6}(T - 273.15)^2$$
$$\text{Å}^3/\text{unit cell} (T \text{ in °K})$$

or

$$V = 23.9341 - 6.64862 \times 10^{-4}(T - 273.15)$$
$$+ 4.56642 \times 10^{-7}(T - 273.15)^2 \text{ cc/mol}$$

(T in °K).

By utilizing these two regression equations, a value of $\Delta V_{\alpha - \beta}$ at 848° K of 0.205 cc/mol is calculated. This number is larger than any of the reported measurements of $\Delta V_{\alpha - \beta}$ presented in Table 7. Polynomial regression of volume data over a range of temperature may minimise the overall uncertainty, but in view of the rapidity of the volume change (increase in $(\partial V/\partial T)_P$) as $T_{\alpha - \beta}$ is approached, specific measurements of $\Delta V_{\alpha - \beta}$, with carefully controlled temperatures are required. Adopting $(dP/dT)_{\alpha - \beta}$ $= 35$ bars/°C and $\Delta V_{\alpha - \beta} = 0.205$ cc/mol gives $\Delta H_{\alpha - \beta}$ $= 146$ cal/mol. If Koster van Groos and ter Heege's (1973) slope (64.5 bars/°C) is used here we obtain $\Delta H_{\alpha - \beta} = 268$ cal/mol. To emphasize the critical dependence of $\Delta H_{\alpha - \beta}$ on $\Delta V_{\alpha - \beta}$ we calculate $\Delta V_{\alpha - \beta}$

Table 7. Selected published measurements of $\Delta V_{\alpha - \beta}$ (cm^3/mol) at 848° K

$\Delta V_{\alpha - \beta}$	Source
0.195	Sosman (1927) (compilation)
0.118	Mayer (1960)
0.11 ± 0.015	Majumdar et al. (1964)
0.0	Bystrikov (1966)
0.154 ± 0.014	Berger et al. (1966)
0.205 ± 0.031[a]	least squares, this paper

[a] Estimate at 848° K to be the minimum value; see Fig. 7. The variance of residuals over the entire regression interval of $-250°$ C to 573° C for α-quartz is 0.031 cm^3/mol

using the Clapeyron slope of Cohen et al. (1974) and the zero hysteresis enthalpy determined above to obtain: $\Delta V_{\alpha - \beta} = 0.128$ cc/mol (0.639 Å^3/unit cell). Inspection of Fig. 7 shows that this result is well within the experimental uncertainty at the transition point and emphasizes the need to carefully assess critical data before thermodynamic quantities are derived from consistency relations. In this case such calculations are only fortuitously consistent with the calorimetrically measured $\Delta H_{\alpha - \beta}$.

Variation of C_P, α_P, β_T, at the $\alpha - \beta$ Transition

Considerable discussion has centered around the evidence pointing toward a first or second order character of the $\alpha - \beta$ transition in quartz. In a first order transformation there are finite changes in volume (V) and entropy (S) which correspond to infinite values of $C_P\{(\partial S/\partial T)_P T\}$ and $\alpha\{1/V(\partial V/\partial T)_P\}$ at the transition temperature, T_t. Typically both C_P and α show little premonitory change below T_t. In second order transformations V and S change continuously through the transition event and consequently C_P and α undergo finite changes at T_t or are smooth functions of temperature. Second order transformations (commonly called lambda transformations, Denbigh, 1970, p. 210; Klotz and Rosenberg, 1972, p. 197) typically show significant increases in C_P below the transition temperature, reflecting structural changes taking place in the substance over a wider temperature interval. Pippard (1957, p. 138) makes a distinction between lambda transitions, which he regards as first order transformations with a substantial premonitory increase in C_P and α, characteristic of order-disorder effects, and strict second order transitions (as in liquid helium). Since all natural substances must, to some extent, disorder before they transform, Pippard's distinction between lambda and first order transitions appears tautological. In this paper we use the terms lambda and second order synonymously.
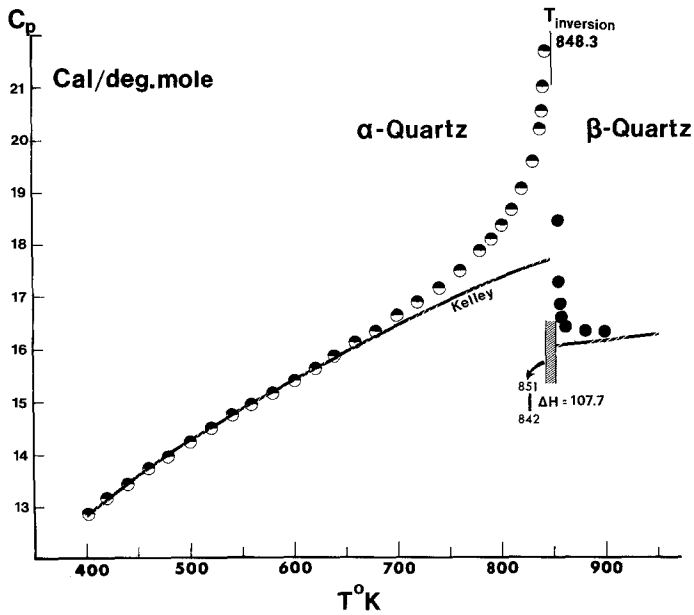
Fig. 8. Heat capacity of quartz as a function of temperature, obtained by heating standard sample "A" and "B" (Table 4). Half circles are values for α-quartz and solid circles indicate β-quartz. The shaded area represents the temperature interval 842–851° K, for which values of $\Delta H_{\alpha-\beta}$ are given in Table 4. The variation of C_P with temperature taken from Kelley (1960) is also shown

