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Thermal release of water from natural quartz

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Abstract

A mass spectrometer was used to monitor the release of water from quartz samples heated to 1200°C in vacuum. Both hydrothermal quartz and granitic quartz show abundant fluid inclusion ruptures over the temperature range from 100°C to 550°C and, in most cases, a prominent water release at the quartz alpha-beta transition (573°C). Fluid inclusion ruptures above this stage are rare. High temperature water release from hydrothermal quartz is negligible, but it is greater (though more variable) for the quartz from granites. No water release can be related to the quartz-tridymite transition.

Introduction

Crystals of many nominally anhydrous minerals incorporate small quantities of water from the surrounding liquid as they grow. This water may be scattered through lattice sites (like other trace impurities), it may be in structural channels or holes, or localized along grain boundaries. However in many minerals most water is physically trapped within large crystal imperfections as fluid inclusions or melt inclusions (depending on whether crystal growth occurred in an aqueous medium or a silicate melt). When the host mineral is heated water may be lost from each type of location in different ways and at different temperatures. In this paper we report on the release of water from quartz samples over the temperature range from 25 to 1200°C but do not attempt to relate each water release to a specific site within the quartz. This study is the first step in a project to develop mass spectrometric techniques for analyzing gases in individual fluid inclusions in deep, late-stage diagenetic cements in sedimentary rocks. Such fluid inclusions provide a means for bringing deep gas samples to the surface without their loss or contamination.

Experimental procedure

Quartz samples weighing approximately 40 mg each were heated in stainless steel tubes attached to an all-metal vacuum system that formed the inlet to a UTI 100C mass spectrometer. Sample temperature was raised linearly at 10°C/min by a TECO TP-2000 linear temperature programmer and the evolved water and other volatiles flowed into the ion source of the mass spectrometer and were then pumped away by an oil diffusion pump. The mass spectrometer was tuned to $m/z = 18$, which is the major response for water, and the analog output displayed on a strip chart recorder as a function of temperature. The mass spectrometer response was quantified by introducing a known amount of water produced by the thermal decomposition of a weighted amount of calcium hydroxide. Blank runs showed that the water contributed by the system was insignificant compared to the water released by heated samples.

Character of water release

Quartz samples from a hydrothermal vein and several granites were analyzed. Water is released discontinuously from all of them. Up to about 150°C water evolution shows a smooth increase with rising temperature, probably due to desorption of adsorbed water. Finely-crushed samples with larger surface areas generally show increased amounts of adsorbed water. As temperature continues to rise the character of the water release changes and sharp bursts of water vapor are recorded over the range from about 150°C to 575°C or higher. Each burst gives an instantaneous rise in water vapor pressure followed by an exponential decay down to background values and appears to be produced by the rupture of an individual fluid inclusion. Some examples of large, isolated bursts are given in Figure 1. A detailed examination of the peaks using an analog-to-digital converter and a minicomputer with the mass spectrometer shows that for the geometry and pumping speed of this system they are about 0.25 seconds wide at half peak height.

Previous studies that used mass spectrometers to monitor gas evolution by scanning a range of mass numbers failed to record the very short bursts of gas (Barker and Sommer, 1974; Killingley and Muenow, 1975; Karzhavin, 1976; Knauth and Epstein, 1982). However bursts of carbon dioxide from rupturing inclusions in olivine heated to 1200°C were reported by Killingley and Muenow (1974), and water, carbon dioxide and sulfur gases were identified in the gases released from inclusions in basaltic

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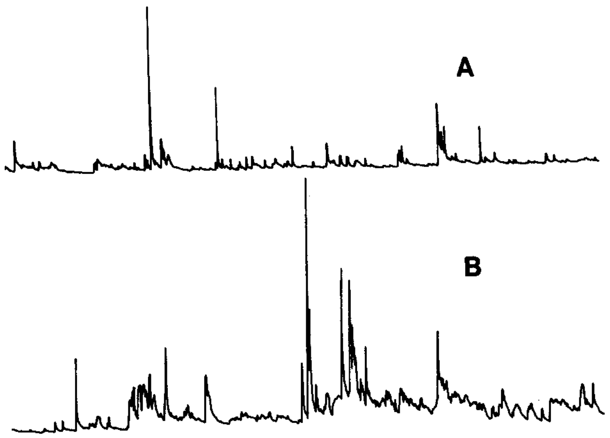

Fig. 1. Mass spectrometer response for water (arbitrary, linear vertical scale) as a function of linearly increasing temperature for a heated hydrothermal quartz. A: 360–410°C, B: 245–295°C.

glass and phenocrysts from basalts. Most bursts occurred above 1000°C (Delaney et al., 1978; Garcia et al., 1979). Coveney (1981) found that CO_2-rich inclusions in quartz associated with gold mineralization ruptured over the range from 180–190°C but no actual traces were given. Water was also identified in these bursts.

