

Synthetic fluid inclusions as recorders of microfracture healing and overgrowth formation rates

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ABSTRACT

Aqueous fluid inclusions have been synthesized within fluorite microfractures ($T = 200\text{ }^{\circ}\text{C}$, $P = P_{\text{sat}}$, $t < 30$ days), quartz microfractures, and quartz overgrowths ($T = 400$ to $300\text{ }^{\circ}\text{C}$, $P = 400$ bars, $t < 20$ days). The experiments were designed to determine the time necessary to form the inclusions, within a minute in a fluorite host, and within a day in a quartz host. The results permit estimation of the time needed to heal microfractures or create overgrowths, which is accomplished by measuring the melting temperature (T_m) of the inclusions in fluorite and the homogenization temperature (T_h) of the inclusions in quartz.

For the fluorite experiments, the results show that fluorite/ NH_4Cl solution equilibrium took 82 hours. Moreover, the healing process appears to be an irregular process along the microfracture. Fluorite experiments mimic boiling processes occurring in natural hydrothermal or epithermal systems and show how a boiling fluid may be progressively salted during vaporization and trapped as fluid inclusions.

For the experiments involving quartz, the quartz/ H_2O - NaCl solution equilibrium was reached on the first day for synthetic quartz and on the sixth day for natural quartz. This difference is linked to the hydration state of the two types of quartz. The decrease in T_h of synthetic fluid inclusions from the core-overgrowth boundary to the external part of the quartz overgrowth shows that the growth of quartz is a progressive and protracted process, which involves a silica oversaturated solution.

INTRODUCTION

Fluid inclusions are often used to delineate diagenetic events (i.e., mineral growth, the healing of microfractures) in time and space. Nevertheless, natural case studies often show poor control on timing of inclusion formation, especially if the inclusions have been reequilibrated, re-filled, or necked-down (Teinturier et al. 2002). The amount of time needed to form fluid inclusions is mainly related to the pressure and temperature of the system, but is also controlled by the fluid chemistry, the dimensions of the crack, and the cementation rates of the host mineral (Brantley 1992). Previously, crack sealing in fluorite crystals was documented in the H_2O - NaCl - CH_4 system over four weeks at a constant temperature of $200\text{ }^{\circ}\text{C}$ (Dubessy et al. 2000). For quartz, crack-healing experiments have been documented at 200 – $600\text{ }^{\circ}\text{C}$ and at vapor pressures up to 2 kbar (Smith and Evans 1984; Brantley 1992; Sawaki et al. 1997; Guillaume et al. 2003). Sawaki et al. (1997) showed that it took several hours to synthesize a small number of inclusions with a pH 13 solution at $300\text{ }^{\circ}\text{C}$ and four days at $200\text{ }^{\circ}\text{C}$ under saturated vapor pressures. With pure water and neutral pH conditions, it takes two weeks to synthesize smaller inclusions in quartz around $300\text{ }^{\circ}\text{C}$ and saturated vapor pressures (Sawaki et al. 1997).

In this paper we aim to study fluid inclusion formation under laboratory conditions, both in fluorite microfractures ($T = 200\text{ }^{\circ}\text{C}$, $P = P_{\text{sat}}$, $t < 30$ days) in the NH_4Cl - H_2O system, and in quartz microfractures and quartz overgrowths ($T = 400$ to $300\text{ }^{\circ}\text{C}$, $P = 400$ bars, $t < 20$ days) in the NaCl - H_2O system. The fluorite experiments were conducted under constant P - T conditions and during a progressive decrease in salinity accomplished by induced leakage, whereas the quartz experiments were carried out at constant pressure by decreasing the temperature by $10\text{ }^{\circ}\text{C}/\text{day}$. Petrographic observations coupled to microthermometric data allowed us to acquire temporal and spatial information about inclusion sealing within the fluorite microfractures and within quartz microfractures and quartz overgrowths. The experimental and analytical procedures described here should allow dating of fluid inclusion formation, which can aid in determining mineral growth kinetics.

EXPERIMENTAL PROCEDURE

Fluorite crystals (SOREM) were thermally fractured by immersing heated crystals in cold water. The quartz experiments were conducted using natural Brazilian quartz fragments ($< 1\text{ cm}$) and synthetic quartz (1 cm in length with a square section of 0.3 mm), which were cut perpendicular to the c axis. Prior to synthesis, samples were heated to $700\text{ }^{\circ}\text{C}$ to eliminate pre-existing inclusions. Quartz was then thermally fractured as above and dried for six hours at $80\text{ }^{\circ}\text{C}$.

