Regional variation in the cell dimensions of metamorphic quartz

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Abstract

Precision unit-cell measurements of eighteen quartz samples from one rock type within a region of classic Barrovian metamorphic zones show variations that correlate with metamorphic grade. Although different samples within each metamorphic zone may show cell-size variations of about 0.01% (ten times the measurement uncertainty), the regional variation is twice as great, and there is a clear trend of increasing cell size with decreasing metamorphic grade. This general increase in cell parameters is consistent with the greater total impurity content and more numerous lattice defects of quartz formed at lower temperatures and pressures.

Introduction

Precision measurements show that the unit cell of quartz from a variety of geological environments varies commonly by as much as 0.03%. A compilation by Baskakova (1973, p. 36) of hundreds of published measurements indicates a spread of up to 2%.

Researchers have tried to correlate these variations with impurity content (Kamentsev, 1962, 1965; Baskakova, 1973; Walenczak and Wiewiora, 1974; Kralik and Weiss, 1974), and to correlate impurity content with growth conditions (Balitzki et al., 1966; Buldakov, 1968; Khadzhi and Lelyakova, 1969; Dennen and Blackburn, 1970; Perry, 1971). They have demonstrated that the unit cell of quartz varies with both structural and interstitial impurities, but conclusions about the effects of specific elements and the relationships between impurity content and growth conditions are partly inconsistent, even contradictory. Correlations have been hampered by the trace nature of most of the impurities, some of which are near or below the detection limit of the analytical techniques that were applied. Even more serious, the impurities occur not only substitutionally (Dennen, 1966; Walenczak and Wiewiora, 1974) and in structural channels (Kamentsev, 1965) but also in the form of solid inclusions (Chernov and Khadzhi,

1968; Korolev et al., 1974; Kralik and Weiss, 1974) and liquid-gas inclusions (Barker and Sommer, 1974).

Solid and liquid-gas inclusions are very common, often abundant. In natural Brazilian and synthetic quartz, for example, the >1 micron inclusions mostly range in size from 2 to 30 microns and in number from 0.4 to 13×10^6 cm⁻² of section (Flicstein and Schieber, 1974). The density of submicron impurities, 200-2000Å in diameter, has been reported as high as 10^{14} cm⁻³ (Morrison-Smith, 1976, p. 412).

The distribution of impurities is mostly uneven (Flicstein and Schieber, 1971, p. 159; Korolev *et al.*, 1974, p. 989), though they often are concentrated along rhombohedral growth surfaces (Chentsova and Butuzov, 1962; Khadzi and Lelyakova, 1969; Lukashev *et al.*, 1970, p. 288).

Any quartz sample of the size used for precision lattice measurements is likely to contain both substitutional and interstitial impurities which affect lattice parameters, as well as solid and liquid-gas inclusions, which contribute to the trace-element content of the sample without affecting unit-cell size. To date, each type of impurity and cell size have not been quantified in the same samples. It is understandable, therefore, that correlations have so far failed to demonstrate consistent quantitative relationships between unit-cell size and composition or between these parameters and the physical conditions of quartz formation, though they have revealed some trends.

We initiated this investigation to learn how variations in the cell parameters of natural quartz relate to crystallization temperature. The factors generally cited as strongly influencing impurity content and thus, presumably, the cell parameters of quartz are growth rate, orientation of the growth surface, concentration of impurities in the growth medium, pH of the growth medium, and growth temperature. A set of natural samples was chosen for which all of these factors might be regarded as essentially constant except crystallization temperature-pressure.

Sample selection

Classic Barrovian zones of chlorite- to sillimanitegrade regional metamorphism are exposed over a several-hundred-square-mile area in north-central Georgia. The zones are regular and uninterrupted, superimposed over folded metasediments of the Great Smoky Group (Hurst, 1973, p. 666). One of the principal rock types of the Great Smoky Group is metagraywacke, in which sedimentary structures and textures are remarkably well preserved. The typical modal composition of the metagraywacke (at biotite grade or higher) is 50% quartz, 25% plagioclase, 15% biotite, lesser muscovite, calcite, and accessory minerals (Hurst, 1955, p. 12). By repeated folding, the metagraywacke is spread over a 20-mile-wide belt, east-west, spanning all the metamorphic zones. Quartz in the metagraywacke recrystallized in response to a thermal gradient that probably was slowly impressed and long maintained. Chemical conditions were comparable throughout the area in beds of the same composition. Only small-scale movements of nutrient at points of recrystallization are evident; all growth surfaces were available. This geological setting appears to offer an unusual opportunity to check cell-size variation in relation to a well-defined thermal gradient, under essentially isochemical conditions.