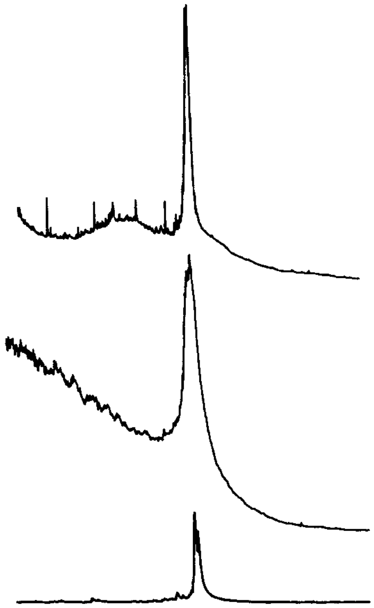

Fig. 2. Character of the water release from quartz over the temperature range from approximately 565 to 580°C. Samples were: top–quartz from Shap granite, England; middle–quartz from Arroyo Hondo granite, New Mexico; bottom–Hot Springs quartz, Arkansas.

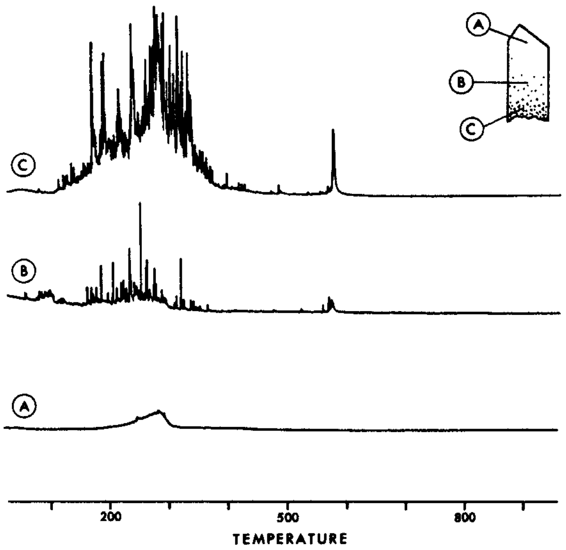

Fig. 3. Character of water release for samples taken from the clear tip (A), slightly cloudy center (B), and milky base (C) of a single Arkansas quartz crystal.

Many of the quartz samples released a significant amount of water at the alpha-beta transition. Selected examples are shown in Figure 2. It appears that the crystallographic readjustments induce fluid inclusion rupture so that in a general way the amount of water released at the alpha-beta transition reflects fluid inclusion abundance. The relative importance of the different water sources to the response observed at the quartz alpha-beta transition is unknown. Melenevskiy and Nikitina (1983)

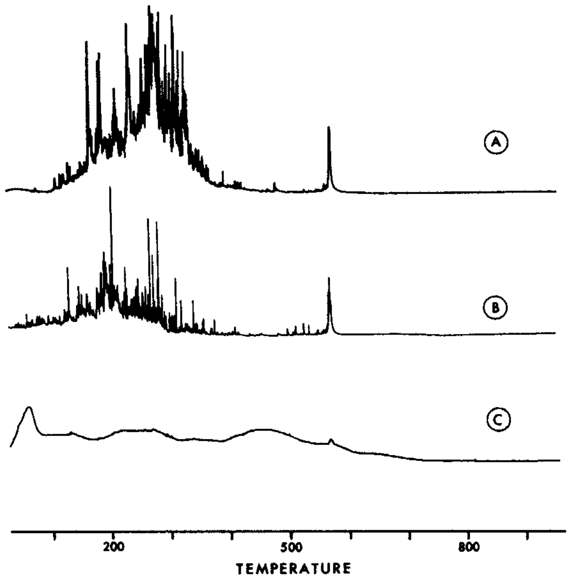

Fig. 4. Character of water release for Arkansas quartz samples with various grain sizes. In each case sample weight was 40 mg and the vertical scale the same. A–coarse (two pieces); B–approximately 40 mesh; C–ground to pass 20 mesh sieve.