Fluorite experiments were carried out in a 150 cm^3 gas-pressure autoclave (Autoclave Engineer), while maintaining equilibrium between liquid and vapor at experimental conditions (Fig. 1). Under these conditions, the homogenization temperatures (T_h) of resulting inclusions are equal to the trapping temperature of the fluid inside the inclusion.

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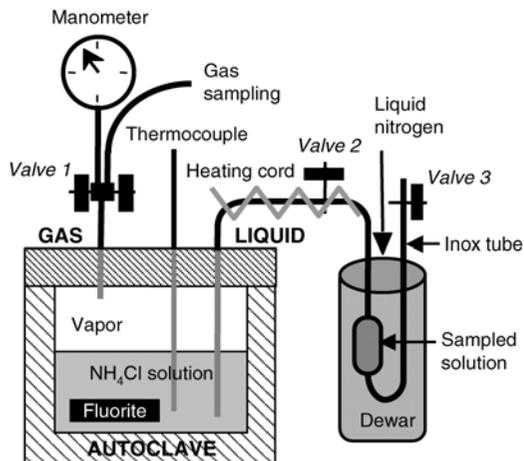


FIGURE 1. Fluorite experiment apparatus. A cold trap is adapted to the end of an Innox tube, which is fixed to the sampling valve (valve 2) of the autoclave. Fluorite crystals and the NH_4Cl solution are heated to 200°C . Solutions are extracted from the sample port (valve 2) of the autoclave at different times, then trapped in the Innox tube and frozen using a liquid nitrogen dewar. The temperature of the tube and the sampling valve (valve 2) is maintained at the autoclave temperature (200°C) by a heating cord. The temperature of the trap is the temperature of the liquid nitrogen and is used to freeze the solution and avoid any vaporization of the sampled solution.

The fluorite crystals and the NH_4Cl - H_2O solution (18 g/l NH_4) were enclosed in an autoclave. The vessel attained a regulated temperature of 200°C within a few hours. The duration of the experiments was 720 hours. The autoclave was purposely allowed to leak slowly, which resulted in a linear increase in the NH_4Cl concentration of the solution with time.

About 1–3 mL of solution was collected during each sampling period (1, 8, 15, and 30 days). The different samplings at different times show that the leakage is constant with time. All samples (liquid phase) were extracted from the sample port (valve 2) and trapped in an Innox tube. The sample was then frozen using a liquid nitrogen dewar. The cold trap was used to avoid any vaporization of the sampled solution. The temperature of the tube and the sampling valve was maintained at the autoclave temperature (200°C) with a heating cord. The solutions were analyzed at room temperature by ion chromatography to determine the NH_4 concentration. Significantly, due to the small sampled volume of the solutions, sampling does not affect the composition of the bulk solution. Indeed, blank experiments have shown that the composition of the sample is equivalent to the composition of the remaining solution in the autoclave. The pressure and temperature were readjusted after each extraction.

The time required to form individual fluid inclusions within fluorite microfractures was determined by correlating the melting temperature (T_m) of the inclusions with the solution analyses. The T_m data were converted to NH_4Cl concentrations using data from Linke (1965). Thus, the microthermometric and ion-chromatography data allow us to obtain a compositional-temperature-time relationship (Fig. 2).

The quartz experiments were conducted in a fluid pressure autoclave (Autoclave Engineer) utilizing gold capsules (Landaï et al. 1989). The duration of each experiment was 480 hours (20 days). Each sample was made up of a quartz crystal, an H_2O - NaCl (1M) solution, and silica gel. The temperature and pressure were 400°C and 400 bar, respectively. However, these P - T conditions were slightly higher during the first 24 hours of the experiment due to manual balancing of the pressure and the temperature. After stabilization, pressure was maintained at 400 bar during all the experiments while temperature was gradually reduced from 400 to 300°C to enhance quartz precipitation and fluid inclusion formation. The cooling is isochoric and occurs on one P - T path (Bodnar and Vityk 1994).

NaCl solutions were used to increase the solubility of quartz and thus enhance fluid inclusion formation (Xie and Walther 1993). The maximum trap-

ping temperatures of the fluid inclusions are thus lower than the critical temperature (425°C) of the NaCl (1M)- H_2O system (Bodnar and Vityk 1994).

