FLUID INCLUSION RE-EQUILIBRATION EXPERIMENTS IN QUARTZ: CHEMICAL POTENTIAL GRADIENTS

BAKKER, R. J.[1], DIAMOND, L. W. [2]

[1] Institute of Geosciences, Mineralogy & Petrology, University Leoben, Austria.

[2] Institute of Geological Sciences, University of Bern, Switzerland.

E-mail: diamond@geo.unibe.ch

The post-entrapment behaviour of fluid inclusions during changing $P–T–f_{fluid}$ conditions in the host rock is still a matter of discussion. So far, only little evidence has been presented from natural samples, although post-entrapment changes are invoked in many studies to explain inconsistent results obtained by petrologic and other methods. Experimental studies over the last decade have not been conclusive and, in part, they are even contradictory. The objective of this study is to continue a series of experiments with synthetic H_2O-CO_2 fluid inclusions in natural quartz to examine the effect of pressure gradients and chemical potential gradients on the bulk fluid-inclusion properties (Bakker & Diamond, 1998 and 1999).

Experimental method

Fluid inclusions were synthesised in natural, pre-fractured quartz according to the method of Bodnar & Sterner (1987). Silver-oxalate and distilled water were used to produce an H_2O-CO_2-rich mixture of 30 mol % CO_2. The syntheses were conducted at 600 °C and 500 MPa for 29 days, within the □-quartz stability field. In order to prevent any pressure differentials, the experimental capsules were brought to the $P–T$ conditions of synthesis and retrieved from these conditions by following the $P–T$ path of the relevant fluid isochore. The locations of about 100 inclusions were precisely documented and then analysed for the following properties: $T_m(CO_2)$, T_m(clathrate), $T_h(CO_2)$, T_h(total), size, distance to quartz surface, and area-ratio of phases at room temperature. The sample was then loaded into an open gold capsule and set under the same experimental $P–T$, again by following the pertinent isochore. Consequently, the argon pressure medium was in direct contact with the quartz surface. A chemical potential gradient in H_2O, CO_2 and Ar was maintained for 27 days between the inclusions and the surrounding pressure medium, at equal internal and external pressures. After termination of the re-equilibration experiments the same inclusions were examined again and characterised according to the previously mentioned properties.

Results

First, the re-equilibrated inclusions modified their morphology by attaining more perfect negative-crystal shapes (Fig. 1). However, the area ratio of vapour/liquid did not change significantly. The changes in microthermometric behaviour are illustrated in Fig.2. $T_m(CO_2)$ of all inclusion has shifted to slightly lower temperatures, approximately -56.8 °C. $T_h(CO_2)$ increased between 1 and 4 degrees. T_m(clathrate) decreased by various amounts to temperatures as low as 4.3 °C, always in the presence of water, liquid CO_2 and CO_2 vapour (Q_2 phase assemblage). The total homogenisation temperature increased significantly (up to >380 °C). The inclusions were analysed by micro-Raman spectroscopy but no gases other than H_2O and CO_2 could be detected.
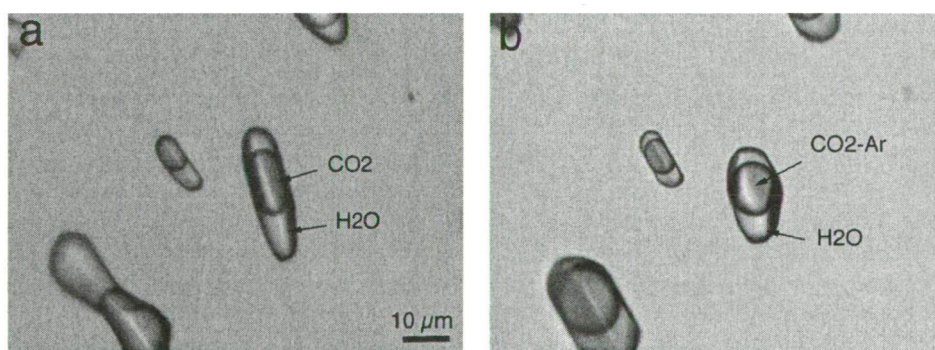
Fig.1. Photomicrograph of several fluid inclusion in quartz, after synthesis (a) and after re-equilibration (b).

