Enrichment of CO_2 in fluid inclusions in quartz by removal of H_2O during crystal-plastic deformation

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Abstract—Ductile strain-induced leakage of H_2O from mixed CO_2 + H_2O fluid inclusions in quartz is proposed as a mechanism for producing occurrences of pure CO_2 fluid inclusions in metamorphic rocks. The H_2O needed for hydrolytic weakening of quartz under stress may be provided by the H_2O in fluid inclusions. With dislocation creep, as dislocations nucleate on the walls of fluid inclusions or intersect them, H_2O can be transported with the dislocations from the inclusion to the grain boundaries. The process should continue so long as there is stress on the host quartz and the inclusion contains H_2O. The H_2O taken to the grain boundaries would, due to its wetting properties, be wicked out along the grain boundaries. If the H_2O is totally removed from an inclusion by a flux of dislocations through the quartz during the crystal-plastic flow, then a residual inclusion bearing components other than water should remain. A mixed CO_2 + H_2O inclusion would, as a consequence of the process, become a pure CO_2 fluid inclusion. During dynamic recrystallization, the CO_2 would collect at grain boundary triple junctions and, following grain boundary migration, would become incorporated into the recrystallized quartz as fluid inclusions. This mechanism of generating pure CO_2 inclusions could result in CO_2 fluid inclusions having densities appropriate for the pressure–temperature conditions during deformation. Using estimates of temperature of deformation, the total confining pressure during deformation could be determined from the density of the CO_2 fluid in these inclusions.

INTRODUCTION

MANY occurrences of CO_2-rich fluid inclusions have been reported in the literature. The most enigmatic of these occurrences are those reported for metamorphic rocks for which nearly pure H_2O was probably the fluid present during metamorphism. Examples include migmatites (Touret & Olsen 1985, Olsen 1987), greenschists (Sisson & Hollister 1990), amphibolite-facies metamorphic rocks (Crawford *et al.* 1979b, Sisson *et al.* 1981) and hydrated granulites (Van Reenen & Hollister 1988), as well as in the well studied occurrences in granulite-facies rocks (Touret 1971, Newton 1986, Lamb 1988).

Most explanations for the occurrence of CO_2-rich inclusions in rocks that crystallized in the presence of an H_2O-rich phase come under two categories: (1) post-metamorphic extraction of H_2O from unmixed CO_2 + H_2O fluids; and (2) selective entrapment of the CO_2-rich fluid of an immiscible fluid system. Both categories have been discussed in the literature (reviewed by Crawford & Hollister 1986, Hollister 1988), and are briefly reviewed here.

(1) Post-metamorphic extraction of H_2O from unmixed CO_2 + H_2O fluids includes preferential removal of the aqueous phase along microcracks which intersect inclusions with unmixed carbonic and aqueous phases ("wicking" of Crawford & Hollister) (Fig. 1).

For unmixed CO_2-rich and H_2O-rich phases, the H_2O-rich phase wets the surfaces of the minerals. This is due to the polar structure of the water molecules which, relative to the non-polar CO_2 molecules, form weak bonds to the mineral surfaces. The H_2O will then be selectively removed, through surface tension, along microcracks that intersect an inclusion (Fig. 1). Watson

& Brenan (1987) experimentally confirmed this process and further pointed out that due to very large differences in wetting characteristics of CO_2 liquid and H_2O liquid (Fig. 2), CO_2 could only leave a rock by hydrofracturing whereas H_2O would naturally be pulled out along microcracks and grain boundaries by the wicking process. The difference in wetting characteristics, which is enhanced by the presence of NaCl (Watson & Brenan 1987), should lead to a natural separation along grain boundaries of CO_2- and H_2O-rich fluids.

