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Differences in the thermal behaviour of natural quartz before and after mechanical grinding as observed by emanation thermal analysis

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Abstract

Emanation thermal analysis, which measures the release rate of radon from a sample previously labelled with trace amounts of thorium-228 and radium-224 on its surface, makes it possible to reveal differences in the thermal behaviour of quartz sand before and after mechanical treatment by milling, and indicates the formation and thermal recrystallization of the highly disordered silica layer resulting from the mechanical activation of the sample.

Keywords: Emanation thermal analysis; Mechanical grinding; Quartz; Radon

1. Introduction

The influence of grinding on the reactivity and structural changes of quartz has been demonstrated by several authors [1] and the increased reactivity of the ground quartz was ascribed to the formation of highly disordered silica layers (thickness from 20 to 500 nm) on the surface of the quartz grains [2–6]. Recently, it was shown by one of us [7] that the thickness of this layer, formed after a mechanical treatment of natural crystalline quartz lasting ten hours, can be estimated from the kinetics of the ground quartz dissolution in 0.5 M HF as being approximately 100 nm. Other authors [5, 8, 9]

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have reported that a thin layer of amorphous silica (thickness lower than 30 nm) is also usually found on the surface of natural quartz.

In this paper the differences in the thermal behaviour of natural quartz samples before and after mechanical grinding are characterized. To do this we have used the radon tracer technique, emanation thermal analysis (ETA).

Emanation thermal analysis [10, 11] is based on the measurement of the rate of radon release from solid samples previously labelled on their surfaces with trace amounts of thorium-228 and radium-224. Due to the recoil energy of the radioactive nuclides formed as the consequence of spontaneous alpha decay, the atoms of Ra-224 and Rn-220 are incorporated into the quartz grains to a depth of about 80 nm from the surface. In this way, layers of this thickness, including amorphous silica layers formed on the surface, can be considered as labelled with the radon radionuclide, the release of which is measured by the ETA method.

In the apparatus used for measurement of the rate of radon release, the labelled sample (0.1 g) was placed in a corundum crucible, over which flowed a stream of air of constant flow rate (40 ml min^{-1}) so as to carry the released radon atoms from the sample into the measuring chamber equipped with a scintillation detector for detection of the alpha radioactivity of radon.

The radon atoms are released from the labelled sample due to the recoil energy they gain during their alpha decay from Ra-224 as well as by the mechanisms of the radon diffusion in the solids. Consequently, according to the theory of ETA given, for example, by Balek and Tölgyessy [10], the values of the radon release rate E measured reflect the changes in the surface area and radon diffusivity taking place in the labelled layers of solids.

2. Samples investigated

The sample of natural quartz sand (NE 34 sand from the Nemours factory, France) was supplied by Sifraco Co. (France). The content of SiO_2 was $\geq 99.6\%$; the presence of Fe_2O_3 (0.030%) and Al_2O_3 (0.080%) was declared by the supplier and a grain size of 100–300 μm represented a surface area of 0.0145 $m^2 g^{-1}$. The mechanically treated sand sample was prepared by grinding the sand for 10 h in a centrifugal mill (Fritsch Ltd., Germany) with agate balls. The specific surface area of the ground sample as measured by the BET was 3.6 $m^2 g^{-1}$, and the average grain size decreased to about 2.5 μm [7].

3. Experimental

The samples were labelled by traces of Th-228 and Ra-224 in acetone solution by adsorption and subsequent drying at 50°C in air. Before the proper ETA measurement, the samples were stored for 3 weeks to allow radioactive equilibrium between radon and its parents to be reached.

The radon release rate from samples of 0.1 g was measured in the ETA apparatus during heating to 1100°C and subsequent cooling in air at the heating and cooling rates of 5 K min^{-1} and 2.5 K min^{-1}, respectively. The ETA results are represented as the temperature dependence of the radon release rate, normalized by the radioactivity of the parent nuclides adsorbed on the sample by the labelling.

