*Thermochimica Acta,* 175 (1991) 293–298
Elsevier Science Publishers B.V., Amsterdam

# INSTRUMENTAL AND PREPARATIVE FACTORS INFLUENCING MEASUREMENT OF $\alpha$–$\beta$ QUARTZ INVERSION TEMPERATURES

M. LISK, K.A. RODGERS * and P.R.L. BROWNE
*Department of Geology, University of Auckland, Private Bag, Auckland (New Zealand)*

(Received 23 July 1990)

## ABSTRACT

Thirty-five measurements made of the $\alpha$–$\beta$ transformation on the quartz samples from the Ohaaki-Broadlands geothermal field and a reference Ceylonese 'rock crystal' gave values ranging from 569.6 to 572.4°C. Rigorous standardization of measurement conditions, however, gave reproducible results and a precision of $\pm 0.35$°C. The instrumental factors and sample characteristics which affected the quartz inversion temperatures include packing density, grain size, and particle size, plus other factors not identified.

## INTRODUCTION

The temperature of the $\alpha$–$\beta$ inversion of quartz can be measured precisely by differential thermal analysis (DTA). This inversion is known to occur over an appreciable temperature range that reflects the paragenesis of the quartz [1,2]. The nature of this relationship is unclear and scant information is available concerning the crystal chemical controls which might affect the inversion temperature. Furthermore, the DTA method is susceptible to instrumental, operator and sampling procedures which affect precision and make comparison of results between different laboratories difficult [1,3]. In the course of a study of controls on $\alpha$–$\beta$ quartz inversion temperatures, it was found necessary to explore the influence of several preparative variables which affect the DTA results. The results supplement the methodology of Rodgers and Howett [3] and are briefly presented here as a guide for other workers.

## INSTRUMENTAL AND EXPERIMENTAL

A Shimadzu differential thermal Analyser (type DT-2B) was used with four Pt–$Pt_{90}/Rh_{10}$ thermocouples, 0.5 mm o.d., arranged at 90°, and Pt/Rh

---

* Author to whom correspondence should be addressed.

crucibles (6 mm o.d. × 17 mm), set in a beryllia sample holder. The original DFC-15 temperature controller unit has been replaced with an EMC #-483 self-contained PID controller module (Electric Measurement and Control). However, the sensitivity of this controller (within 1° C) failed to provide the precision ($\pm 0.3°$ C) reported in earlier quartz inversion studies [1,3,4], but manual control of the voltage output, using an initial voltage of 39.5 V, yielded a gentle, non-linear temperature curve which was reproducible and had an acceptable precision of $\pm 0.35°$ C over the appropriate temperature range.

The quartz inversion temperatures were measured using the procedure of Rodgers and Howett [3] by employing an internal standard of water-free, analytical grade potassium sulphate blended with the quartz. Cryolite, diluted by ignited alumina, served as a reference material. Successive experimental determinations were made which included the thermal responses of quartz, $K_2SO_4$ and cryolite, for both rising and falling furnace temperatures. The linear distances between the peaks projected onto the chart baseline were measured with calipers and direct proportion was used to calculate the temperature of the quartz inversion peak relative to the 20.8° C spacing difference between the $K_2SO_4$ and cryolite peaks. Inversion temperature determinations were made in duplicate for each sample, with several in triplicate.

A wide range of quartz specimens have now been measured by the authors. Results from three typical samples are considered here, by way of example: a Ceylonese 'rock crystal', a large piece of which has been adopted as a secondary standard by the Auckland University thermal laboratory, and two quartz separates, BR1 and BR2, obtained from two altered rhyolites from the Broadlands geothermal field, Ohaaki, New Zealand.

## VARIABLES

The key to obtaining precise results lies in rigorous standardization of all experimental procedures [1–3]. The shape and position of the DTA curve depend on both instrumental factors and sample characteristics.

### *Instrumental factors*

The instrumental factors include furnace atmosphere, sample arrangement, thermocouple composition and heating rates. In most laboratories, inversion temperatures are measured in air at ambient pressure, while sample arrangement and thermocouple compositions for a particular machine are usually pre-determined by the manufacturers.

Little information is available concerning the influence of heating rate on quartz inversion temperatures. Rodgers and Howett used a PID-determined

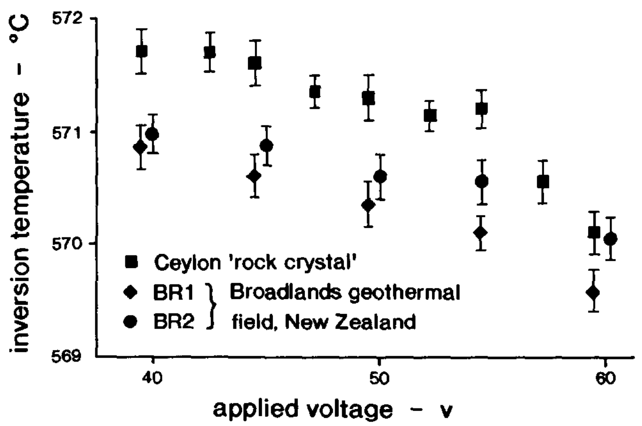

Fig. 1. Variation in $\alpha-\beta$ inversion temperature with heating rate, expressed as applied voltage, for three quartz samples.