Special cases

Some of the inclusions decrepitated during the total homogenisation measurements following the initial syntheses. These inclusions became dark and apparently lost all their H_2O, leaving low-density CO_2 fluid inclusions. All the other inclusions that had not decrepitated were checked for stretching by monitoring changes in $T_h(CO_2)$. After the re-equilibration experiments most of the decrepitated inclusions had completely disappeared. The quartz crystal was completely restored without any trace of the previously present inclusions. A small proportion of the decrepitated inclusions were filled again with a substantial amount of H_2O, which in some cases even exceeded the H_2O/CO_2 ratio in the original fluid composition. These examples suggest that H_2O did not leave the quartz crystal upon decrepitation of the inclusions, but remained present, probably in thin films in micro-cracks or channels (such as dislocations).
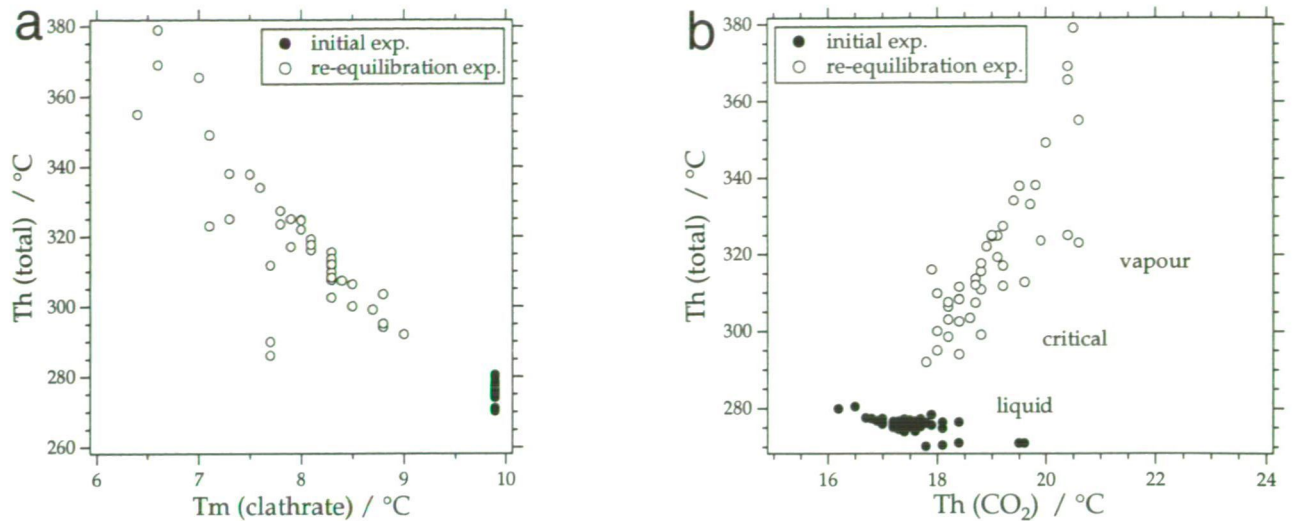
Fig.2. Microthermometric results of initial syntheses and re-equilibration of fluid inclusions. Clathrate melting occurs at Q_2 conditions (a). Inclusions from the initial synthesis homogenise to the liquid phase (LV□L) (a and b). After re-equilibration most of the inclusions homogenise to the vapour phase (LV□V). Partial homogenisation of the CO_2-rich phases (b) is always to the liquid (L_{CO_2}V□L_{CO_2}).

Discussion and conclusions

As no Raman-active gases were detected in the fluid inclusions other than CO_2 and H_2O, we attribute the large observed changed in T_m(clathrate) and $T_m(CO_2)$ to diffusion of argon (which is not Raman active) into the inclusions from the pressure medium of the re-equilibration experiments. Argon is known to enter into a clathrate solid-solution with CO_2, and for low Ar concentrations, this solid-solution is thermally less stable than pure CO_2 clathrate. The large increase in T_h(total) is also consistent with admixture of volatile Ar. Diffusion of argon through quartz into fluid inclusions appears to be effective at 600 °C and 500 MPa under the high imposed fugacity gradient of the present experiments. The possibility of Ar diffusion was apparently overlooked in previous re-equilibration experiments (e.g. Sterner et al., 1995), but it may explain some of the conflicting results in the literature. Owing to the masking effects of diffusing Ar, the mobility of H_2O and CO_2 cannot be evaluated conclusively from our experimental set-up. However, the change in mode of total homogenisation, from LV□L in the initial syntheses to LV□V following re-equilibration, may indicate a decrease in bulk density. Our size measurements show that the total volume of the inclusions did not change significantly upon re-equilibration. Therefore, if Ar diffuses into the inclusions, a decrease in density can only be obtained if H_2O and/or CO_2 diffuse out of the inclusions (as expected from the imposed fugacity gradients). Future experiments in a pure H_2O environment and a pure CO_2 environment will give information of the effectiveness of H_2O and/or CO_2 diffusion through quartz as a consequence of chemical potential gradients at equal pressures.

References

BAKKER, R. J., DIAMOND, L. W. (1998) Reequilibration of synthetic CO_2-H_2O fluid inclusions in quartz (abst.) PACROFI VII (Las Vegas), Programs and Abstracts, 10.

BAKKER, R. J., DIAMOND, L. W. (1999) Reequilibration of synthetic CO_2-H_2O fluid inclusions in quartz : isofugacity experiments (abst.) ECROFI XV (Potsdam), Terra Nostra, **99/6**, 20-21.

BODNAR, R. J., STERNER, S. M. (1987) Synthetic Fluid Inclusions. In G. C. Ulmer & H. L. Barnes (eds.): Hydrothermal experimental techniques. John Wiley & Sons, Inc., New York, 423-457.

STERNER, S. M., HALL, D. L., KEPPLER, H. (1995) Compositional re-equilibration of fluid inclusions in quartz. Contribution to Mineralogy and Petrology, **19**, 1-15.