

A method to synthesize large fluid inclusions in quartz at controlled times and under unfavorable growth conditions

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ABSTRACT

A new synthesis technique allows large fluid inclusions to be produced at conditions under which one normally would obtain only small inclusions, with the additional advantage that the timing of fluid entrapment can be controlled. In the first step, primary fluid inclusions are grown at *P-T* conditions under which it is relatively easy to produce large inclusions. In the second step, which can be performed either during the same experiment or during a separate experiment after a desired time of pre-equilibration, some of the primary inclusions produced during the first step are re-opened by in-situ fracturing, causing partial replacement of the inclusion content. The sample is then left at high pressure and temperature until the cracks leading to the re-opened inclusions are healed. To test the method and quantify the efficiency of fluid replacement in the re-opened inclusions, we produced primary inclusions at 700 °C/200 MPa and re-opened them during a second experiment in the presence of a compositionally different fluid at 500 °C/70 MPa. Laser-ablation ICP-MS (LA-ICP-MS) analyses of eight primary and 11 refilled inclusions demonstrate that in the latter more than 97% of the original fluid was replaced by new fluid. Thus, the refilled inclusions are representative of the surrounding fluid at the time of in situ fracturing.

Keywords: Synthetic fluid inclusions, experimental technique, LA-ICP-MS, H₂O-salt

INTRODUCTION

Synthetic fluid inclusions in quartz have been used extensively to study phase relations and *P-V-T-X* properties of fluids at high pressure and temperature (e.g., Sterner and Bodnar 1984, 1991; Bodnar and Sterner 1985, 1987; Bodnar et al. 1985; Diamond 1992; Lamb et al. 1996, 2002). In fact, most of our knowledge about the *P-V-T-X* properties of fluids at >500 °C has been gained from such studies. Synthetic fluid inclusions have also been used to gain information about element solubility and speciation in magmatic-hydrothermal fluids (e.g., Ballhaus et al. 1994; Loucks and Mavrogenes 1999; Hanley et al. 2005; Berry et al. 2006; Hack and Mavrogenes 2006; Duc-Tin et al. 2007; Simon et al. 2007a, 2007b; Spandler et al. 2007; Evans et al. 2007; Ulrich et al. 2008), and to study element partitioning in two-phase fluid systems (e.g., Simon et al. 2005, 2006, 2008; Nagaseki and Hayashi 2008). Since the advent of laser-ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS), which combines high-analytical sensitivity with fast measuring time and simple quantification procedure (e.g., Günther et al. 1998; Heinrich et al. 2003), the number of solubility and partitioning studies has increased dramatically. Limitations are set by the inclusion size (if the inclusions are too small the required detection limits may not be reached), and by the fact that fluid may be trapped before it has reached equilibrium with respect to all components of the system. The latter problem has been addressed by Sterner (1992), who modified the original technique described in Sterner and Bodnar (1984) in such a way that the cracks used for fluid entrapment can be generated at a specific

time during the experiment by in situ fracturing. However, both the original method of Sterner and Bodnar (1984) and the in situ fracturing technique of Sterner (1992) have the disadvantage that the resulting fluid inclusions are relatively small in experiments performed at conditions of low quartz solubility (typically <20 µm if their volume is recalculated to a spherical shape). This is not a problem for studies dealing with *P-V-T-X* properties because microthermometric and Raman spectroscopic measurements can be performed easily on inclusions of this size. For LA-ICP-MS analyses, however, larger inclusions are required for the detection of element concentrations in the parts per million range in fluids of low density and salinity—even with optimized sensitivity (e.g., Guillong and Heinrich 2007). Large (>50 µm diameter) fluid inclusions have been produced by using quartz pieces with laser-drilled holes (Loucks and Mavrogenes 1999) or by using etched-quartz pieces as a starting material (Duc-Tin et al. 2007). However, both of these techniques have the disadvantage that they do not allow for the controlled timing of fluid entrapment, which can lead to systematic errors in experiments that require long equilibration times (e.g., Duc-Tin et al. 2007). Here, we describe a technique that combines the advantage of the etched-plate technique with that of the in situ fracturing technique, by using a two-stage synthesis approach in which large fluid inclusions are produced during a first step, and then re-opened and refilled with new fluid during a second step.