DTA measurements of C_P have been made on quartz powders near the transition temperature (Mayer, 1960; Sinelnikov, 1953; Coenen, 1963). The heat capacity of quartz as measured by differential scanning calorimetry on standard samples "A" and "B" (Table 4) and calibrated against the heat capacity of NBS sapphire # 720 is displayed in Fig. 8. The data[4] have been fitted to a Maier-Kelley type function with extended hyperbolic terms asymptotic about the transition temperature (see Appendix) to yield:

$$C_P = 10.31 + 9.116 \times 10^{-3}\, T - \frac{1.812 \times 10^5}{T^2}$$

$$-5.630 \times 10^{-2}\frac{T}{(T-848)} - 0.3553\frac{T}{(T-848)^2}$$

$$-0.9011\frac{T}{(T-848)^3}\ \text{cal mole}^{-1}$$

(α-quartz, $400 - 842°$ K, $r^2 = 0.9890$, $\sigma = 0.1680$), and

$$C_P = -318.8 + 0.2532\, T - \frac{8.687 \times 10^7}{T^2}$$

$$+0.1603\frac{T}{(T-848)^4}\ \text{cal mole}^{-1}$$

(β-quartz, 851–900° K, $r^2 = 0.7708$, $\sigma = 0.2299$)

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[4] Tabulated values of C_P may be obtained by writing to the authors

Below 400° K or above 900° K the heat capacity expressions of Kelley (1960) or Robie et al. (1978) should be used.

The heat capacity shows a marked premonitory rise over that reported by Kelley (1960). The difference between the two curves amounts to a heat effect of 108.1 and 14.5 cal/mol below and above the transition, respectively, Integrating the heat capacity expressions given above and combining these results with the transition enthalpy gives the total heat effect $(H_{900} - H_{400})$ associated with the quartz $\alpha - \beta$ transition: 7875.3 cal/mol. This value compares quite favorably with 8089.8 cal/mol calculated from Kelley (1960) and 7930.1 cal/mol obtained from Robie et al. (1978). C_P measurements on the single crystal standard "A" gave results nearly identical to standard "B", showing that the form of the C_P function displayed in Fig. 8 has not been affected by sample preparation.

The pressure and temperature derivatives of volume change drastically at $T_{\alpha-\beta}$. Finite difference derivatives of the regression curve shown in Fig. 7 permit the calculation of the coefficient of thermal expansion, $\alpha\,(\equiv(1/V)(\partial V/\partial T)_P)$ at 1 bar. Regression of these derivatives yields a polynomial fit (with maximized multiple r^2 used as a criterion for polynomial degree) for both α- and β-quartz with the following results:

α-quartz (−250° C to 580° C)

$$\alpha_P = 35.3232 \times 10^{-6} + 5.25526 \times 10^{-8}(T - 273.15)$$

$$-2.43439 \times 10^{-10}(T - 273.15)^2$$

$$+8.21877 \times 10^{-13}(T - 273.15)^3 °\,\text{K}^{-1}$$

(multiple $r^2 = 1.00000$, variance of residuals $= 0.09604 \times 10^{-6}$)

and for β-quartz (580° C to 1050° C)

$$\alpha_P = -28.0422 \times 10^{-6} + 3.85184 \times 10^{-8}$$
$$(T - 273.15)°\,\text{K}^{-1}.$$

(multiple $r^2 = 1.00000$, variance of residuals $= 0.001527 \times 10^{-6}$).