Metagraywacke samples were collected from the Copperhill Formation throughout the area from the Blue Ridge-Ellijay axis westward to the Great Smoky Fault. Eighteen samples similar in chemical composition, relict grain size, and lithological association were selected. Their geographic positions with respect to the Barrovian zones are shown in Figure 1. From each sample, crushed just enough to free most of the grains, a clean concentrate of quartz was handpicked under a binocular microscope.

Lattice parameter measurements

The unit-cell parameters of each handpicked quartz sample were measured at 25°C with copper radiation and a Philips back-reflection symmetricalfocusing camera, 60 mm radius, modified for temperature control.

Temperature control was achieved by adding to the regular camera a specially constructed brass specimen holder 5 cm long, 3.2 cm high, and 0.7 cm thick, milled to fit the curvature of the camera and attached by 4 small screws to the rocking arm of the camera. Into the inner, curved surface of the sample holder a sample cell 2.8 cm long, 1.3 cm high, and 0.8 mm deep was milled. Two microheaters (Hotwatt Model SC-121) and one thermister (Fenwal glass probe 500-4000 ohms, nominal 1050 at 25°C) were mounted in the brass specimen holder adjacent to the sample cell. Temperature was controlled by an RFL Industries Model 70-115 controller connected to the two microheaters. Resistance of the thermister was read with a Fluke 8000A Digital Multimeter. The efficiency of this control method depends upon the temperature of the room being fairly stable and being set several degrees below the temperature of the sample holder. For these measurements, room temperature was adjusted to 18°±3°C with an air conditioner and monitored with a Hewlett-Packard Model 7127A recorder.

Each sample was ground to pass a 325-mesh (44μ) sieve. The generation of submicron particles was minimized to prevent fine-particle line broadening. The ground sample was moistened with a binder (20 parts acetone, one part lacquer) and packed into the cell of the sample holder with a spatula so as to ensure close conformity of the sample surface with camera curvature. Specimen temperature was equilibrated at 25±0.02°C, as measured with the sample thermister, before the X-ray shutter was opened. With room temperature varying no more than ±3°C, sample temperature varied no more than ±0.02°C during the X-ray exposure.

Twenty-six lines, twelve of them $K\alpha_1-K\alpha_2$ pairs, were read in the range 59-80° θ . Each was read at least 3 times; when the readings differed by as much as 0.02 mm, at least 6 readings of the line were averaged. For each line, *a* and *c* were calculated with Cu $K\alpha_1 = 1.540562$, Cu $K\alpha_2 = 1.544390$ Å (Bearden, 1967). The *a* and *c* values were plotted against (cos² θ /sin θ + cos² θ/θ), the extrapolation function of HURST AND STORCH: CELL DIMENSIONS OF QUARTZ



Fig. 1. Location of samples with respect to metamorphic zones. Heavy dotted lines mark the first appearance of the index mineral.

Nelson and Riley (1945). While the preferred extrapolation function for the symmetrical-focusing method is $\phi \tan \phi$, where $\phi = \pi/2 - \theta$ (Klug and Alexander, 1954, p. 464), several plots against both functions showed that the Nelson and Riley function gives a slightly better extrapolation. Each value of the unit-cell parameter was refined by three successive graphical approximations. The graphical method was used instead of the least-squares method for ease in weighing the quality of diffraction measurements.

The precision of the measurements was checked by comparing the values obtained by three different individuals, each of whom measured three different films of the same sample. The nine determinations of a and c were within 0.00005Å of the mean value.

For a comparison with measurements made by another method, in a different laboratory, a 5-mm cube cut from a large clear Brazilian quartz crystal was measured by Dr. Robert L. Barns of Bell Telephone Labs, Murray Hill, by the single-crystal method of Bond (Bond, 1960; Barns, 1972). The same cube then was crushed and measured with the modified camera and procedure described above. Dr. Barns measured (00.6) at 23.7°C and (33.1) at 24.1°C. His fully corrected values for 25°C and CuK α_1 = 1.540562Å are: $a = 4.91350\pm0.00003$, $c = 5.40511Å\pm0.00002$. Our values are: a = 4.9134(9), c = 5.4050(0)Å. Agreement is closer than might ordinarily be expected of interlaboratory measurements (Parrish, 1960; Barns, 1972).