EXPERIMENTAL METHODS

The principle of the approach is illustrated in Figure 1 and can be described as follows. In the first step, numerous large, primary fluid inclusions are produced at high temperature and pressure by growing a layer of new quartz over an etched-quartz substrate. In the second step, which can be performed either during the same

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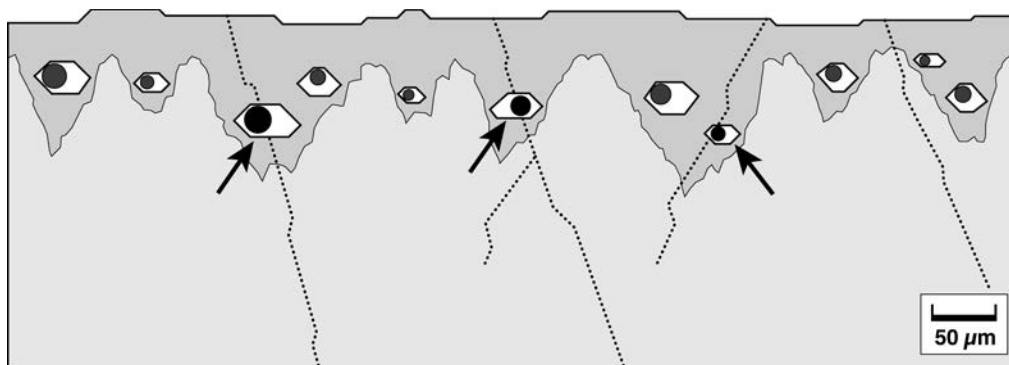


FIGURE 1. Schematic cross-section through the uppermost 0.3 mm of a quartz piece recovered from the second experiment. Light gray color shows the etched quartz before it was used in the first experiment. Dark gray color represents quartz that grew over the etched substrate during the first experiment, leading to the entrapment of large, primary fluid inclusions in former etch channels. Dotted lines represent cracks that were generated by in situ fracturing during the second experiment and subsequently healed to form planes of small, secondary inclusions. At each location where such a crack intersected a primary inclusion (arrows) the original fluid content was replaced by new fluid.

experiment as the first step or later in a separate experiment, some of these primary inclusions are re-opened by in situ fracturing. This is achieved by allowing the Au capsule to drop from the hot end of the vertical autoclave to the water-cooled end such that the Au capsule is quickly quenched (Matthews et al. 2003). This action causes numerous cracks to develop in the quartz piece due to thermal stress. At each location where a crack intersects a primary fluid inclusion, its original fluid content is replaced by new fluid. The capsule is then moved back to the hot end of the autoclave again, where the fluid in the re-opened inclusions can further equilibrate with the surrounding fluid until the fractures are healed. In the following, we describe a feasibility test that was conducted in two separate experiments, the second of which was performed at conditions under which one would get only small inclusions by using standard synthesis techniques.

