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THE EFFECT OF PARTICLE SIZE ON THE DETERMINATION OF QUARTZ BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

Analysis by DSC and powder XRD techniques for quartz occurring in claystones and minerals has indicated severe discrepancies between the results. The decrease in quartz particle size below 20 μm produces a significant reduction in peak area of the quartz $\alpha-\beta$ reversible transition, thus affecting DSC estimates of the quartz content of the sample.

INTRODUCTION

Quartz is essentially ubiquitous and occurs in many different types of geological environment. Recently the application of differential scanning calorimetry (DSC) to the analysis of mineral mixtures containing quartz, was reported [1]. Essentially the technique involves measuring the peak area of the $\beta-\alpha$ cooling transition of quartz, which appears alone since other interfering minerals (e.g. clays) are dehydrated irreversibly and yield no thermal response on cooling.

In an attempt to develop a rapid technique for quartz analysis in claystones and other minerals, the above approach was followed. This communication indicates the limitations of DSC in analysing for quartz in this manner.

EXPERIMENTAL

Thermal analysis curves were recorded on a Rigaku Denki Thermoflex 8100 series instrument. The DSC unit possessed a range of ±0.5 to 16 mcal s^{-1} and was operative to about 900 °C. Calibrations were carried out as described elsewhere [2]. Runs were performed using platinum pans with corresponding lids. Calcined alumina was used as the thermal reference material. Experiments were carried out in static air. Sample masses were in the range 5–30 mg and heating rates 10 °C min^{-1}. Peak areas were measured using a Planix 7 Tamaya planimeter.

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TABLE 1

Comparison of DSC and XRD determination of quartz in claystones and rock samples

Sample [a]	% Quartz (XRD)	% Quartz (DSC)
Dickite	24	15
Metabentonite	37	13
Illite	24	7
Attapulgite	10	4
Pyrophyllite	36	28
Chalcedony	95	25
Pyrolusite	29	26
Siliceous Siltstone	66	65

[a] Name refers to major clay or mineral species present.

X-ray diffraction (XRD) scans were carried out on a Siemens D-500 diffractometer using copper K_α radiation and a graphite monochromator. The internal standard method [3] was used to determine quartz levels in claystone and mineral specimens.

Samples were milled in a Siebtechnik mill. Size distributions of the mineral specimens were obtained using a Micromeritics Sedigraph recorder. The claystone and mineral samples analysed are shown in Table 1. Fine granular quartz (Merck Art. 7536) was used as a suitable reference material. Particle size fractions of quartz were obtained by sieving; below 40 μm fractions were collected using an ATM Corp. Sonic Sifter.

RESULTS AND DISCUSSION

The quartz content of each sample was determined by the method described earlier [1]. The β–α cooling exotherm of quartz was found to be variable, being reasonably strong for some samples but weak to almost absent in others. Yet in almost all cases, XRD indicated a substantial quartz content. The results obtained by the two techniques are shown in Table 1.

It is clear that with the exception of several samples a large discrepancy occurs between the DSC and XRD values. In some instances, as with chalcedony and attapulgite, the DSC value is about a quarter the XRD result.

The anticipated source of the problem was the particle size of the materials. Particle size distribution using the sedimentation technique showed that the coarser samples, with bulk sizes predominantly above 20–30 μm (pyrolusite and quartz rich siltstone) yielded results in agreement with XRD. Claystones of finer particle size, predominantly below 20 μm, yielded poor agreement.

However, since the particle size distribution using the sedimentation technique (Sedigraph) yielded the overall bulk distribution this did not necessarily reflect upon the size of the quartz particles present.