Results

Table 1 gives 18 sets of precision lattice-parameter measurements, with calculated c/a ratios and unit-cell volumes.

The regional variation of unit-cell volume is

Sample no.	<u>a</u>	<u>c</u>	$ca^2 Sin 60^0$	c/a
4	4.9136	5.4051	113.01	1.1000
8	4.9134	5.4048	113.00	1.1000
9	4.9137	5.4049	113.01	1.1000
24	4.9139	5.4051	113.03	1,1000
25	4.9135	5.4047	113.00	1.1000
26	4,9137	5.4046	113.01	1.1000
34	4.9134	5.4049	113.00	1.1000
35	4.9139	5.4050	113.03	1.1000
36	4.9136	5,4046	113.01	1.1000
45	4.9140	5.4052	113.03	1.1000
46	4.9134	5.4051	113.01	1.1001
47	4,9137	5.4052	113.02	1.1000
51	4,9137	. 5.4048	113.01	1.1000
54	4.9134	5.4046	112.99	1.1000
55	4.9136	5.4050	113.01	1.1000
56	4,9133	5.4044	112.99	1.1000
58	4.9135	5.4046	113.00	1.1000
60	4,9142	5,4054	113.05	1,1000

Table 1. Lattice parameters of quartz in 18 samples of Ocoee metagraywacke from north-central Georgia

shown by Figure 2. Characteristically, the low-grade metamorphic quartz has a larger unit-cell volume than the high-grade quartz.

The variability of the lattice parameters with respect to metamorphic zones is shown in greater detail in Figure 3, prepared by projecting all values for aand c and unit-cell volume along strike to a common line cross-cutting the metamorphic zones. This common line is the abscissa of Figure 3; a vertical line through any point connects the three values for one sample. This figure shows the variability of a, c, and unit-cell volume from sample to sample in a given zone, a variability greater than 10 times the measurement uncertainty, and discloses also a clear trend of decreasing lattice parameters and unit-cell volume with increasing metamorphic grade.

The c/a ratios of 17 of the 18 samples are identical to 5 significant figures. Changes in unit-cell volume generally are due to changes in both a and c.



Fig. 2. Regional variation of the unit-cell volume of metamorphic quartz.

Discussion

The quartz initially sedimented in what is now metagraywacke to the Great Smoky Group was derived largely from medium- to coarse-grained crystalline rocks. This is inferred from the metagraywacke's mineralogical composition, grain size, and excellently preserved primary clastic textures. Throughout the sampled area, medium to coarse grains of single-crystal feldspar well preserve the size and shape of clastic grains prior to metamorphism.

Each measured quartz sample consists of several hundred grains from a metagraywacke outcrop. If all the grains in a sample did not come from a single source and were not homogenized by physical conditions subsequent to deposition, *i.e.*, by regional metamorphism, then some grain-to-grain variability in unit-cell parameters might be expected. Such variability could show only as a broadening or splitting of the diffraction peaks. Densitometer profiles show single, symmetrical, unbroadened peaks and thus give no indication of unit-cell variation among the grains of a given sample.

From outcrop to outcrop, however, within each metamorphic zone, there is considerable variation, as shown by the scatter of a and c values in Figure 3. These outcrop-to-outcrop variations must relate either to differences in sediment source or to local differences in metamorphic conditions.

The clearest pattern of variation, the overall trend of decreasing unit-cell parameters from northwest to southeast, correlates with increasing metamorphic grade. For this set of samples, the regional trend is hardly attributable to any factor known to affect unit-cell size except those factors which vary with temperature or pressure of recrystallization.

Effect of impurities on unit-cell size

Some impurities, such as Fe, Al, and Ge, substitute readily in the quartz structure; others such as B, Ti, Cu, P, and As are incorporated less readily (Brown and Thomas, 1960). Because the ionic radius of Si is smaller than that of any cation likely to replace it, substitutional cations might be expected to increase the unit cell of quartz, as reported by Kamentsev (1962, 1963, 1967), Buldakov (1968), Baskakova (1973), Kralik and Weiss (1974), and Walenczak and Wiewiora (1974). According to these investigators, unit-cell volume increases directly with Al and Li, two of the principal impurities. The c dimension increases directly with substitutional Al (Kamentsev, 1967) and a increases more with interstitial than with substitutional impurities. Conversely, the removal of



Fig. 3. Plot of quartz lattice parameters vs. position with respect to metamorphic zones.

impurities decreases the cell parameters (Butuzov *et al.*, 1975): both a and c decrease as Ca, Fe, Li, Mg, and Mn are removed electrolytically, Al remaining constant. The above conclusions have to be weighed against the fact that substitutional impurities were distinguished from interstitial impurities more by interpretation than by observation.