The T_h and T_m of fluid inclusions within thin fluorite samples were measured on a Linkam MDS 600 stage. For inclusions in thick, natural and synthetic quartz samples, a USGS type stage was used (Goldstein and Reynolds 1994). The stages were calibrated with pure H_2O - CO_2 inclusions ($T_m = -56.6^\circ\text{C}$) and low-salinity synthetic inclusions ($T_m = -0.4^\circ\text{C}$) at subzero temperature, and by melting of organic crystals at positive temperatures. Phase transitions were observed with a petrographic microscope equipped with Olympus 50 \times and 80 \times objective lenses.

For quartz-hosted fluid inclusions, the T_h measurements were corrected using the Zhang and Frantz (1987) EOS with known pressure and molalities to give true trapping temperatures (T_t). The timing of formation of fluid inclusions within quartz overgrowths and/or microfractures can therefore be read directly from the P - T - t diagram in Figure 3. All positive temperatures mentioned in the text and figures are true T_t .

Ion chromatography was used to quantify NH_4^+ and Cl^- contents of the solution in contact with fluorite. Measurements were conducted at the CNRS analytical laboratory at Vernaison, France. A 3 cm^3 sampling device was adapted to collect the solution through the output valve of the autoclave. After collecting, the solution was quenched by rapid cooling with liquid nitrogen and stored at low temperature until analysis.

RESULTS

Fluorite experiments

Numerous fluid inclusions were formed within microfractures in the fluorite material. Most of the inclusions are less than $10\ \mu\text{m}$ in diameter (Fig. 4) but some are 20 – $25\ \mu\text{m}$ in size. Measured T_h values were constant at $200 \pm 2^\circ\text{C}$. Figure 2 shows the variation of T_m and NH_4 concentration of each studied inclusion as a function of time. Sampling intervals are also represented on the plot. The induced leakage is constant and has been calcu-

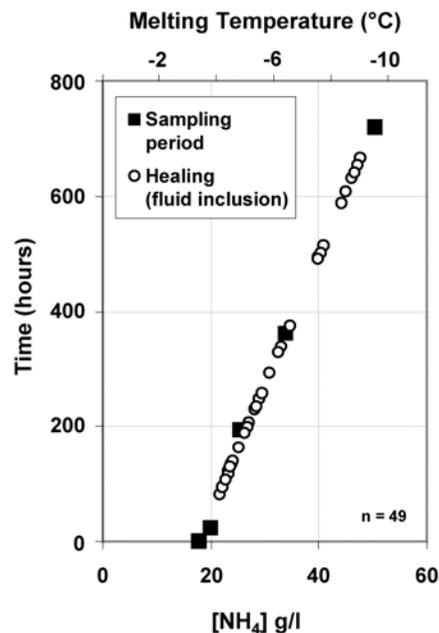


FIGURE 2. Time of formation of synthetic fluid inclusions inside fluorite microfractures. Graph showing variations of the autoclave fluid and fluid inclusion composition with time. Filled squares represent the compositions of 1–3 mL aliquots of autoclave fluid taken at 1, 8, 15, and 30 day intervals (see text) and the open circles are fluid inclusion compositions projected onto the regressed aliquot data.

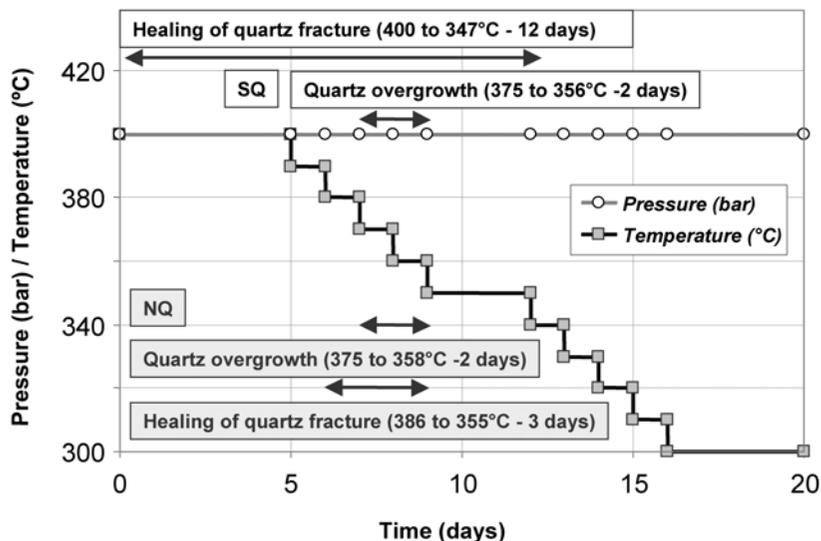


FIGURE 3. Experimental conditions of natural (NQ) and synthetic quartz (SQ) experiments in the NaCl-H₂O system (400 bar; 400 to 300 °C) for the healing of quartz microfractures and the growth of quartz overgrowths. Indicated temperatures are corrected trapping temperatures (T_i) for the aqueous fluid inclusions.