Diffusion along dislocations (pipe diffusion) may be considered as a special case of wicking. A dislocation tube which connects an inclusion to the grain boundary probably has similar properties, with respect to the factors controlling the wetting properties of fluids, as microcracks. Water molecules would be wicked out along the tube, thus draining the inclusion of H_2O and leaving behind CO_2.
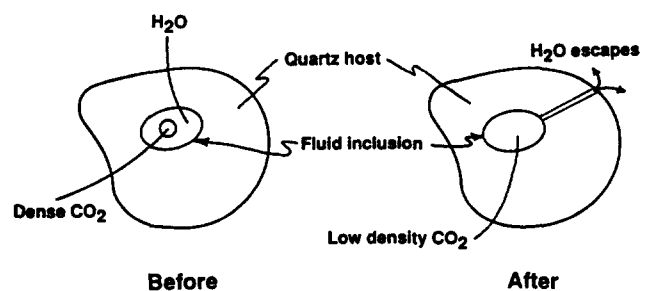

Fig. 1. Schematic illustration of the process of 'wicking' (Crawford & Hollister 1986). The sketch on the left shows a fluid inclusion for a temperature at which liquid CO_2 occurs as a separate phase with liquid H_2O. If a microcrack intersects this inclusion, as in sketch at right, the H_2O will be drawn out to the grain boundary. The liquid CO_2 will expand to fill the original cavity, leaving a fluid inclusion containing only CO_2, but with lower density than in the original inclusion.
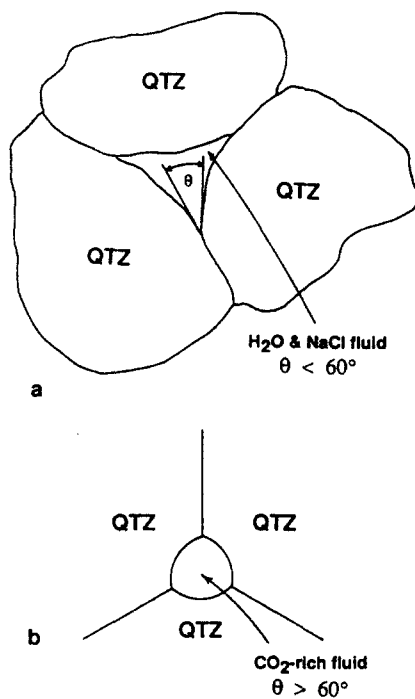
Fig. 2. Sketches illustrating wetting angle (θ) for intergranular fluids for θ less than $60°$ (a) and more than $60°$ (b). The former case holds for H_2O + NaCl solutions; the latter for CO_2-rich fluids. Adapted from Watson & Brenan (1987).

(2) Preferential trapping of the nearly pure CO_2 phase of a two-phase system is a reasonable hypothesis based on observation, experiment and theory. Hollister & Burruss (1976) and Hendel & Hollister (1981) proposed, based on observational data, that fluid immiscibility could occur during greenschist- and at least to the lower amphibolite-facies of metamorphism. These observations find support from the experimental work of Takenouchi & Kennedy (1965) on CO_2 solubility in brines of variable salt content. Experiments of Gehrig et al. (1979) and theoretical analysis by Bowers & Helgeson (1983) and Skippen & Trommsdorff (1986) have since shown that fluid immiscibility can occur at least to 600°C for salt-rich systems. Observations by Mercolli (1982) demonstrated fluid immiscibility to 500°C for a natural CO_2 + H_2O + NaCl fluid system; and, recently, based on Cl + F contents of hydrous minerals, Henry (1988) suggested fluid immiscibility may occur into the granulite-facies for very saline brines. An important conclusion from the work of Pichevant et al. (1982), Bowers & Helgeson (1983) and Skippen & Trommsdorff (1986) is that the amount of H_2O dissolved in the CO_2-rich phase diminishes with increased salt content, and, for saturated brines, may be as little as 5 mol % even at temperatures of 500°C. Thus, if only the CO_2-rich phase were trapped as fluid inclusions, even on cooling to temperatures low enough for phase separation, the aqueous phase would be an invisible film on the wall of the inclusion (Roedder 1972). The large difference in wetting characteristics of CO_2-rich fluids and brines described by Watson & Brenan (1987) implies that the CO_2-rich fluid of a two fluid system would collect at imperfections and grain boundary triple junctions and

therefore would preferentially be trapped and preserved as fluid inclusions. This explanation was used by Sisson et al. (1981) to interpret fluid inclusion populations in amphibolite-facies metacarbonate rocks, and by Mullis (1976) to explain apparently pure CH_4 inclusions in greenschist-facies vein quartz.