4. Results

4.1. *Quartz sample before mechanical treatment (Fig. 1)*

The increase of radon release rate in the temperature interval from room temperature to 110°C reflects the liberation of adsorbed water from the quartz surface. The surface, once free of water, has a higher radon release rate. The decrease in E on subsequent heating up to 180°C can be ascribed to further drying of the sample, which increases the probability for radon Rn-220 atoms formed by the decay of Ra-224 to be

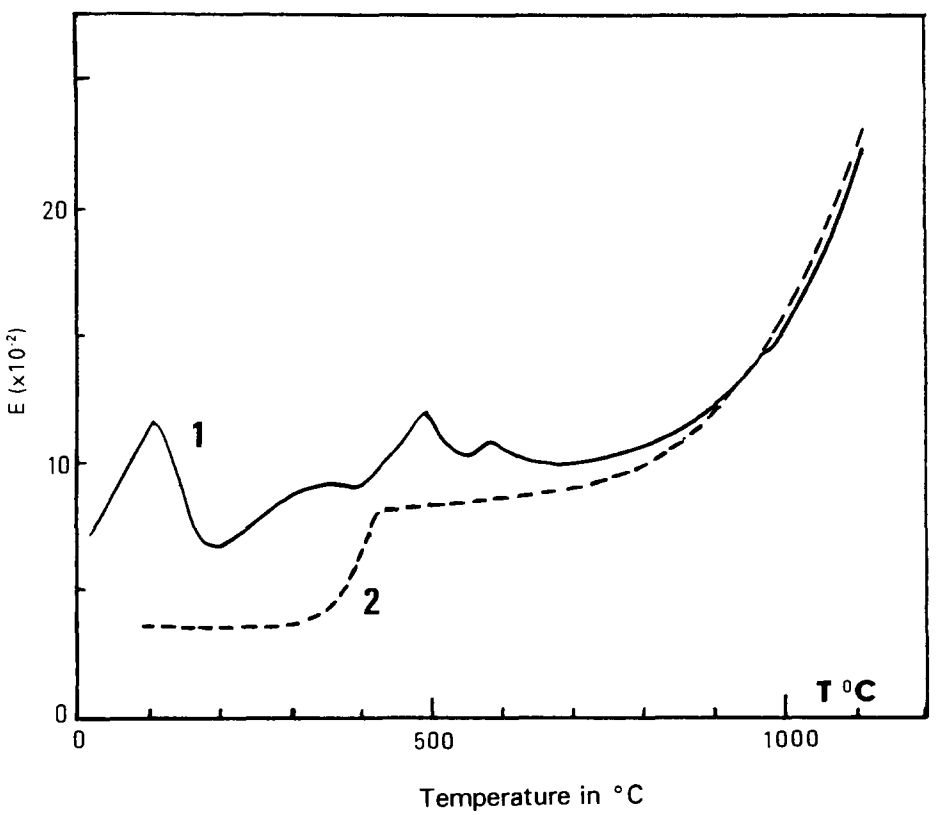

Fig. 1. ETA curves of the starting quartz (original sample) on heating (1) and cooling (2): E, radon release rate (arbitrary units).

incorporated into the neighbouring grains by recoil energy. This leads to a decrease of the probability of radon release from the sample grain aggregates.

The slow increase of radon release rate from 180°C to about 500°C characterizes the diffusion of radon from the sample aggregates, especially in the intergranular space of the aggregates. The decrease of E in the temperature range from 500 to 550°C reflects the sample densification taking place in the labelled surface layers of the quartz sand. This may be promoted by the formation of the first nuclei of β-quartz [12]. The α–β quartz transition takes place in the whole volume of the sample in the temperature range from 550 to 573°C as indicated by classical DTA or DSC experiments on this sample. On further heating, the densification of the structure is reflected by the slow decrease in E up to the temperature where heat-induced radon diffusion takes place. This usually starts from a temperature of 0.5 T_{fus} which for the quartz sample is about 720°C.

The quartz sample was heated up to 1100°C and subsequently cooled to room temperature, the ETA curve being measured during sample cooling. From the ETA cooling curve, the radon diffusion characteristics of the heat-treated quartz sample can be estimated. As follows from the cooling curve, a change in the diffusion mechanism takes place at 430 ± 10°C. This phenomenon, which does not correspond to any transition of crystalline silica, will be investigated separately.

4.2. Quartz sample submitted to mechanical treatment (Fig. 2)

As mentioned above, a layer of highly defective silica to a depth of approximately 100 nm was produced by grinding the quartz. The layer labelled by recoiled radium atoms is at least 65 nm deep. Consequently, the amorphized silica layer produced by mechanical treatment on the quartz is almost totally labelled by the recoiled Ra and Rn atoms, and, moreover, the core of the crystalline quartz is not labelled.