lated at approximately -0.008 °C/h in terms of T_m and approximately 0.045 g(NH₄Cl)/l/h in terms of concentration gain. The first sign of healing occurs after 82 hours with an inclusion that contains 21.67 g/l of NH₄Cl. This early inclusion is characterized by the lowest T_m (-4.1 °C). The last inclusion, formed after 665 hours, contains 47.65 g/l of NH₄Cl and has a T_m value of -8.7 °C. Overall, microthermometric results show that most of the fluorite microfractures healed between 82 and 257 hours.

Quartz experiments

Numerous fluid inclusions were formed within the healing microfractures, but comparatively few were formed within the quartz overgrowths. The inclusions located along the quartz microfractures are rarely greater than 30 μm in length (Fig. 4) and those inside overgrowths never exceed 8 μm in maximum dimension. Measured T_m values were constant at -3.4 ± 0.3 °C.

Two types of fluid inclusions were identified in the quartz microfractures: (1) Fluid inclusions with variable liquid/vapor (L/V) ratios (30–40% and 60–70%) and high T_i (385–418 °C) (Fig. 5). These inclusions (<15 μm) are found exclusively in quartz microfractures and are located near the surface of the synthetic quartz. These inclusions display a near-critical behavior. Indeed, T_i is near the critical temperature of 420 °C for an H₂O-NaCl (1M) system (Bodnar and Vityk 1994). These aqueous inclusions were synthesized within the first 24 hours, during the stabilization of the P - T conditions at the beginning of the experiment. (2) Fluid inclusions with constant gas filling (around 25%), which are trapped within larger microfractures (up to 30 μm). These aqueous inclusions show a wide range of T_i , from 385 to 347 °C in synthetic quartz and from 386 to 355 °C in natural quartz. Healing of these quartz microfractures occurred within 12 days for synthetic quartz and three days for natural quartz (Fig. 3).

Therefore, the results show that the synthetic quartz/H₂O-NaCl solution equilibrium was reached within one day whereas the natural quartz/H₂O-NaCl solution equilibrium was reached after six days.

In the quartz overgrowths, the T_i of the fluid inclusions in

natural (from 375 to 356 °C) and synthetic quartz (from 375 to 358 °C) are nearly identical and coincide with the decrease in temperature during the experiment (Figs. 3 and 5). Figure 6 shows an example of a synthetic quartz overgrowth, which grew within two days. Aqueous inclusions located inside quartz overgrowths are rare and small. Thus, few T_i values were measured. The core-overgrowth boundary is characterized by a relative large band (15 – 20 μm) containing numerous tiny inclusions, which have constant T_i of 368 °C. The T_i of aqueous inclusions decreases from the core-overgrowth boundary (368 °C) to the external part of the overgrowth (356 °C), suggesting that the quartz grew rapidly and continuously over this temperature range. Moreover, the continuous decrease in T_i is proof that fluid has not accessed the inner part of the overgrowth at a later time.

In natural samples from this study, T_i from microfractures and overgrowths are very similar, suggesting that the processes of healing and quartz growth occurred over the same time frame.

Aside from the healing of synthetic quartz microfractures,

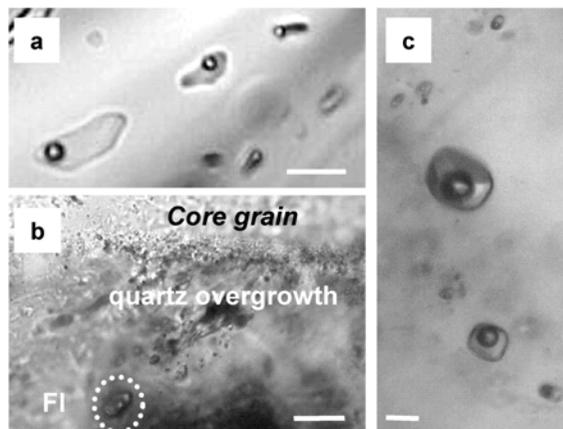


FIGURE 4. Photomicrograph of synthetic fluid inclusions (a) inside fluorite microfractures, (b) inside Brazilian quartz overgrowths, and (c) within synthetic quartz microfractures. Bar scale = 10 μm .