Oriented quartz pieces measuring $3 \times 3 \times 6$ mm were cut from inclusion-free, natural quartz such that their longest dimension was parallel to the c-axis of the quartz crystal. By using a rough blade for the cutting and then treating the quartz pieces for 1 h in concentrated hydrofluoric acid, a rough surface consisting of deep, narrow etch channels was produced. In the first experiment, two etched quartz pieces were loaded into a gold capsule (4 cm length, 5.0 mm outer diameter, 4.6 mm inner diameter) together with 0.05 g of silica glass and 100 μ L of an aqueous solution containing 10 wt% NaCl solution and ~ 1000 ppm Rb, Cs, Sr, Mn (Table 1). The Au capsule was then arc welded shut and left in the oven at 150 $^{\circ}$ C for 24 h to check for leaks. Subsequently, the Au capsule was loaded into a rapid quench vertical autoclave of the design described in Matthews et al. (2003), using water as the pressure medium. This design allows for the Au capsule to be held in the hot end of the vertical autoclave by a magnetic clip at the end of the capsule holder, which itself is held in place by an external magnet. During quench, the magnet is dropped down to the base of the extended autoclave allowing for the capsule holder to drop down as well such that the Au capsule is now located in the water cooled region of the autoclave allowing for rapid quench within a few seconds. Experimental run conditions were reached by first raising the pressure to 200 MPa, and then raising the temperature isobarically to 700 $^{\circ}$ C. These conditions plot 80 MPa above the limit of the fluid immiscibility field in the system H_2O -NaCl at 700 $^{\circ}$ C (Bodnar et al. 1985), ensuring that the fluid was single-phase. Overall uncertainties in the recorded pressures and temperatures are about 3 MPa and 10 $^{\circ}$ C, respectively. The sample was held at these P - T conditions for three days, and then the autoclave was removed from the furnace and allowed to cool to room temperature within about 30 min. During cooling, the pressure inside the autoclave followed an isochoric path defined by the volume of the autoclave plus that of the pressure line.

In the second experiment, the quartz pieces recovered from the first experiment were loaded together with silica glass and a solution of 10 wt% KCl and ~ 1000 ppm Ba into a new Au capsule, and heated in the same autoclave isobarically to 500 $^{\circ}$ C/70 MPa. These P - T conditions plot slightly below the fluid isochore defined by the conditions of the first experiment, resulting in ~ 14 MPa overpressure in the primary fluid inclusions. The conditions of 500 $^{\circ}$ C/70 MPa plot 10 MPa above the limit of the two-phase field in the H_2O -KCl system at 500 $^{\circ}$ C (Liebscher 2007), again ensuring that the fluid was single phase. Twenty-four hours after the start of the second experiment the capsule was dragged rapidly to the cold end of the

TABLE 1. Overview of run conditions and compositions of starting solutions

	Starting solution	T ($^{\circ}$ C)	P (MPa)	ρ (g/cm 3)
1st experiment	9.54 wt% NaCl; 958 ppm Rb; 944 ppm Sr; 963 ppm Cs; 948 ppm Mn	700	200	0.63
2nd experiment	9.60 wt% KCl; 1038 ppm Ba	500	70	$\sim 0.60^*$

* Estimated based on the system H_2O -NaCl.

autoclave and left there for about 30 s. Subsequently, the capsule was moved back to the hot end of the autoclave and left there for another three days such that the cracks generated by in situ fracturing could heal. The autoclave was then removed from the furnace and the Au capsule allowed to cool isochorically to room temperature within about 30 min.

Quartz pieces recovered from the second experiment were gently polished to remove excess quartz on the sample surface. Individual fluid inclusions were analyzed by LA-ICP-MS at the Bayerisches Geoinstitut, using a Geolas M 193 nm ArF Excimer laser (Coherent/Lambda Physik) attached to an Elan DRC-e quadrupole mass spectrometer (Perkin Elmer Instruments). The laser was operated at a frequency of 10 Hz and an output energy of 80 mJ, which resulted in an energy density of ~ 10 J/cm 2 at the sample surface. The sample chamber was flushed by using helium gas at a rate of 1 L/min. Measured isotopes were ^{23}Na , ^{29}Si , ^{39}K , ^{55}Mn , ^{85}Rb , ^{88}Sr , ^{133}Cs , and ^{137}Ba , using 10 ms dwell time per isotope. We used NIST SRM 610 glass as external standard and the concentrations of Na and K in the starting solutions as internal standard for primary and refilled inclusions, respectively. Ablation of NIST SRM 610 glass using a laser pit of 50 μ m and a repetition rate of 10 Hz indicated an oxide rate of 0.08% (based on ThO), a rate of doubly charged ions of 0.06% (based on ^{42}Ca vs. ^{21}Ne), and a U/Th signal intensity ratio of 1.007 (see Günther and Hattendorf 2005, for discussion about these parameters). Overall uncertainties are about 10–20% relative for elements well above the detection limit, but may be higher for elements close to the detection limit (Heinrich et al. 2003). More details about the instrument and the quantification procedure can be found in Günther et al. (1998) and Heinrich et al. (2003).