Touret (1971), Newton et al. (1980) and others have argued that, for some occurrences of granulite-facies rocks, the nearly pure CO_2 fluid inclusions are trapped samples of a supercritical primary fluid. The proposal of 'carbonic metamorphism' is based on these occurrences. Carbonic metamorphism consists of a pervasive flow of CO_2 fluid through the crust which dehydrates and heats the lower crustal rocks to produce granulites (Newton et al. 1980, Janardhan et al. 1979). The fact that a granite gneiss can be charnockitized locally by CO_2 fluids has been demonstrated for several localities in southern India (e.g. Hansen et al. 1984, Raith et al. 1988). However, whether this is a phenomenon of limited scope or has led to the conversion of large regions of granitic gneiss to charnockite has yet to be demonstrated. O'Nions & Oxburgh (1988) argue that the flux of carbon from the mantle through active tectonic areas is too little to do the necessary dehydrating to form extensive granulite-facies terranes.

A third category of explanation for generating CO_2-rich fluid inclusions in rocks which crystallized in the presence of an H_2O-rich fluid is to invoke a process of selective extraction of H_2O into the quartz lattice from inclusions containing a homogeneous CO_2 + H_2O fluid mixture. A proposal that this occurs during ductile strain is the subject of the present paper. It has, however, been previously suggested that water may be lost from metamorphic inclusions by simple hydration of the host quartz (Roedder 1984). This hypothesis is based on the length of time that quartz is held at the temperatures of metamorphism, and on the finite solubility of H_2O in quartz (White 1973). However, Gerretsen et al. (1989) showed that the content of structural water in quartz is up to one order of magnitude less than previously thought, and several studies (e.g. Hollister & Burruss 1976, Stout et al. 1986) have shown that mixed CO_2 + H_2O fluids have survived apparently intact from near peak metamorphic conditions. These inclusions occur in quartz in pressure shadows and in synmetamorphic extension veins; this quartz had not experienced crystal-plastic deformation after inclusion formation. If hydration of quartz were important for removing H_2O from inclusions, it should happen for all long duration, high-temperature situations. It appears not to.

The purpose of the present paper is to examine the possibility that crystal-plastic deformation could lead to preferential extraction of H_2O from inclusions containing homogeneous mixtures of CO_2 and H_2O. The proposed mechanism would apply for all situations in which the quartz host of the inclusions had been ductilely deformed. The idea is that H_2O in an inclusion promotes hydrolytic weakening when the host mineral is under stress, and that, during dislocation creep, H_2O can be quantitatively removed from the inclusion as dislo-

cations leave the site of the inclusion, leaving CO_2 and other components that were originally mixed with the H_2O. Although this mechanism may operate after peak metamorphism, it is likely also, for reasons developed below, that it operates synchronously with metamorphism. The proposed mechanism may account for some of the pure CO_2 fluid inclusions reported in metamorphic rocks.

It is emphasized that many CO_2-rich fluid inclusions in metamorphic rocks occur along healed fractures which transect entire quartz grains and cross grain boundaries. Reasonable explanations for these occurrences already exist. Many are likely the result of 'hydro' fracture of predecessor fluid inclusions overpressured during exhumation. Such inclusions have proven useful in deducing the retrograde portions of metamorphic $P-T$ paths (Hollister *et al.* 1979, Hames *et al.* 1989). The origins of these inclusions are not discussed in the present paper. Other explanations for pure CO_2 fluid inclusions include formation of fluid inclusions from the CO_2-rich fluid remaining after formation of hydrated retrograde minerals (Lamb 1988, Morrison & Valley 1988) and, of course, entrapment of the fluid given off by decarbonation reactions.

DESCRIPTION OF PROPOSED MECHANISM

In most metamorphic rocks, at temperatures in excess of 300°C, and in the absence of retrograde reactions, quartz is the softest silicate phase (Suppe 1985, p. 146). Deformation is enhanced by the presence of quartz because it deforms by crystal-plastic flow at relatively low temperatures. Evidence for the crystal-plastic flow of quartz incorporates the observation of intracrystalline strain features, such as undulatory extinction and, at higher temperatures, recovery and recrystallization.