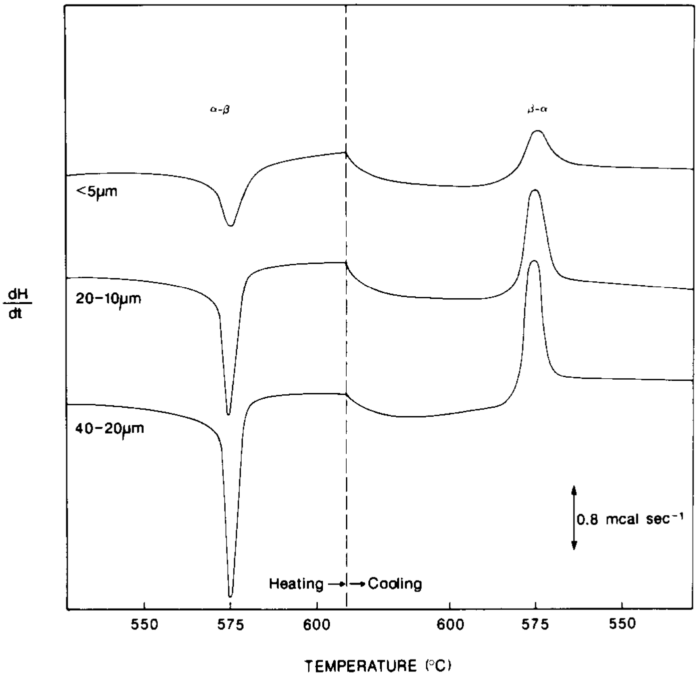

Fig. 1. DSC curves determined for the α–β (heating) and β–α (cooling) transitions for quartz of various particle size (sample mass 31.5 mg).

To establish the effect of particle size upon DSC measurements of quartz, pure quartz granules were used. Fractions of a given particle size, within the range 400 μm to less than 5 μm were prepared.

In each case the same weight of quartz was heated under identical conditions. The heating and subsequent cooling curves for several size fractions are shown in Fig. 1. The peak areas for the reversible α–β transitions were measured and averaged. For a given fraction the area of the heating and cooling phase are essentially equal, as noted earlier [1]. A plot of the peak area vs. particle size is shown in Fig. 2. Clearly the magnitude of the quartz inversion is affected by the particle size. No significant variation occurs in the range 400 μm to approximately 20–25 μm. Below 20 μm, however, the peak area decreases, and markedly so below 10 μm. For a particle size range below 5 μm a threefold decrease in area is observed. From Fig. 1 the quartz inversion can be seen to weaken and broaden with decreasing particle size.

These results explain the observation that the DSC of coarser materials agree with the XRD result, and why the fine claystones, containing finely dispersed quartz particles, yield low results. By contrast XRD of quartz samples in the range 50–5 μm showed little change in peak intensity. No problem occurs with this technique since it is at its optimum in analysing particles in the range of approximately 10 μm [4].

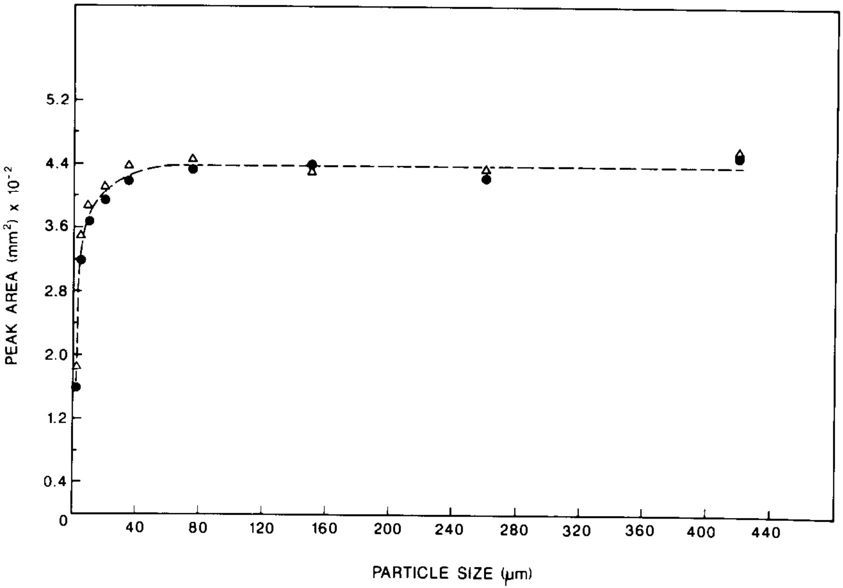

Fig. 2. Plot of quartz particle size vs. peak area for the $\alpha-\beta$ (●) and $\beta-\alpha$ (△) transitions.

It is concluded that the determination of quartz using the DSC technique is limited by particle size effects, and is not suitable for samples less than 20 μm in size. More generally, the possible change in the thermal profile of a sample as a function of particle size should be considered whenever DSC is to be employed as a quantifying technique.

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