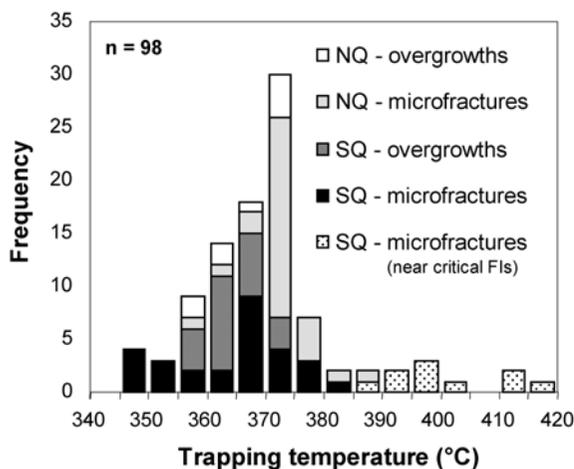


FIGURE 5. Trapping temperatures (T_i) of synthetic fluid inclusions in synthetic quartz (SQ) and natural quartz (NQ) microfractures and overgrowths.

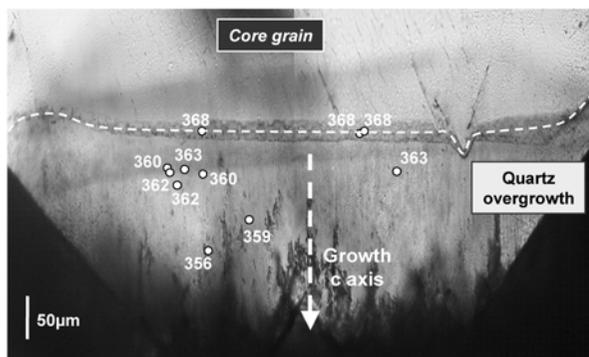


FIGURE 6. Growth direction and temperature characterization of a synthetic quartz overgrowth using corrected T_i of synthetic aqueous fluid inclusions (white circles). Data indicate that the overgrowth formed in two days.

all fluid inclusion formation seems to have halted just before the temperature step at 350 °C (ninth day), suggesting that the solution became undersaturated with silica during and after this step.

DISCUSSION

Rates of microfracture healing and overgrowth formation

For experiments involving fluorite, the data demonstrate that at 200 °C an aqueous solution of NH_4Cl requires three or four days to equilibrate (saturate) with the fluorite and allow the formation of inclusions. To better understand and visualize the formation of fluorite microfracture healing in time and space, 3D continuous surfaces (Fig. 7) were by triangulation and discrete smooth interpolation using the GOCAD software (Mallet 1992). The surface intersects all inclusions that belong to a fracture plane. Each inclusion is characterized by its properties (i.e., T_m , NH_4 concentration, time, and depth below the

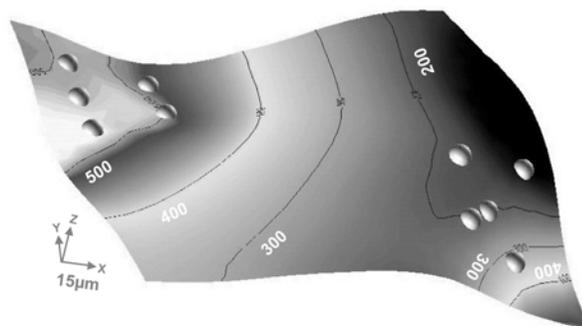


FIGURE 7. Spatial and temporal representation of fluid inclusions (white circles) in a single fluorite microfracture (3D continuous surface). Shades of grey represent interpolation between isochron time-lines (black lines). The isochron time lines are in hours.

sample surface). The results show that these inclusions were randomly sealed between the 117th and 513th hour of the experiment and that healing is not a continuous or linear process with time. Indeed, the total cementation of a single microfracture was shown to be completed over several days, or sometimes up to 20 days.

For quartz experiments, the data demonstrate that, between 400–350 °C and 400 bar, an aqueous solution of NaCl requires one day to saturate with the synthetic quartz, and six days to saturate with natural Brazilian quartz. This difference could be related to differences in hydration state and quartz surface morphology. The healing of quartz microfractures generally occurs prior to the quartz overgrowth formation and does not necessarily need an external silica supply in contrast to quartz overgrowth formation. The results also showed that overgrowths are enhanced by decreasing the temperature from a maximum silica oversaturated pore fluid. A relatively slow cooling rate and a smooth quartz surface will enhance quartz overgrowth formation but should minimize the number of fluid inclusions. Low P - T conditions (<350 °C, 400 bar) and weak silica supply will considerably reduce the quartz fracture healing and overgrowth formation rates. Indeed, in the quartz experiments, growth appears only to have been halted by a limited supply of silica, suggesting that the solution became undersaturated with silica.