Hollister (1988, p. 469) suggested that, when the pressure in the inclusion (P_i) exceed the confining pressure (P_c) on the host crystal, dislocations would nucleate on the walls of the inclusions, such as was described by Wanamaker & Evans (1989) for olivine with $P_i > P_c$. In principle, this could allow entrance of H_2O into the quartz coupled with a defect as discussed by McLaren *et al.* (1983). The combination of a coupled defect and of conditions for $P_i > P_c$ was suggested by Pêcher & Boullier (1984) to explain an apparent loss of H_2O from inclusions during experiments with variable P_i relative to P_c. Roedder (1981) and Hollister (1988) suggested ductile strain might also be a driving force for the selective loss of H_2O.

According to McLaren *et al.* (1989), dislocations nucleate on fluid clusters (ultra-small fluid inclusions) when stress is applied to the host. They suggest that the low yield stress of synthetic quartz may be due to the large number of dislocations generated at these clusters of water molecules, and that glide of these dislocations is what enhances strain in 'wet' synthetic quartz relative to 'dry' natural quartz. Although McLaren *et al.* (1989) suggested that the greatly enhanced generation of dislo-

cations in 'wet' quartz was responsible for its weakness, an active role for H_2O in promoting dislocation mobility is likely (Blacic & Christie 1984, Ord & Hobbs 1986, Paterson 1989). This role, called hydrolytic weakening by Griggs & Blacic (1965), can be thought of as breaking Si–O–Si bonds by H_2O to form Si–OH HO–Si, thus reducing the energy needed to move the defects to achieve dislocation climb, which in turn permits dislocation creep at lower stress. Objections to hydrolytic weakening in experimental systems center on the problem of getting the H_2O into the quartz (Gerretsen *et al.* 1989). This problem may not apply to the metamorphic situation, where, during strain and at high fugacity of H_2O during dehydration metamorphic reactions, H_2O is available to hydrolyze bonds at dislocations nucleated on grain boundaries; and H_2O can be provided at the interior of the quartz from fluid inclusions formed during healing of hydrofractures.

Strain will be concentrated where quartz is the weakest, and where dislocation creep can be facilitated by hydrolytic weakening. Fluid inclusion walls are likely sites for dislocation nucleation, and the fluid in the inclusion can provide the H_2O needed for dislocation creep. With a continuous flux of dislocations from or through the fluid inclusions during strain, the inclusions will be drained of their water. The dislocations will pass through the crystal during strain to the grain boundary along with the H_2O bound as Si–OH HO–Si. After being reconstituted at the grain boundary, the H_2O will be drawn out of the rock along the grain boundaries by the wicking effect discussed above. By this mechanism, the amount of H_2O dissolved in the quartz at any instant need not be greater than the trace amounts believed to occur in quartz (Gerretsen *et al.* 1989).

The role of water in aqueous inclusions in promoting dislocation creep has been previously proposed by Kerrich (1976). However, for mixed CO_2–H_2O inclusions, because CO_2 is not known to break Si–O bonds and/or because of its non-polar nature and size, CO_2 is not likely to lower the energy barrier for motion of dislocations. The CO_2 is expected to remain in the inclusions unless they decrepitate for high $P_i > P_c$. The wetting properties of CO_2 are such that the most likely mechanism of removing small amounts of CO_2 from a quartz host is by hydrofracture only (Watson & Brennan 1987).

Tullis & Yund (1980) envisaged that H_2O entered quartz along microcracks in initially anhydrous (and therefore brittle) quartz and that the water structurally weakened the quartz in the vicinity of the microcracks and promoted the observed weakening. However, because any crack would quickly heal, leaving a plane of fluid inclusions where the fracture initially occurred (Smith & Evans 1984), the source of the water for the hydrolytic weakening during subsequent strain would more likely be from the fluid inclusions (Fig. 3). Although a completely satisfactory explanation for hydrolytic weakening has yet to be found (Gerretson *et al.* 1989, McLaren *et al.* 1989, Paterson 1989), there seems little doubt that H_2O in some way reduces the strength of quartz. An active role for H_2O-bearing fluid

inclusions in the deformation process provides a mechanism for concentrating, as a restitic component, CO_2 in fluid inclusions.