RESULTS AND DISCUSSION

Quartz pieces recovered from the second experiment contained ~ 10 – 20 healed cracks that cut through about twice as many fluid inclusions. Most fluid inclusions (both primary and refilled ones) measured 20–40 μ m in diameter, with some reaching sizes of 100 μ m (Fig. 2). Because the salinity and density of the fluid in the second experiment was similar to that of the first experiment,

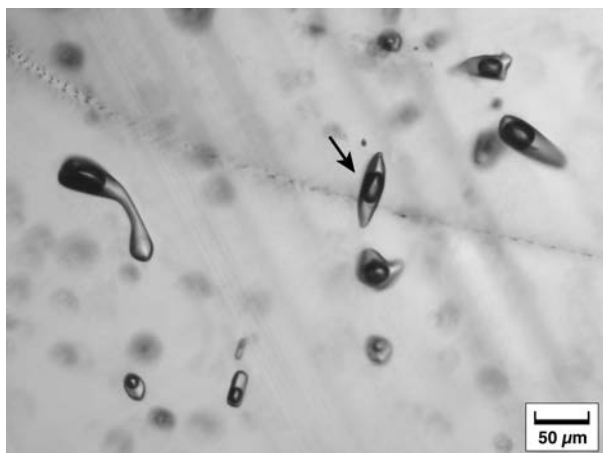


FIGURE 2. Photomicrograph of a sample after the second experiment showing several primary inclusions and one that was re-opened by in-situ fracturing during the second experiment. Note the small size of fluid inclusions generated by simple crack healing (transmitted light).

refilled inclusions can be distinguished optically from primary inclusions only by the fact that the former are intersected by cracks (Fig. 2). There is no evidence that the 14 MPa overpressure in the primary inclusions during the second experiment caused them to decrepitate, as they contain only components of the first solution (see below) and are not surrounded by cracks or halos of secondary inclusions (Fig. 2). In principle, primary fluid inclusions could also be re-opened by a large pressure drop instead of thermal quenching (e.g., Sterner and Bodnar 1989; Vityk and Bodnar 1995). However, decrepitation of fluid inclusions due to overpressure commonly results in fractures that are so thin that they seal immediately, allowing only fluid to move out, but no new fluid to move in. Furthermore, pressure drops are likely to result in fluid immiscibility if the run conditions are close to the solvus. Thermal quenching is thus preferable to pressure quenching for the application described here.

Eight primary and 11 refilled fluid inclusions were analyzed by LA-ICP-MS. Typical signals of both inclusion types are shown in Figure 3, and compositional data are listed in Table 2. Primary inclusions contain only Na, Rb, Sr, Cs, and Mn, but no detectable K and Ba (Table 2; Fig. 3a). Average concentrations of Rb, Sr, and Cs in these inclusions, calculated based on 3.72 wt% Na as internal standard, are 9–13% lower than their original concentrations in the starting solution, and in the case of Mn there is up to 81% missing. The latter element probably was lost to the gold capsule, since gold can take up ~11 wt% Mn at 700 °C (Predel 1991). The reason for the apparent loss of Rb, Sr, and Cs is not clear.

