

Preferential water leakage from fluid inclusions by means of mobile dislocations

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THE fluid density, carbon dioxide content, and therefore the pressure-temperature conditions derived from fluid inclusions in metamorphic rocks are commonly inconsistent with coexisting mineral assemblages. Here we report hydrothermal experiments mimicking isobaric cooling and isothermal decompression, which indicate changes in density and composition without significant change in volume of H₂O-CO₂ inclusions in quartz. A simultaneous change to CO₂-rich compositions and lower densities indicate that water leaking from the inclusions. We argue that preferential water leakage is made possible by microscopic unmixing of the H₂O-CO₂ mixture caused by physical and chemical interactions with the inclusion wall. Water transport then occurs by movement of water-saturated dislocations through the hydrothermally recrystallizing quartz.

Significant discrepancies often exist both between the measured densities of gas-rich fluid inclusions and those calculated from metamorphic pressure-temperature conditions as inferred from mineral assemblages, and between observed and calculated values of water content in fluid inclusions for appropriate mineral assemblages (for example, studies on Rogaland, Norway^{1,2} and Naxos, Greece³⁻⁶). The discrepancies have led to suggestions concerning re-equilibration of fluid inclusions during post-peak deformation, for example by dynamic recrystallization⁷⁻⁹. As such, deformation during isobaric cooling (for Rogaland²) or isothermal decompression by syn-metamorphic tectonic extension (for Naxos¹⁰) have been proposed.

Experimental re-equilibration of fluid inclusions resulting only in density changes, has been achieved by (1) volume changes without significant diffusion of H₂O through quartz¹¹; (2) decrepitation¹²⁻¹⁶; and (3) diffusion of H₂O through the quartz lattice^{14,15} as point defects (interstitial molecules^{17,18} and substitutes^{19,20}) or as water-related species through dislocation lines^{16,21-23}. Depending on temperature and crystallographic orientation with respect to deviatoric stress state, H₂O may diffuse

through dislocation lines due to activation of glide systems. Until now, no compositional change of H₂O-CO₂ fluid inclusions has been experimentally studied by hydrothermal re-equilibration²⁴.

In this study, fluid inclusions were synthesized at 200 MPa and 835 K for 38 days according to the method of Sterner and Bodnar²⁵ in cores drilled out of optically clear Brazilian quartz. The fluid composition was 79 ± 3 mol% H₂O and 21 ± 3 mol% CO₂ with no additional salt, hydroxide or acid, in order to avoid rapid quartz recrystallization and incorporation of imperfections. Flat fluid inclusions were selected from a three-dimensional inspection with a U-stage to characterize their morphology and volume percentages of the gas species (Fig. 1). A microthermometric study yielded an average homogenization temperature (T_H) of the CO₂ phases at 304.2 K and of the total H₂O-CO₂ content at 574.4 K (Table 1). Electron microscopy (TEM) was performed to identify defect structures in the healed crack. The thin foils were prepared from quartz cores from duplicate experiments in order to keep the core, intended for further re-equilibration, undamaged (see below).

Isobaric cooling was experimentally reproduced by a second anneal at 673 K and 200 MPa for 21 days (Fig. 2). A pure H₂O environment of the quartz core was chosen to distinguish newly formed fluid inclusions from the original CO₂-bearing fluid inclusions from the first run. The identical individual fluid inclusions were again photographed (Fig. 1b) and T_H was remeasured (Table 1). Comparison of morphologies of these flat inclusions assures that the volumes changed less than 4 vol% and presumably, this may hold for all fluid inclusions. The quartz was re-examined by TEM after microthermometry. The foils were made of small, 0.5-mm-thick slices of the same core used in both synthesis and re-equilibration experiments. Direct comparison of the dislocations before and after re-equilibration was impossible. As result of the second run, a few pure H₂O fluid inclusions were synthesized in cracks, which were not completely annealed after the first run. Their average density of $0.0445 \text{ mol}\cdot\text{cm}^{-3}$ reflects the new conditions. The identical H₂O-CO₂ fluid inclusions from the first run now contained lower densities than after the first run as illustrated by volume increases of the vapour and liquid CO₂ bubbles at the expense of H₂O volume (Fig. 1a, b). The T_H of the CO₂ phases is now in the range 266.0-304.1 K, whereas T_H of the total content is in the range 541.0-595.4 K (Table 1).