It is well known that high shear strains result in grain size reduction, and it is known that during dynamic recrystallization fluid inclusions become concentrated along subgrain and grain boundaries (Kerrich 1976). However, for CO_2, assuming H_2O had been lost by the proposed mechanism, tiny (submicroscopic?) fluid inclusions of pure CO_2 would be expected to decorate the grain boundaries. We have observed this situation in some of our metamorphic samples. During recrystallization, these tiny droplets would merge to make bigger pockets at triple junctions between recrystallized quartz grains. Subsequent grain boundary migration would result in incorporation of these pockets of CO_2 as fluid inclusions wholly within single quartz crystals. Thus, in recrystallized quartz, although dislocation creep may have operated to separate H_2O from CO_2, the location and size of the CO_2 inclusions may be controlled in part by processes associated with dynamic recrystallization.

The proposed mechanism for draining H_2O from CO_2 + H_2O fluid inclusions provides a reasonable explanation for why pure CO_2 fluid inclusions can occur in metamorphic rocks at all grades: most metamorphic rocks are foliated, and the presence of foliation is generally due to crystal-plastic deformation; thus, most matrix quartz and strained quartz veins have experienced crystal-plastic deformation. However, quartz precipitated in pressure shadows has not undergone crystal-plastic deformation and may therefore contain compositions closer to those of the intergranular metamorphic fluids. This appears to be the case for the studies of Hollister & Burruss (1976) and Stout et al. (1986).

DISCUSSION

Metamorphic reactions generally involve devolatilization, and arguments have been made (Walther & Orville
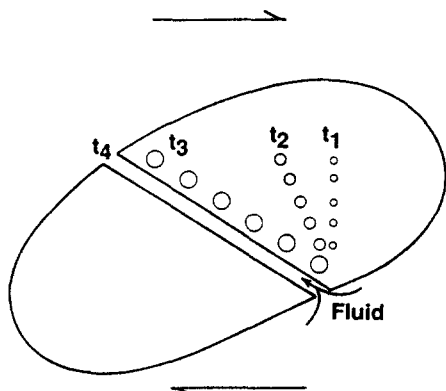
Fig. 3. Schematic illustration of the formation of a fluid-filled fracture and the subsequent effect of simple shear on the fluid inclusions. The inclusion trail t_1 formed at time t_1 (the earliest) following opening of a fracture such as illustrated at t_4. The inclusions at t_1 are interpreted to have formed immediately after a tension fracture opened, such as at t_4 and which is illustrated at t_3. With progressive strain, the inclusions would lose water and shrink, which is represented by the row of smaller inclusions at t_2 and, after further strain, by the even smaller inclusions at t_1.

1982, Crawford & Hollister 1986) that the fluid would escape along hydrofractures. These hydrofractures would be oriented parallel to local σ_1 (Fig. 3). Healing of the fractures would occur rapidly after fluid pressure had fallen back to lithostatic pressure. After an episode of hydrofracturing, fluid remaining along the grain boundaries would be wicked out and migrate to lower pressure regions, thus reducing the grain boundary fluid pressure to below lithostatic pressure. The quartz would then deform by crystal-plastic flow laws (if at high enough temperature). Where the resulting healed planes of fluid inclusions occurred in quartz, they would be available to enhance subsequent ductile strain. This strain would be synchronous with metamorphic mineral growth if the rock on the whole had a foliation defined by the metamorphic minerals. Graham et al. (1983) argued that ductile deformation in metamorphic rocks is localized at the sites of active metamorphic reactions. Here it is argued that during devolatilization reactions one step in the development of this synmetamorphic strain is the formation of fluid inclusion-filled healed fractures in quartz.