Refilled inclusions are dominated by K and Ba, but smaller amounts of Na, Cs, Rb, and Sr are detectable as well (Fig. 3b), suggesting that the original fluid content of these inclusions was not fully replaced by the new fluid. Efficiencies of fluid replacement, calculated based on K as the internal standard and either Cs, Rb, Sr, or Na as a measure of the remaining amount of original fluid, are shown graphically in Figure 4. Interestingly, replacement efficiencies, calculated based on Cs, Rb, and Sr,

TABLE 2. LA-ICP-MS analyses of primary and refilled fluid inclusions

Inclusion type	Size (μm)	Na (ppm)	K (ppm)	Mn (ppm)	Rb (ppm)	Sr (ppm)	Cs (ppm)	Ba (ppm)
Primary	40	37160*	<1800	570	860	910	880	<52
Primary	35	37160*	<2400	840	880	930	830	<44
Primary	30	37160*	<690	210	880	930	850	<14
Primary	40	37160*	<1900	690	800	890	740	<26
Primary	35	37160*	<990	670	870	930	880	<18
Primary	50	37160*	<480	180	800	730	800	<10
Primary	30	37160*	<2600	600	820	840	810	<65
Primary	40	37160*	<540	560	960	750	920	<11
Refilled	30	1220	50340*	<19	13	16	10	840
Refilled	35	762	50340*	<34	8	7	5	950
Refilled	40	1140	50340*	<14	14	18	12	970
Refilled	45	490	50340*	<9	7	6	6	890
Refilled	35	880	50340*	<24	7	6	7	940
Refilled	50	1490	50340*	<25	7	6	7	840
Refilled	30	580	50340*	<16	7	6	6	970
Refilled	35	1660	50340*	<28	19	18	16	830
Refilled	40	700	50340*	<18	10	7	7	980
Refilled	35	700	50340*	<10	10	9	8	800
Refilled	35	1420	50340*	<27	<8	7	7	860

* Internal standard.

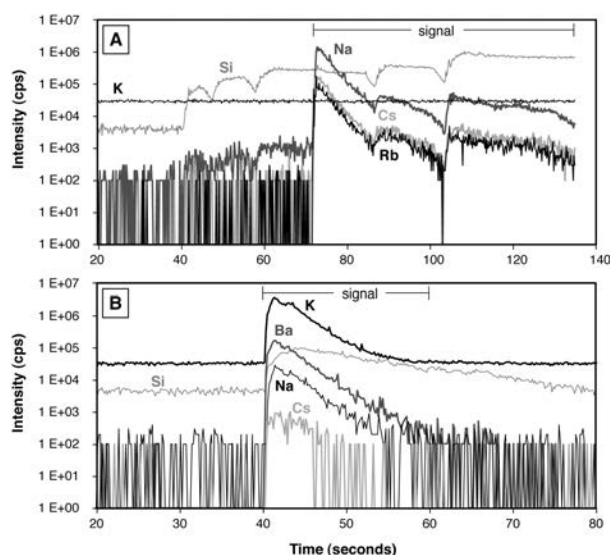


FIGURE 3. (a) LA-ICP-MS signal of an unopened, primary inclusion; (b) LA-ICP-MS signal of a refilled inclusion. Note the presence of Na and Cs in the refilled inclusion, suggesting that not all of the original fluid was replaced during the refilling. The concentrations of Cs, Rb, and Sr in this inclusion imply a replacement efficiency of 99.2–99.4%.

are in relative good agreement with each other, whereas those calculated based on Na are significantly higher and less systematic. Weight fractions of residual fluid calculated based on Na are 80–430% (relative) higher than those calculated based on Cs, Rb, and Sr, which is far higher than the 9–13% difference caused by the partial loss of Cs, Rb, and Sr during the first experiment. We interpret this observation as evidence for Na migration into the refilled inclusions after they became sealed, with the Na originating from nearby primary inclusions. Sodium and other elements with small ionic radii that fit into interstices in the quartz lattice (i.e., H^+ , Li^+ , Ag^+ , Cu^+) are very mobile in quartz at magmatic and hydrothermal conditions, displaying a diffusion coefficient similar to that of diffusion in liquids (Verhoogen 1952; Rybach and Laves 1967; Frischat 1970; Kamenetsky and Danyushevsky