Water content was calculated by density measurements and volume estimations of the fluid species based on surface measurements. A few fluid

TABLE 1 Duration of the experiment, range of homogenization temperatures (K) of CO₂ and CO₂-H₂O mixtures of the original and new experiments

	Duration (in days)	Homogenization CO ₂ phases			Homogenization H ₂ O-CO ₂ phases		
		T_{\min}	T_{\max}	T_{av}	T_{\min}	T_{\max}	T_{av}
Original experiment	38	303.5*	304.4*	304.2*	573.1	575.7	574.4
New experiment	21	266.0	304.1	-	541.0	595.4	-

There were 57 measurements per experiment

* Temperatures of inclusions that homogenize in the liquid phase (others homogenize in the gas phase). The original fluid inclusions yield a narrow range of both homogenization temperatures, whereas the recrystallized fluid inclusions in the new experiment display a broad range.

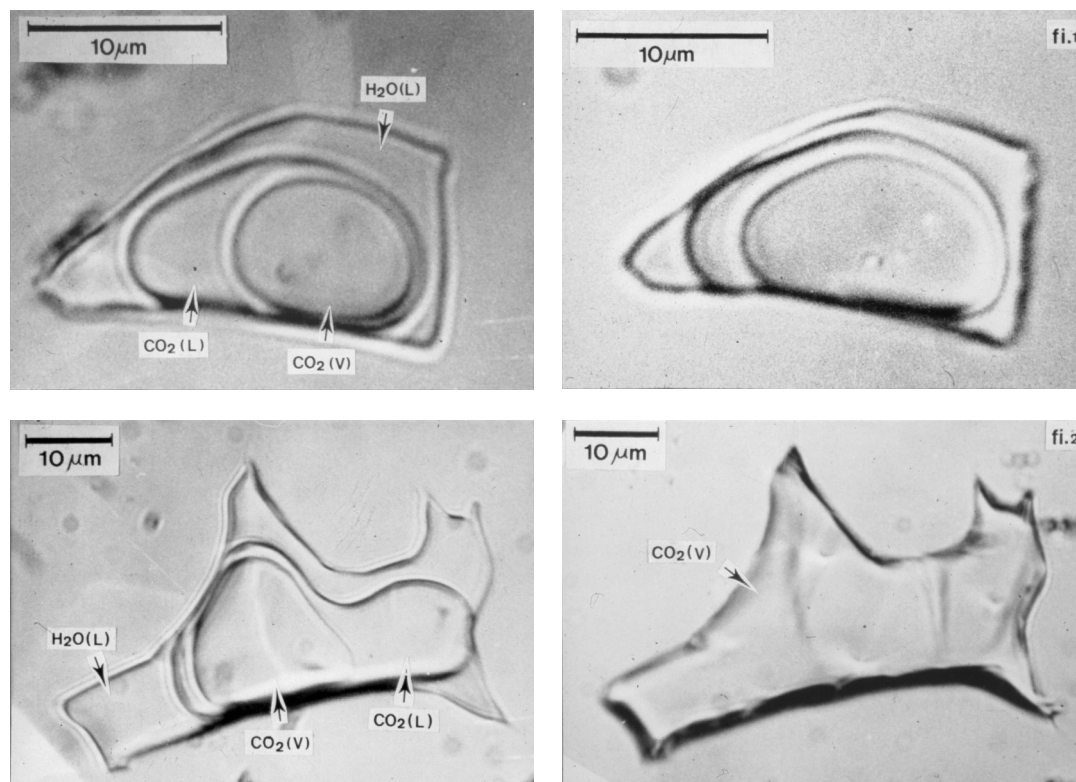


FIG. 1 a, Photomicrographs of three-phase fluid inclusions generated in the original experiment, with 21 mol% CO_2 . At 293 K, the volume percentages of $\text{H}_2\text{O}(\text{l})$, $\text{CO}_2(\text{l})$ and $\text{CO}_2(\text{v})$ are 40, 39, 21 respectively. Both inclusions homogenize at 304.3 K for the CO_2 and at 574.8 K for the CO_2 - H_2O phases. b, Photomicrographs of the identical inclusions after the new experiments, simulating isobaric cooling. Only minor solution and precipitation is illustrated. At 293 K the volume percentages of