The extraordinary curvature $(d^2\alpha/dT^2)$ below the inversion temperature is noteworthy and analogous to heat capacity trends in the same temperature interval.

Analysis of data on the compliances of α- and β-quartz as a function of temperature (Mayer, 1960) results in a value for the adiabatic compressibility $(-(1/V)(\partial V/\partial P)_S)$ at zero pressure:

$$\beta_S = S_{11} + S_{12} + S_{33} + 2(S_{33} + S_{13} + S_{12}).$$

Utilizing the relationship:

$$\beta_T\ (\text{isothermal}) = \beta_S + V\,T\,\alpha_P^2/C_P$$

Table 8. Published measurements on $(dP/dT)_{1\,bar}$ of the $\alpha - \beta$ transition

(dP/dT) bars/K	(dT/dP) K/kbar	Pressure range	Material	Source
48	21	0–2640 bars	single crystal	Gibson (1928)
34.8	28.7	524–10,000 bars	crushed >200, <35 mesh	Yoder (1950)
38.5 ± 1.5	26 ± 1	6–35 bars	single crystal	Cohen and Klement (1967)
38.8 ± 0.5	25.8 ± 0.3	1–5 kbars	single crystal	Coe and Paterson (1969)
64.5 ± 0.5	15.5 ± 0.11	1–1000 bars	crushed: composite dune sand and single crystal	Koster van Gross and ter Heege (1973)
35.0 ± 0.1	28.6 ± 0.08	1–997 bars	single crystal	Cohen et al. (1974)
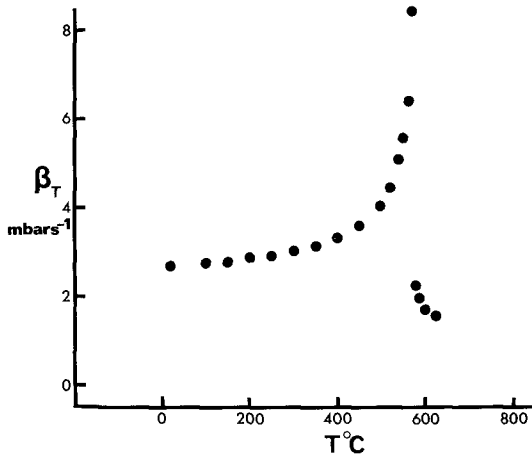
Fig. 9. Isothermal compressibility $(\beta_T = -(1/V)(\partial V/\partial P)_T)$ of quartz, calculated from V, $(1/V)(\partial V/\partial T)_P$ (obtained from Fig. 7) and values of C_p and the adiabatic compliances in Mayer (1960), as a function of temperature

with values of α_p and V from the equations given above and C_p from Mayer (1960) yields the isothermal compressibility for both α- and β-quartz at zero pressure as a function of temperature (Fig. 9). These data are entirely consistent with those of Birch (1966) and can be regressed to hyperbolic type functions ($f = a + bT + \sum_i c_i T/(T-848)^i$) with coefficients determined at the 95 % confidence level, as above, to give:

$$\beta_T = 2.279 + 9.393 \times 10^{-4} T - 0.1047\, T/(T-848)$$
$$- 0.6953\, T/(T-848)^2$$
$$- 38.35\, T/(T-848)^5\ \text{mbars}^{-1}$$

(α-quartz, 293–848° K, $r^2 = 0.9998$, $\sigma = 0.04124$, T in °K),

and

$$\beta_T = 6.057 - 5.106 \times 10^{-3} T - 3.364 \times 10^{-3}\, T/(T-848)$$

(β-quartz, 853–900° K, $r^2 = 0.9994$, $\sigma = 0.01927$, T in °K).

Finite difference derivatives of β_T with respect to temperature can be related through $(\partial\beta/\partial T)_P = -(\partial\alpha/\partial P)_T$ to the pressure dependence of the thermal coefficient of expansion. These data can be fitted in an analogous way to give:

$$(\partial\beta/\partial T)_P = 3.165 \times 10^{-3} - 9.113 \times 10^{-6}\, T$$
$$- 1.786 \times 10^{-3}\, T/(T-848)$$
$$+ 6.478 \times 10^{-3}\, T/(T-848)^2\ \text{mbars}^{-1}\,{}^{0}K^{-1}$$

(α-quartz, 333–838° K, $r^2 = 0.9999$, $\sigma = 0.0011$) and

$$(\partial\beta/\partial T)_P = -1.327 + 1.496 \times 10^{-3}\, T$$

(β-quartz, 855–886° K, $r^2 = 0.8805$, $\sigma = 0.0174$).

