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Implications for Geothermometry of Aluminum Substitution in Quartz from Kings Mountain, North Carolina

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Abstract. The aluminum concentration of quartz from contact-metamorphosed, Al_2SiO_5 bearing quartzite at King's Mountain, North Carolina shows a regular variation with distance from an intrusive contact. Presumably this is the result of temperature-dependent solubility of aluminum in quartz, but critical comparison of these results with other recently published data shows that detailed calibration of this geothermometer has not yet been achieved.

Introduction

I proposed earlier (Perry, 1963) that a correlation might exist between temperature of metamorphism and aluminum concentration in quartz from rocks containing an Al_2SiO_5 polymorph. Initial results confirmed this prediction, but the restricted composition of applicable rocks and the tedious procedures required to obtain quartz free of aluminous phases in these rocks appeared to make this a rather unsuitable geothermometer. More recently, Dennen *et al.* (1970) have expanded on this work and have found that the chemical potential of aluminum required to produce aluminum-saturated quartz is less than that required to produce a separate Al_2SiO_5 phase and, in fact, that most natural quartzes appear to be saturated in aluminum. This new background data provides a framework for discussion of my original study. Theoretical considerations are discussed by Perry (1963) and elaborated by Dennen *et al.* (1970).

Geology

Kyanite- and/or sillimanite-bearing quartzites in the vicinity of Kings Mountain, North Carolina were selected for study because mapping by Espenshade and Potter (1960) revealed a regular metamorphic gradient from greenschist to amphibolite facies that is spatially related to the Yorkville Quartz Monzonite. A narrow zone (C6, Fig. 1) within the sampled area contains the triple point assemblage kyanite-sillimanite-andalusite. The intruding Yorkville Quartz Monzonite is described by Espenshade and Potter (1960) as a dominantly coarse-grained porphyritic rock having a flow structure defined by parallel orientation of feldspar phenocrysts (An_{25-38}) and biotite; zoned plagioclase phenocrysts are common, and most microcline phenocrysts are perthitic.

Analytical Data

Analytical data are given in the Table. Analyses were made with a 3 meter quartz-glass Littrow mounted prism spectrograph. Detailed analytical procedures are described in Perry (1963). The final column of the Table lists values reported by

Table. Aluminum and Lithium Analyses of quartz from Aluminous Quartzites, Kings Mountain, North Carolina

Sample	Al (ppm)	σ (ppm)	ca ^a (%)	Li (ppm ^b)	Al (ppm ^c)
C 5	109	± 6.7	± 6.1	nd	114
C 18	77	± 7.1	± 9.2	0.3	85
C 21	52	± 4.2	± 8.1	nd	—
C 23	39	± 8.5	± 22	nd	40

^a Class interval.

^b Detection limit, less than 0.2 ppm.

^c Comparison analysis reported by Dennen (1966).

Dennen (1966) for my samples; the close correspondence of these results indicates that our analytical data may be compared directly.

More controversial than the analytical techniques is the adequacy of the steps taken to obtain a pure quartz phase in the presence of fine-grained, highly aluminous impurities (Perry, 1963). The final separation step consisted of ultracentrifugation of 12–20 μ particles at 40 000 g (25 000 RPM). The heavy liquid used was a mixture of 9.1 ml bromoform and 0.9 ml ethanol to which about 7 mg of n-hexylamine-HCl was added to neutralize surface charges and prevent clotting of fine particles. Aluminum concentrations for Kings Mountain samples fall well within the range for natural quartzes (Bambauer, 1961, Dennen *et al.*, 1970), and several estimates of purity suggested relatively low levels of physical contamination. A grain count of kyanite and rutile grains in the final separate of C18 gave a kyanite/rutile volume ratio of between $1/3$ and $1/5$. The spectrographically measured titanium concentration of this sample (50 PPM) was all considered to come from rutile, giving a maximum estimate of the rutile concentration. From this the maximum Al content contributed by kyanite impurities was calculated to be: $0.47 \cdot (1/3) \cdot (\text{PPM Ti}) = 7.8 \text{ PPM}$, or about 10% of the sample value.

Discussion

Fig. 1 has as its ordinate the aluminum concentration of quartz from assemblages saturated with Al_2SiO_5 (kyanite in C 18, C 21, and C 23, sillimanite in C 5). Bambauer (1961) showed that aluminum commonly occurs in quartz in coupled substitution with hydrogen or lithium. Analyses of lithium (Table) show that this element is unimportant in any of the Kings Mountain samples, whereas the presence of hydrous phases in all assemblages suggests that hydrogen was sufficiently abundant not to control Al substitution.

The abscissa of Fig. 1 is the distance of the sample locality from the nearest outcrop of Yorkville Quartz Monzonite. Presumably this is related in some direct way to the maximum temperature of metamorphism. Thus, a relationship of solubility of aluminum to temperature is demonstrated; but the evaluation of temperature is difficult.