$\text{H}_2\text{O}(\text{l})$, $\text{CO}_2(\text{l})$ and $\text{CO}_2(\text{v})$ have been changed to 31, 29 and 40 respectively for inclusion 1 (fi.1) and 10, 0 and 90 respectively for fluid inclusion 2 (fi.2). The $\text{H}_2\text{O}(\text{l})$ phase of fi.2 is concentrated in the edges of the inclusion. The homogenization temperatures of the CO_2 and the CO_2 - H_2O phases for fi.1 have been changed to 303.6 and 579.5 K, respectively and for fi.2 to 269.8 and 552.8 K. The calculated mol% CO_2 for fi.1 and fi.2 are 26 and 46, respectively.

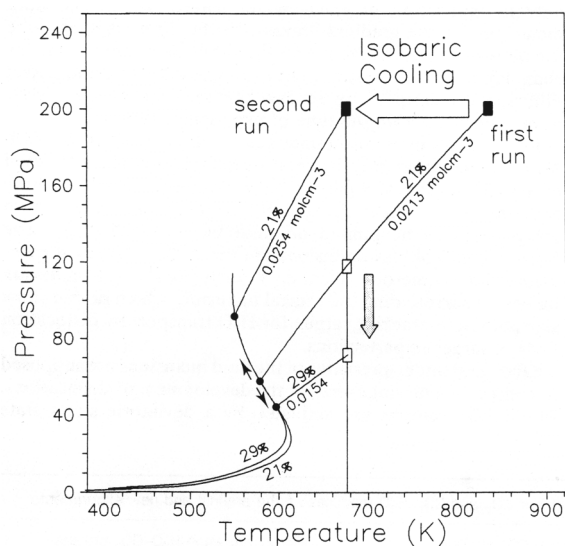


FIG. 2 Pressure-temperature diagrams display the experimental conditions (black squares). The curved lines are the projections of the experimentally determined H_2O - CO_2 mixing areas³⁷ for 21 and 29 mol% CO_2 . The corresponding isochores and their densities ($\text{mol}\cdot\text{cm}^{-3}$) are calculated as nearly straight lines with the MRK equation of state³⁸. Isobaric cooling is indicated with the large open arrow. The shaded arrow indicates the development of the underpressure in the fluid inclusions due to preferential leakage of H_2O at new experimental conditions (see text). The P_{intern} at new conditions is indicated.

inclusions retained their original water content values, but most were lower than the original values. Any volume adjustments and infiltration of H_2O would result in lower T_{H} (Fig. 2). Seemingly contradictory, preferential leakage of H_2O is responsible for instantaneously higher T_{H} and simultaneous internal pressure drop. Fugacity-, chemical- and pressure-gradients are considered as driving forces, resulting only in infiltration of H_2O . Water leaked out of the fluid inclusions, so the gradients cannot be the direct driving force for outward H_2O diffusion and the diffusion cannot occur by channelized cracks or pores. The available data for point-defect diffusion in quartz²⁶⁻²⁹ prove that this mechanism is too slow to be effective within the time of experimentation.

Dislocations in hydrothermal quartz were imaged with TEM. Most of the apparently isolated inclusions end in dislocation arrays (Burgers vectors parallel to (a) were determined by tilting experiments) or larger channel-like imperfections. Dislocation arrays seem to be pinned on fluid inclusions (Fig. 3). The formation of bubbles on dislocation lines^{20,30,31} after heat treatment and numerous secondary inclusions^{12,15} ("implosion haloes"¹¹) surrounding the central inclusion, which do not show signs of micro-cracking, argue for H_2O transport by dislocation lines or larger imperfections.