Examination of the behavior of all thermodynamic quantities across the $\alpha - \beta$ transition zone demonstrates that considerable disorder ensues in the α-quartz lattice in anticipation of the structural changes that accompany the $\alpha - \beta$ transition. The interpretation of these phenomena as evidence for a strict 2nd order transition however is inconsistent with the finite values of $\Delta V_{\alpha-\beta}$ and $\Delta H_{\alpha-\beta}$ reported here and in the literature. In light of the experimental difficulties involved with measuring small changes in physical and energetic properties at 848° K, it is unlikely that the physical distinctions between first and second order may ever be realised.

Conclusions

The experimental data presented and discussed above allow the following generalizations to be made: (1) The variability in the lattice parameters of natural volcanic quartz does not correlate with any other measurable physical property, within the limits of experimental error. (2) An increase in the $\alpha - \beta$ inversion temperature is inversely correlated to Al content, and provides a weak indication of the growth or equilibration temperature of quartz phenocrysts. (3) The $\alpha - \beta$ transition temperature hysteresis reflects sample preparation and is a function of grain size. It

has a strong correlation with the enthalpy of the $\alpha - \beta$ transition which for zero hysteresis is taken to be 92.0 ± 1.4 cal/mol. In contrast for a single crystal the enthalpy change is 107.7 ± 1.4 cal/mol. (4) The discontinuities in various physical properties that occur at the $\alpha - \beta$ transition (e.g. instantaneous increase in the anharmonicity of the O lattice vibrations) are superimposed over a broader series of structural changes that are reflected in the behavior of the derivatives of free energy with respect to T and P, as a function of temperature.

Appendix

Measurements of the heat capacity of quartz were fitted to an equation of the form:

$$C_P = a + bT + \frac{c}{T^2} + \sum_{i=1}^{n} d_i \frac{T}{(T-848)^i} \tag{1}$$

where a, b, c, and d_i to d_n are regression coefficients. With n arbitrarily chosen as 10, extended Maier-Kelley terms were entered or removed during the regression by testing for significance at the 5% level.

The form of Eq. (1) was adopted for ease of integration in order to obtain entropy, enthalpy, and free energy as a function of temperature. Since $(\partial H / \partial T)_P = C_P$, we have:

$$\Delta H \bigg|_{T_{ref}}^{T} = aT + \frac{b}{2} T^2 - \frac{c}{T} + d_1 \{T + 848 \ln |T - 848|\}$$
$$+ d_2 \{\ln |T - 848| - 848/(T - 848)\}$$
$$+ \sum_{i=3}^{n} d_i \left\{ \frac{-848}{(i-1)(T-848)^{i-1}} - \frac{1}{(i-2)(T-848)^{i-2}} \right\} \bigg|_{T_{ref}}^{T}, \tag{2}$$

and from $(\partial S / \partial T)_P = C_p / T$, we have:

$$\Delta S \bigg|_{T_{ref}}^{T} = a \ln T + bT - \frac{c}{2T^2} + d_1 \ln |T - 848|$$
$$+ \sum_{i=2}^{n} d_i \left(\frac{1}{1-i} \right) (T - 848)^{1-i} \bigg|_{T_{ref}}^{T}. \tag{3}$$

Finally, using $(\partial G / \partial T)_P = -S$, and adopting S_{ref} as a symbol for the reference temperature entropy:

$$\Delta G \bigg|_{T_{ref}}^{T} = -\left\{ a(T \ln T - T) + \frac{b}{2} T^2 + \frac{c}{2T} \right.$$
$$+ d_1 \{(T - 848) \ln |T - 848| - T + 848\} + d_2 \ln |T - 848|$$
$$\left. + \sum_{i=3}^{n} d_i \left(\frac{1}{1-i} \right) \left(\frac{1}{2-i} \right) (T - 848)^{2-i} \right\} \bigg|_{T_{ref}}^{T}$$

$$+ \left\{ a \ln T_{ref} + b T_{ref} - \frac{c}{2 T_{ref}^2} + d_1 \ln |T_{ref} - 848| \right.$$
$$\left. + \sum_{i=2}^{n} d_i \left(\frac{1}{1-i} \right) (T_{ref} - 848)^{1-i} \right\} (T - T_{ref}) - S_{ref} (T - T_{ref}). \tag{4}$$

Substitution of the appropriate a, b, c, and d_i's (provided in the text) into Eqs. 2-4 yields the enthalpy. entropy, and free energy of quartz over the temperature range 400-900° K.

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