2° C min$^{-1}$ heating rate [3]. In the present study, heating rates were in the range 1–2° C min$^{-1}$, as determined by the 39.5° C initial constant voltage setting. This returned consistent and reproducible results.

It was found that a reduction in measured inversion peak temperatures occurred with all three quartz samples when the initial voltage was increased, i.e. as the heating rate increased (Fig. 1). The variation in inversion peak temperature lay within the level of precision where the applied voltage was below 40 V and the heating rate did not exceed 2° C min$^{-1}$. Between settings of 40 and 55 V, a progressive decrease in the measured peak temperature occurred which averaged about 0.05° C per volt. Above 55 V, heating rates were in excess of 8° C min$^{-1}$ and a marked decrease in the measured inversion temperatures occurred as the rates increased, with results obtained from all three samples tending to converge towards common values.

This decrease in measured peak temperature with increasing heating rate contrasts with reports of measurements made on minerals other than quartz, e.g. [5–7]. It is regarded as reflecting the nature of the particular quartz samples measured, in which both homogenization of defect structures and the decrepitation of fluid inclusions within the quartz grains are believed to have assisted in triggering the structural changes.

## *Sample preparation*

Variations in the method of sample preparation can influence the position of peak temperature and the shape of DTA curves [1].

1. Both the original grain size and the sample particle size of the crushed sample can affect inversion temperatures of some minerals. Wendlandt noted that peak temperatures increase with decreasing sample particle size

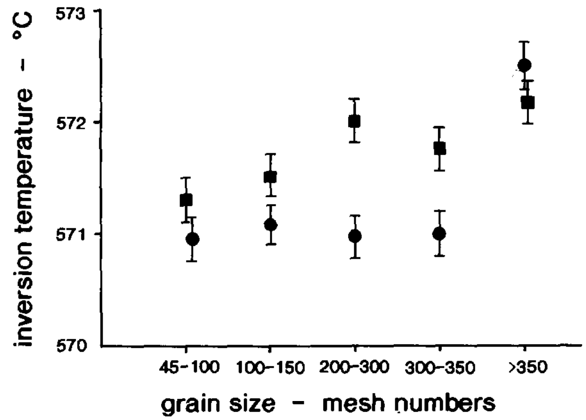

Fig. 2. Variation in $\alpha-\beta$ inversion temperature with sample particle size for two quartz samples. Abscissa scale is arbitrary. Symbol key as for Fig. 1.

for both kaolin and silver nitrate [5]. Bayliss [8] and Berkelhamer and Speil [9] both found that peak temperatures decrease with decreasing grain size for kaolin. Smykatz-Kloss [1] observed that the width at half height of the dehydration peak of montmorillonite and halloysite is a function of grain size. Few data have been reported as to how either the original grain size or the sample particle size might affect quartz measurements.

Figure 2 shows results from the present study. These indicate that an increase in peak temperature may occur with decreasing sample particle size, as in the case of the Ceylonese rock crystal; however, the Broadlands quartz has no significant variation among mesh sizes coarser than 350. In this latter case, factors other than sample particle size apparently have a greater influence on peak temperatures.

Crushing during sample preparation is known to affect the degree of disorder in the quartz lattice. Hofmann and Rothe noted, for example, that excessive grinding can reduce the long range structure of quartz [10]; the defect character of the grains increases and the physical properties change, affecting the $\alpha-\beta$ inversion [1]. McDowell and Vose found that extremely fine grained quartz had a sluggish thermal response [11]. These reports, however, have little relevance for the coarser sample particle sizes and the briefer grinding times used in the present study. The main effect of finer sample particle sizes may be little more than to help reduce the effects of fluid inclusion decrepitation, or to increase the packing density.

Further measurements with other samples suggested that a 100–200 mesh particle-size fraction returned the most reproducible results and this has been used in subsequent studies.

2. High packing densities promote higher heat conductivities and thus reduce thermal gradients within a sample, affecting the peak position of the differential curve at temperatures up to 600 °C [1,5]. The resulting quicker

response between the temperatures of sample and sample holders produces a DTA curve which returns to the zero line faster and produces a sharper peak at a slightly lower temperature [1]. It was not possible to quantify the effect of packing density in this study, but an attempt was made to standardize each sample by hand tamping gently five times with a metal rod.