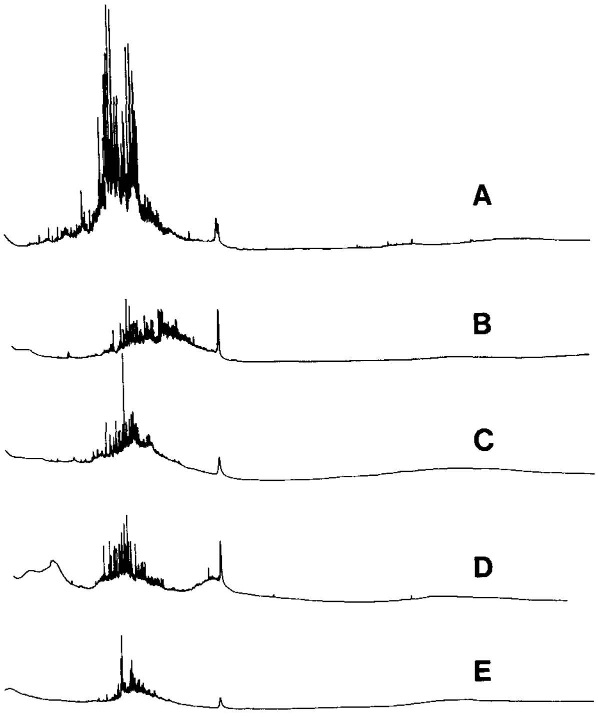

Fig. 5. Selected water release curves for quartz from granites. A–Dartmoor (Burrator), England. B–Dartmoor (Two Bridges), England. E–Rosalie granite, U.S.A. Temperature range in all cases is from 20°C to 975°C.

also reported water release at the quartz alpha-beta transition. In all samples fluid inclusion ruptures are common at temperatures below the transition but rare above it. The amount of water released at the alpha-beta transition was in the range from <0.01 to 0.04 mg H_20/g of quartz, and, for example, the cloudy base of an Arkansas quartz crystal (Fig. 2C) released 0.025 mg H_20/g of quartz. It is difficult to assign any particular water release to the quartz–tridymite transition because this phase change seems to be much more variable in temperature and to release water (if at all) over a wide temperature range. Much of the high temperature release of water from granitic quartz is continuous. This could be due either to diffusional loss of water or to rupturing of many small inclusions.

Hydrothermal quartz

The response shown in Figure 3C for quartz from Arkansas is typical of the water release from low temperature, hydrothermal quartz. Homogenization temperatures for fluid inclusions in the Arkansas quartz were found to range from 140°C to 180°C, with most clustering around 160–165°C. However, on heating in vacuum they rupture at temperatures from 100°C to over 300°C with a maximum around 230°C. The range of values is probably broadened by the presence of secondary fluid inclusions (possibly of several generations) (Leroy, 1979), and because inclusions are located at various depths below the surface and at differing distances from planes of weakness, such as fractures, so that they can therefore tolerate various degrees of overpressuring.

A single crystal of Arkansas quartz of dimensions 6 cm × 1 cm × 1 cm was selected for study because inclusions were very common in the cloudy base but diminished in abundance toward the clear tip. Samples removed from the base, middle section and tip gave the water release curves shown in Figure 3. Not surprisingly the number of inclusion ruptures recorded was very high for the cloudy base sample, and this piece of the crystal also showed the largest water release at the alpha-beta transition, and the inclusion ruptures were at somewhat higher temperatures. As expected crushing also diminishes the number of fluid inclusion ruptures observed and essentially none were recorded for a sample crushed to pass a 200 mesh sieve (Fig. 4). Decreased grain size also leads to a smaller alpha-beta peak and enhances amounts of adsorbed water due to the increased surface area per unit mass.

Quartz from granites

The water release curves for quartz from granite resemble those for hydrothermal quartz in showing evidence for rupturing fluid inclusions at low temperatures. They also show prominent water release peaks at the alpha-beta transitions at 573°C, and because granites crystallize above this temperature this suggests that growth temperature is not a factor influencing water release at this crystallographic transition. Granitic quartz also differs from the hydrothermal quartz in that quartz from granite shows significant water evolution at higher temperatures, and this often continues up to the 1200° limit used in the experiments (Fig. 5). The character of this high temperature release varied somewhat from one rock to another. A few samples showed some fluid inclusion ruptures but most showed either a rather smooth water release or a somewhat "hummocky" trace. This may possibly have been produced by release of water from rupturing small silicate melt inclusions (although none were observed by microscopic examination).

Acknowledgments

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