In Perry (1963) I constructed a heat flow model in which the temperature at triple point locality (C 6, Fig. 1) was constrained to be 360° C, a value near the



Fig. 1. Relative contact

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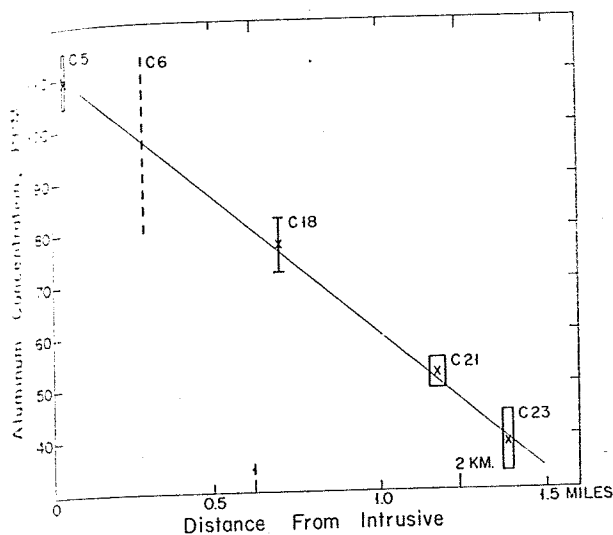


Fig. 1. Relation of Al concentration in quartz to distance from Yorkville quartz monzonite contact

upper limit of experimental error of the $300^{\circ} \pm 50^{\circ} \text{C}$ reported by Bell (1963) as the temperature at which kyanite, sillimanite, and andalusite coexist. Fig. 1 of Zen (1969) illustrates the ambiguity in the determination of the temperature and pressure of the Al_2SiO_5 triple point. Probably, the best estimate at present is 622°C and 5.5 kilobars (Richardson *et al.*, 1969), fully 322°C above the original value of Bell (1963). The difficulties in establishing equilibrium in experimental studies of Al_2SiO_5 are probably paralleled by metastable persistence of phases in natural systems but, as Richardson *et al.* (1969) point out, the replacement of both kyanite and andalusite by sillimanite (which occurs at Kings Mountain) implies a temperature above the triple point temperature.

Dennen *et al.* (1970) report that a linear relationship exists between aluminum concentration in quartz and the temperature at which the quartz grew or equilibrated. They further report that the Kings Mountain quartz samples fit this relationship; this is true, however, only if the old Al_2SiO_5 triple point data is used. If Richardson *et al.* (1969) have correctly determined the triple point, the maximum temperature at locality C 5 was probably greater than 622°C and may have been about 650°C . This temperature corresponds to 170 ppm Al on the curve of Dennen *et al.* (1970) instead of the observed value of 109 ppm (Table). This 60% discrepancy is in the wrong direction to be attributable to poor separations of quartz for analysis and, in fact, lends confidence in the quality of the quartz separates. Since quartz from these highly aluminous rocks does not follow the relationship reported by Dennen *et al.*, that relationship and its applicability to metamorphic rocks should be carefully examined.

Other possible discrepancies may be considered. The least metamorphosed of the Kings Mountain samples (C 23, 39 ppm Al) corresponds to a temperature of 160°C on the curve of Dennen *et al.*, and, using the Al_2SiO_5 triple point pressure as an estimate, this would correspond to a thermal gradient of 25°C/kb . This value

seems low and is also inconsistent with the isograd map of Espenshade and Potter (1960). Most of the temperatures given in Table 4 of Dennen *et al.*, with the notable exception of Missouri rhyolite, also seem exceptionally low.

There are at least three possible reasons for the discrepant results.

1. The Al_2SiO_5 triple point determination is seriously in error. It seems unlikely that the value of Richardson *et al.* (1969) will be changed sufficiently to reconcile the concentration differences reported here.

2. Synthetic quartz does not contain equilibrium concentrations of aluminum. This is likely inasmuch as equilibrium was not demonstrated.

3. Reequilibration to low temperatures is likely to occur in natural systems if nucleation of new phases is not involved. This may well have occurred at Kings Mountain and is consistent with redistribution of oxygen isotopes between phases during cooling in a large, wet thermal aureole as noted by Perry and Hall (1969) and in preparation).

Clearly, the usefulness of aluminum substitution in quartz as a geothermometer requires further evaluation. It may be that there are few chemical parameters in mineral systems, except those dependent on nucleation energy, which turn on or off at geologically interesting temperatures.

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Si-Al Orderi

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Abstract. Differences in the basis of five crystallographic laboratory treatments of nepheline and independent tetrahedra ordered than a sequence

Very little is known about rock-forming conditions and detailed structural framework structure of a variable degree of order, particularly since the order could conceivably

Recent crystallographic preliminary estimates of Nepheline structure at Bancroft, Canada and Peacor, 1969, Norway (Dollase and Monte Somma specimen of 48 hrs. (Two 24 hrs. order to remove

The five structural sites, however, is not symmetric of the order and positional order occurs in all sites oxygens to the T_1 , T_2 and T_3 sites per 32 oxygen sites (1) sites of the oxygen