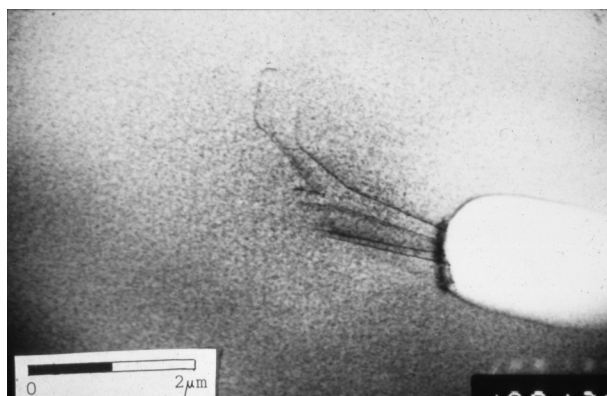


FIG. 3 The bright field electron micrograph (TEM) of a synthetic fluid inclusion (white) produced in the original experiment illustrates a suite of six pinned dislocations.

Over- and under-pressure of the fluid inclusions are supposed to constitute a driving force for the development of dislocations. Mobile dislocations are activated by a deviatoric stress state around the fluid inclusions due to the lattice discontinuity and their mobility may result in an episodic tapping of fluid inclusions. The dislocations may become saturated with water from the fluid inclusions. The dislocation loops, which move from the interior of the crystal to the surface, can be considered as "water-bucklers", able to operate in both internal over- and under-pressure conditions. Because of the high length:diameter ratio, the volume of H_2O transport may be larger than the claimed volume decrease of fluid inclusions by pore collapse. Also, fluid inclusions are principally major imperfections and they may act as sources of dislocation multiplication. The mechanism does not explain preferential leakage of water from a single phase CO_2 - H_2O mixture in fluid inclusions during experimentation. Local unmixing on near-molecular scale must occur for the preferential leakage. This may be caused by the following: (1) The physical and chemical surface interaction between hydrophile quartz and water dipoles. The surface of the fluid inclusions, the channel-like imperfections and the dislocation lines may be wetted by a molecular film of H_2O attached to interfacial silanol groups. On a larger scale, similar surface interactions, which may prevent CO_2 molecules from escaping through dislocations, have been proposed for fluid wetting of microcracks and grain boundaries in rocks³². Fluids with high CO_2 content ratios form isolated drops at grain corners, whereas at high H_2O contents a three-dimensional continuity of a fluid film exists. (2) The restriction of the dislocation size^{33,34}. The dislocations may be too small in diameter for effective molecular pipe-diffusion of CO_2 molecules, which are larger than H_2O molecules. (3) The formation of H_2CO_3 molecules, by the association of CO_2 and H_2O . These molecules influence the original fluid composition for small CO_2 contents. The dimensions of H_2CO_3 molecules are even larger than CO_2 molecules, enforcing argument (2).

We conclude that a wide range of fluid-inclusion compositions can be generated from one type of metamorphic fluid, by preferential H_2O leakage as a

result of local variations in the degree of hydrothermal synmetamorphic recrystallization, even within a single trail. In experimental hydrothermal simulations of isobaric cooling (described here) and isothermal decompression³⁵ a decrease of density was caused by preferential leakage of water.

In theory, compositions of practically pure N_2 - CH_4 - CO_2 gaseous fluid inclusions are thermodynamically forbidden at high-grade peak metamorphic conditions (for Rogaland³⁶). The argued H_2O leakage out of originally water-rich fluid inclusions containing CH_4 , CO_2 and N_2 may result in extremely gas-rich fluid inclusions.

The density of CO_2 -rich fluid inclusions in metamorphic quartz lenses (for Naxos^{3,4}) are adjusted to post-main metamorphic conditions by H_2O leakage and therefore, the CO_2 content is too high compared with the calculated CO_2 content derived from mineral equilibria.

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