Relevance to fluid inclusion studies

The result of this study has implications for how we undertake microthermometric analysis and how fluid inclusions should be selected for analysis with respect to the fluid inclusion assemblage (FIA) principle (Goldstein and Reynolds 1994).

Synthetic fluid inclusions within healed microfractures are representative of the experimental conditions. The compositions of the fluid inclusions (T_m) are representative of the parent fluid composition and its evolution during the experiments. The measured T_m range within the same FIA is therefore significant because each inclusion of the FIA has recorded a fluid composition at one time. Regarding T_m and or T_h histograms, the maximum peak of the broadened histogram is usually taken, mistakenly, as the average value representing the parent fluid in terms of composition and/or temperature. The variance of T_m and T_h between fluid inclusions having varying or similar

size, shape, and content within the same FIA requires a relatively large amount of data collection in order to determine the full range of variability.

In the fluorite samples, the different T_m values indicate progressive salt-enrichment of the fluid during the experiment. This process of vaporization has a great impact on fluid composition and can strongly modify T_m values. At 200 °C, the initial T_m values of around -3.4 °C (corresponding initial NH_4Cl aqueous solution) evolve to higher T_m values of around -9.4 °C (corresponding final NH_4Cl aqueous solution) over a period of 30 days. Therefore, such a system requires a relatively large number of T_m measurements to correctly follow and describe the evolution of the fluid (paleo)-composition during vaporization, locate which fluid inclusions are pre- or post-boiling processes, and identify the composition pole from which the boiling fluid originated.

Relevance to natural systems

The fluorite experiments mimic boiling processes in natural hydrothermal or epithermal systems and show how a boiling fluid may be trapped as fluid inclusions. Indeed, the boiling process induces a progressive salt-enrichment of the fluid during vaporization, which is recorded by the fluid inclusions. The changes in fluid composition and T_m values is important at the experimental conditions (200 °C, 30 days, $-9.4 < T_m < -3.4$) and should be enhanced in natural hydrothermal systems according to the fluid concentration and the vaporization period (geological time scale). During homogeneous trapping in an autoclave, the fluid inclusions are trapped at constant temperature without external liquid or gas supply, resulting in inclusions with constant T_h , similar L/V ratios, but different T_m due to steam loss. Heterogeneous trapping is not possible because the samples are bathed in the liquid phase, effectively isolating the gas phase from the sample. When boiling processes occur in natural systems, fluid inclusions often show a large range of T_m but can also show a large or narrow T_h range and constant or variable L/V ratios (Simmons and Browne 1997; Scott and Watanabe 1998; Kiliyas et al. 2001). In that case, heterogeneous trapping, if it occurs, is explained by the presence of an "effervescent" fluid containing a mixture of liquid water and gas bubbles. Fluid inclusions thus trap both liquid brine and vapor. Note that external fluid(s) entering an opened natural system could increase the complexity of such systems.

In diagenetic reservoirs, P - T variations can involve liquid-gas unmixing processes along the oil-water-gas column by modifying the salinity of fluid inclusions and/or the methane concentration (Guillaume et al. 2003). Moreover, this study has shown that the healing of a single microfracture is not an instantaneous process but can occur within several days at various salinities and temperatures. This protracted healing of a single microfracture could explain the frequent variability of salinity and temperatures of natural aqueous inclusions.

Extrapolation to natural systems, which operate at low temperatures and over long periods of time, can be formulated. Fluorite microfractures from this study healed in less than 30

days at 200 °C and P_{sat} . Quartz overgrowths formed between 350 and 400 °C within 10 days and reached 200 to 400 μm in size. In natural systems, microfracture healing and the formation of quartz overgrowths seems possible from 50 and 80–90 °C, respectively (Teinturier et al. 2002). In this case, quartz overgrowths from natural systems can easily reach 100–150 μm (from 80 to 150 °C) in less than 5 Ma. This requires that the flow rates of the aqueous fluid, its silica saturation state, and the silica supply are relatively high. On the other hand, the healing processes could occur over a relatively short time interval (several months or years) as well as relatively long periods (over several million years). Fluid inclusions can thus also record rapid events such as salinity, P - T conditions, or local reequilibration processes.

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