The effect of water released from the sample surface and its intergranular spaces on the radon release is more pronounced with this ground quartz sample, due to the higher surface area and the increased defect concentration of the surface layer. The increased rate of radon release, observed in the temperature interval from 180 to 550°C, reflects (as in the case of the non-ground sample) the diffusion of radon in the intergranular spaces. The decrease of E starting at 550°C reflects the densification of the sample (as in the non-ground sample but the peak at about 573°C does not appear, which shows that the labelled surface of the ground sample is not yet affected by the α–β transition of quartz). However, the decrease is greater, indicating the increased reactivity to the densification of amorphous silica formed on the grain surface. The increase of E observed on further heating at 800°C is controlled by the heat-enhanced radon diffusion. It reflects a slightly different character of the thermal behaviour of this sample with respect to the original quartz sand. Now, in the temperature range from 800 to 1100°C, the thin, highly disturbed surface layer of the quartz grains may recrystallize [4]. This recrystallization phenomenon may be responsible for the discontinuity of the ETA curve between 940 and 990°C. After heating the sample to 1100°C, the ETA curve was measured during cooling (Fig. 2, curve 2). It is practically the same as the ETA cooling curve of the non-ground quartz sample from 1100 to 950°C (Fig. 1, curve 2),

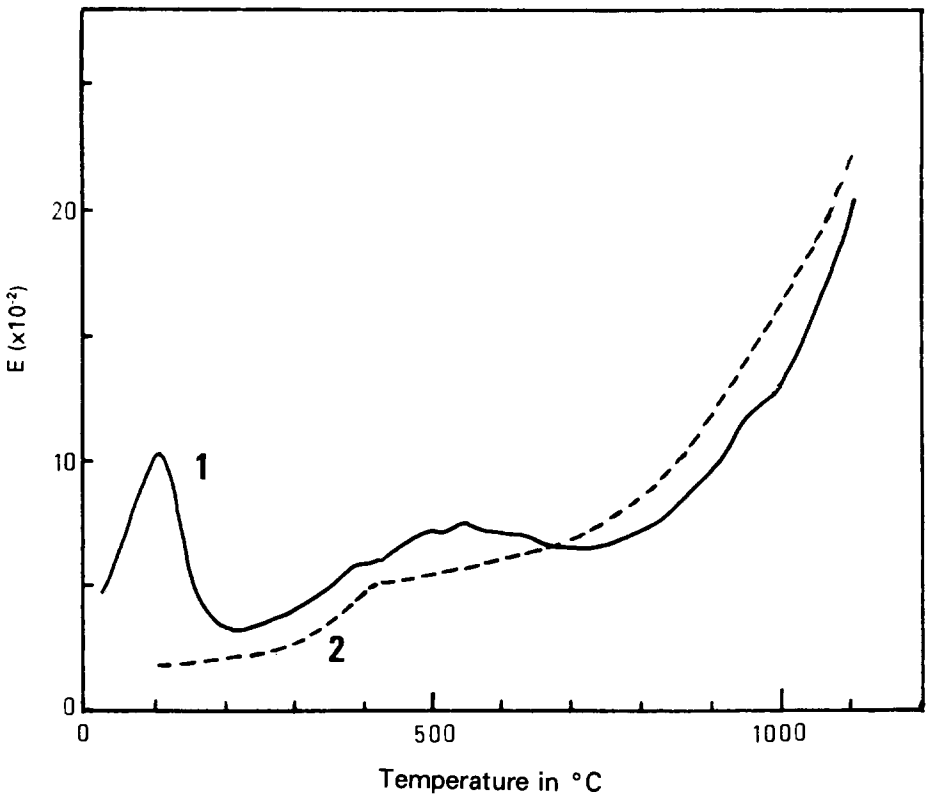

Fig. 2. ETA curves of quartz ground for 10 h, on heating (1) and cooling (2): E, radon release rate (arbitrary units).

which means that the recrystallization of amorphous silica to crystalline silica took place before the heating to 1100°C. The difference in the ETA heating and cooling curves observed in the temperature region 700–1100°C results from the changes in the diffusion properties of radon due to the presence of the highly disordered silica layer and its recrystallization before 1000°C.

However, this difference between the heating and cooling curves is not apparent on the curves of the unground sample, except perhaps above 970°C. Effectively, if a layer of highly disordered silica exists on the surface of the sample before grinding, its thickness is certainly lower than some nanometers and it was not detected by the sensitive dissolution technique previously used to investigate the role of grinding on the properties of quartz [7].

5. Conclusion

We have demonstrated that the radon tracer technique, emanation thermal analysis, makes it possible to reveal differences in the thermal behaviour of quartz sand before

and after its mechanical treatment by milling. The temperature dependences of the release rate of radon from the samples characterize the differences in the diffusion properties (permeability) of the highly disordered silica layer in the reactivity of the ground sample towards consolidation with respect to the original non-mechanically treated sample.

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