Packing density may also affect the size of a peak. Although the authors found no variation in either peak shape or area with varying grain size, Berkelhamer [12] reported differences in peak shape with finer size fractions, but not peak area, i.e. heat of reaction. However, other sample and instrument variables may affect peak shape, particularly homogeneity. Both Smykatz-Kloss [1] and Rodgers and Howett [2] reported variation in size and shape of quartz inversion curves which they ascribed, in part, to inhomogeneity of the samples.

3. Several generalizations apply to sample size assuming that the selected size truly represents the whole. While larger sizes enhance sensitivity they reduce resolution. However, in order to obtain a clean thermal effect where the heat of reaction is relatively small, as is the case with quartz, the amount of sample used must exceed a certain minimum size, although Smykatz-Kloss considered that samples involved in structural transformation studies should not exceed 200 mg [1]. An effective way of increasing sample size, while retaining high resolution, is to add to it an inert dilutent of similar thermal capacity, such as $Al_2O_3$, which has been prepared in an identical fashion.

The results for five different sample sizes of quartz, see Fig. 3, showed no consistent relationship between peak temperature and bulk sample size. As with the particle size results, the authors believe that factors other than sample size have a greater bearing on the measured inversion temperatures. For example, thermal gradients exercise a major influence on heat transfer in DTA apparatus where sample sizes of up to 100 mg are used [7]; the

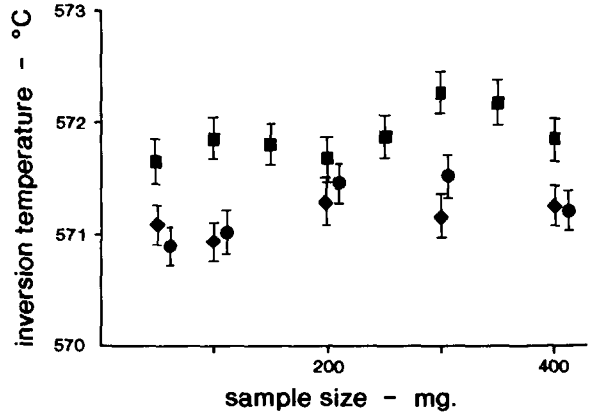

Fig. 3. Variation in $\alpha-\beta$ inversion temperature with sample size for three quartz samples. Symbol key as for Fig. 1.

present results may merely reflect anisotropic heat distribution within the samples.

## CONCLUSIONS

The present results emphasize, yet again, the need to standardize rigorously procedures used in thermal analysis, particularly where recorded data are to be compared between samples, operators, instruments and laboratories. The influence of heating rates alone on recorded peak positions underlines this conclusion. The unpredictable effect of sample particle size makes it essential that any contribution it, or a similar factor, has on the final result, has an equal bias on all samples. Even the inconclusive results obtained for sample size sound a note of caution when trying to compare results from samples of different mass. Nevertheless, the authors have found that when these variables are constrained and instrumental procedures standardized, quartz inversion temperatures can be measured so as to yield sensible isothermal patterns for samples from specific geological environments such as geothermal fields.

Note that, as in most conventional differential thermal studies, it is desirable that sample and reference material should possess similar thermal capacities, and be prepared in identical fashion. Our experience reconfirms that this may be achieved satisfactorily in measuring quartz inversion temperatures by using alumina plus cryolite [$Na_3AlF_6$]) as reference material, together with potassium sulphate [$K_2SO_4$] plus quartz in the sample crucible [1,3]. Where necessary, thermally inert alumina can be used as a dilutent to balance the amount of the sample size (quartz + potassium sulphate) with that of the reference (cryolite and alumina).

## REFERENCES

1 W. Smykatz-Kloss, Differential Thermal Analysis: Applications and Results in Mineralogy, Springer-Verlag, New York, 1974.
2 K.A. Rodgers and N.M. Howett, Neues Jahrb. Mineral., Abh., 159 (1988) 1.
3 K.A. Rodgers and N.M. Howett, Thermochim. Acta, 87 (1985) 363.
4 W. Smykatz-Kloss, Contrib. Mineral. Petrol., 26 (1970) 20.
5 W.M. Wendlandt, Thermal Analysis, John Wiley, New York, 3rd edn., 1986.
6 H.E. Kissinger, Anal. Chem., 29 (1957) 1702.
7 J.W. Dodd and K.H. Tonge, Thermal Methods, John Wiley, Chichester, 1987.
8 P. Bayliss, Nature, 201 (1964) 1019.
9 L.H. Berkelhamer and S. Speil, Mine Quarry Eng., 10 (1945) 221.
10 U. Hofmann and A. Rothe, Z. Anorg. Allg. Chem., 357 (1968) 196.
11 I. McDowell and W. Vose, Nature, 170 (1952) 366.
12 L.H. Berkelhamer, Rep. Invest. U.S. Bur. Mines Rep. Invest., 3763 (1944).