Temperature in relation to unit-cell size and impurity content

A general decrease in lattice parameters with increasing crystallization temperature has been reported by Keith (1950), Kamentsev (1967), and Baskakova (1973) and is clearly indicated by our data (Fig. 3). This implies a general decrease in impurity content with increasing crystallization temperature, if cell size relates mainly to cationic impurities.

Several investigations of impurity content in relation to crystallization temperature have yielded inconsistent conclusions. For example, Keith and Tuttle (1952) found that the substitution of trace elements in quartz may increase or decrease with increasing growth temperature. Balitzki *et al.* (1966), distinguishing substitutional from admixed Al by electron paramagnetic resonance and temperature by homogenization of liquid-gas inclusions, concluded that substitutional Al decreases with decreasing temperature, while total Al (admixed plus substitutional) increases. Kamentsev (1967), determining Al by precision measurement of c, having earlier concluded that c varies linearly with Al (1962), and determining temperature again by homogenization of liquid-gas inclusions, concluded that Al (substitutional by his interpretation) increases with decreasing temperature. Dennen and Blackburn (1970) concluded that total Al (interpreted as substitutional) increases linearly with temperature. Scotford (1975), comparing total Al with probable crystallization temperature for 18 quartz samples from diverse geologic environments, concluded that no direct relationship exists between Al content and crystallization temperature. A further test of the idea that Al might vary directly with crystallization temperature was made by Browne and Wodzicki (1977), who studied optically clear hydrothermal quartz crystals from the Broadlands geothermal field in New Zealand. They compared direct drillhole and fluid-inclusion temperatures with those deduced from the Al vs. temperature curve of Dennen and Blackburn, and concluded that Al content is an unreliable geothermometer.

Quite clearly, crystallization temperature is not the only factor determining the trace element content or the unit-cell parameters of quartz. Several other possible factors have been identified. Buldakov (1968) pointed out that growth pH can strongly influence the substitution of Al in quartz. At low pH, where Al³⁺ exists as a cation, its substitution for Si is hindered because the Al-O bond is much longer than the Si-O bond in a silica tetrahedron and the Al³⁺ ion is not an analogue of Si4+; at high pH, on the other hand, where Al exists as an anion, its bond with oxygen is shorter, due to greater covalency, and its electron shell more closely resembles that of Si⁴⁺ in quartz. Pavlishin et al. (1978) concluded that pH is the dominant control over the substitution of Al for Si in hydrothermal quartz.

Laboratory experiments have shown that the impurity content of quartz can vary not only with temperature and pH but also with the concentration of impurities in the growth medium, the orientation of the growth surface, and particularly the growth rate. Experimenting with quartz growth in 3% NaOH over the range 280–480°C and 1100–1300 kg/cm² pressure, with variable temperature gradient, Khadzhi and Lelykova (1969) found that Al uptake is inversely related to growth rate within the temperature interval 300–400°C; at other temperatures, the Al content was minimal at an intermediate growth rate, and increased at both higher and lower growth rates. Rapidly grown synthetic quartz contains abundant colloidally-dispersed non-structural impurities (Chernov and Khadzhi, 1968). At high temperatures, the concentration of colloidal complexes binding Al and other elements is markedly reduced and so is their mechanical incorporation in the growing lattice (Khadzhi and Lelykova, 1969).

An interpretational summary of previous studies is that total impurity content, the proportion of interstitial to substitutional impurities, and the lattice parameters of natural quartz all generally decrease with increasing crystallization temperature, but they may vary as well with other factors. Among these are concentration of impurities in the growth medium, pH, orientation of growth surface, and growth rate.

Growth pressure is a probable additional factor. Keith's (1950) correlation of decreasing cell size with increasing growth temperature might as well be a correlation with increasing growth pressure. Likewise, the trend of decreasing cell size with increasing metamorphic grade, reported here, correlates as well with increasing pressure.