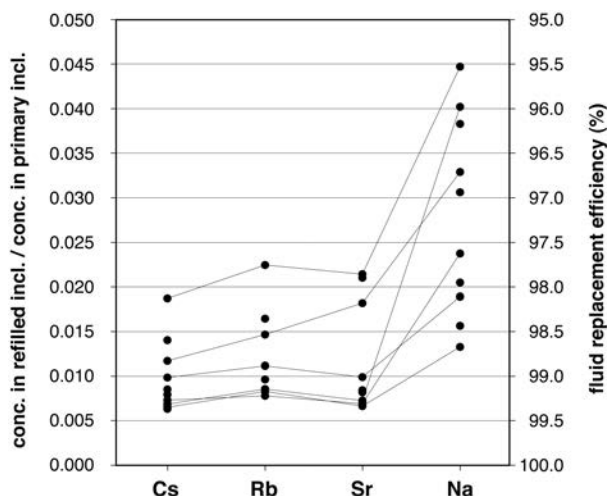


FIGURE 4. Concentration of Cs, Rb, Sr, and Na in refilled inclusions normalized to the average concentration of these elements in primary inclusions. The vertical scale on the right indicates corresponding fluid replacement efficiencies in weight percent. Notice that replacement efficiencies calculated based on Cs, Rb and Sr agree well with each other, whereas those calculated based on Na are higher and less systematic.

2005; Zajacz et al. 2008). It was demonstrated experimentally that silicate melt inclusions in quartz can lose more than 90% of their Na content if equilibrated for 1–3 days at 710 °C in a Na-free, aqueous fluid, and that originally Na-deficient melt inclusions can gain the same amount of Na during the same time period (Zajacz et al. 2008). Thus, it is not surprising if small amounts of Na diffused from primary into refilled inclusions during the three days at which the sample was held at 500 °C following in situ fracturing. We conclude that the concentrations of Cs, Rb, and Sr in the refilled inclusions are probably more representative of the calculated degree of fluid replacement than the concentration of Na. Consequently, the data in Figure 4 suggest that all re-opened inclusions were filled to >97.5% by new fluid, and that in eight out of the 11 inclusions the efficiency of fluid replacement was ≥99%. Possibly, the degree of fluid replacement could have been raised even more by cycling the capsule several times between the hot and the cold end of the autoclave, but this option was not explored in this study.

Generally speaking, the efficiency of fluid replacement was very high, implying that the refilled inclusions are a good representative of the surrounding fluid at the time of in situ fracturing. The amount of residual fluid from the first experiment is so small that it does not have a significant effect on the density and microthermometric behavior of these inclusions. With respect to LA-ICP-MS analyses, any contribution from the remaining fluid can easily be subtracted mathematically. Caution needs to be exercised in experiments in which the thermal quenching could result in the precipitation of dissolved species. Although elements which precipitate rapidly should also re-dissolve rapidly once the sample is brought back to run conditions (Stern 1992), one should verify that the fractures did not heal before the fluid re-attained equilibrium with respect to all solids.

The main advantages of this technique are threefold: (1) it allows large fluid inclusions to be synthesized at conditions under

which one would get only small inclusions utilizing standard techniques; (2) the timing of fluid entrapment can be controlled (i.e., it is possible to wait until equilibrium is attained before the entrapment of the fluid is initiated); and (3) the inclusions are arranged on a single plane, which greatly facilitates sample preparation for subsequent analysis. The two-stage synthesis approach can be applied either during a single experiment if one would like to take advantage of the controlled timing of fluid entrapment, or it can be applied in two separate experiments if the *P-T-X* conditions of the second experiment do not allow large enough fluid inclusions to be produced by other means.

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