A direct relationship between growth pressure and structural water in quartz has been reported by Barker and Sommer (1974), who distinguish three types of water: (1) fluid inclusions and adsorbed water, which can be driven off at temperatures below 650°C, (2) water along grain boundaries and dislocations, released at 1150-1300°C, and (3) structural water released only at the melting point of quartz. They found that only the structural water increases directly with growth pressure. Additional evidence for a direct relationship between growth pressure and structural water might be adduced from Bambauer et al. (1962, 1963), who used IR absorption in the 3μ region to quantitatively determine H in 400 quartz crystals from fissure veins throughout the central Swiss Alps. They report that H is highest in the higher-grade metamorphic rocks, presumably formed at higher pressures, and drops off regularly with decreasing metamorphic grade. Notably, their measurements do not include the type (1) water of Barker and Sommer, but do include types (2) and (3). The quantities of both type (1) and type (2) water in natural crystals are much greater than the quantity of type (3) water (Barker and Sommer, 1974, Fig. 1). Bambauer (1961) earlier studied the trace-element content of 250 quartz crystals from the central Swiss Alps. He concluded that total Al in the quartz correlates positively with H and that "high trace element contents produce a measurable lattice expansion." His conclusions appear to be, but are not necessarily, inconsistent with the interpretational summary above. His positive correlation of Al and H involves total Al but only partial H. His conclusion about lattice expansion is based on only three measurements, two of which give the same cell volume, within stated reproducibility. If the scatter of values in Figure 3 is typical of regional metamorphic areas, then three measurements are hardly sufficient to establish a regional trend.

As a general rule of crystal growth, higher pressures increase growth rate and improve the mechanical quality of silicate crystals (Takubo et al., 1971). Whether higher growth pressures decrease the cell size of quartz is yet to be directly established. In another silicate group, mullite-sillimanite (Hariya *et al.*, 1969), a decrease in cell size has been associated with increasing growth pressure, possibly due to a higher degree of structural order at higher pressure.

Order-disorder in relation to lattice parameters

High disorder is associated more often with high than with low impurity content. Mechanically disordered quartz would be expected to have larger cell dimensions than better crystallized quartz. These expectations are compatible with observations. Synthetic quartz rich in colloidal inclusions has low structural order (Khadzhi and Lelyakova, 1969, p. 45). More nearly perfect quartz crystals have minimal impurities. Authigenic quartz characterized by high mechanical admixtures also may have high substitutional impurities (Kralik and Weiss, 1974). If the larger cell of the low-grade Ocoee quartz connotes a more defective lattice, then low-grade conditions must have generated it, because the initially sedimented quartz was derived largely from crystalline rocks formed at a higher temperature.

The sympathetic variation of a and c, as shown by near-constancy of the c/a ratio, suggests that orderdisorder might not be a significant factor in cell size variations of the Ocoee quartz, because structural ordering usually is accompanied by a variation in axial ratio (C. Frondel, personal communication).

Conclusions

Published efforts to relate impurity content of quartz to variation in unit-cell parameters and growth conditions have yielded some inconsistent conclusions. Several reasons for the inconsistencies are apparent: a clear distinction between substitutional and interstitial impurities was not made, or the degree of order and number and type of defects were not determined, or only a few of the factors known to influence impurity content and cell size were taken into account. When the conclusions are adjusted to the apparent limitations imposed by the data, the inconsistencies largely vanish, leaving the following generalizations.

(1) The unit-cell parameters of quartz generally increase with substitutional impurities.

(2) Substitution of a sole multivalent impurity may increase or decrease with increasing crystallization temperature, but when several multivalent elements are present, a coupling can take place during growth with the result that the coupled substitution commonly decreases with increasing temperature. The coupling of Al and P is an example. The solubility in hydrothermal fluid of AlPO₄ is inversely related to temperature, while the solubility of SiSiO₄ is directly related. Thus the solid solution of AlPO₄ in quartz is favored more by low than by high temperature.

(3) Total impurities, the number of structural defects, and the lattice parameters are commonly greater in quartz formed at lower temperatures and pressures and in quartz grown rapidly.

(4) A single characteristic of quartz, such as cell size or content of one impurity, does not generally define a growth parameter. Al content, for example, does not alone define growth temperature, nor water content alone define growth pressure. Expectably, though, a combination of characteristics—accurate unit-cell parameters, quantitative distinctions between interstitial and substitutional impurities, type and density of defects—might succeed, once their interrelationships are more clearly defined.

The foregoing conclusions are drawn largely from published data, as referenced, and partly from unreported experiments.

Our measurements show that the unit-cell parameters of quartz in metasediments in north-central Georgia are largest in low-grade rocks and decrease in the direction of increasing metamorphic grade. The pattern of variation in cell size correlates well with the pattern of regional metamorphism and is consistent with the expectation that quartz formed at higher temperatures and pressures would be characterized by lower total impurities, higher quality, and smaller cell size.

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