During synmetamorphic deformation, new fluid inclusion-filled healed fractures would form episodically. As fluids were evolved by metamorphic reactions, hydrostatic pressure would rise and when it exceeded the lithostatic pressure by the tensile strength of quartz, hydrofractures would be generated. After the fall of fluid pressure as fluid was drained out along the grain boundaries to lower pressure regions, the process would be repeated, assuming continuing heat input to drive the metamorphic reactions. Thus, there would be a steady supply of H_2O for synmetamorphic hydrolytic weakening of the quartz.

Figure 3 schematically illustrates progressive strain on fluid inclusions which originated along healed fractures. It is assumed that the original trapped inclusions consisted of a supercritical mixture of CO_2 and H_2O. As strain progresses, H_2O is taken from the inclusions and the interior of the grain along with the dislocations. When the H_2O reaches the grain boundaries, it is wicked away. Continuous episodes of opening of fractures by hydrofracture when fluid pressure exceeds lithostatic pressure by the tensile strength of quartz can provide a fresh supply of H_2O to the interior of the grains for enhancing the creep of dislocations. During the intervening episodes of crystal-plastic flow of the quartz, pure CO_2 fluid inclusions will form from the primary supercritical CO_2 + H_2O fluids.

Stretching and shrinking of quartz around inclusions for $P_i > P_c$ and for $P_i < P_c$ has been demonstrated by the hydrothermal experiments at 700°C reported by Sterner & Bodnar (1989). They were able to demonstrate partial to total reequilibration of fluid density in inclusions in response to changes in confining pressure. Pêcher & Boullier (1984) conducted similar experiments with similar results. Sterner & Bodnar (1989) could not confirm actual loss or addition of H_2O during the shrinking or stretching. The amount of water necessary to enter the quartz to facilitate dislocation creep to accom-

modate the stretching is not known, but the processes involved must be the same as those for crystal-plastic deformation. Under conditions of continuing strain as discussed in this paper, a flux of H_2O, from the inclusion into the lattice near a dislocation line and through the crystal during dislocation movement, would be required to facilitate high strains of the host quartz. The generation of pure CO_2 fluid inclusions by crystal-plastic deformation could, thus, result in CO_2 densities appropriate for $P_{fluid} = P_{lithostatic}$ during deformation.

This conclusion differs from that of Sterner & Bodnar (1989) who point out that stretching and shrinkage would result in loss of density information at the time of original trapping, but not loss of the primary fluid composition. Here, it is proposed that, as H_2O is lost, the cavity size accommodates this loss during strain. Thus, the density of the inclusion would reflect the $P-T$ conditions during strain or subsequent recrystallization, but the fluid composition would not reflect the ambient intergranular fluid composition. Such a result is consistent with the observations that pure CO_2 fluid inclusions are common in metamorphic rocks at all grades and that many have densities consistent with metamorphic conditions. It is further suggested that a fluid inclusion will shrink or stretch in response to changing conditions so long as there is some H_2O available to facilitate dislocation creep. If all H_2O were lost during strain, then perhaps no further re-equilibration of the pure CO_2 fluid inclusions could occur, except by hydrofracture, even if $P_i \neq P_c$. Of course, even if the inclusion is pure CO_2, stress may be concentrated at the inclusion which would promote fracture of the quartz at the site of the inclusion under conditions of applied external stress.

EXAMPLES FOR WHICH THE PROPOSED MECHANISM MAY APPLY

Selective leakage of H_2O from $CO_2 + H_2O$ inclusions by crystal-plasticity in quartz may explain some of the data reported by Sisson & Hollister (1990), who found mainly pure CO_2 fluid inclusions, with densities appropriate to the metamorphic conditions, in rocks for which an H_2O-rich fluid was present during the metamorphism. The samples used in that study were collected from an area in southcentral Maine which has been the subject of study by Ferry (1986, and references therein) who argued for larger volumes of water to have passed through the area during progressive metamorphism. Precise calculations by Ferry, which showed the fluid composition was mainly H_2O, were based on metamorphic mineral assemblages, mineral compositions, and the P and T of metamorphism.

Sisson & Hollister (1990) argued that the densities of the fluid inclusions were set during metamorphism because the isochores of the CO_2-rich fluid inclusions in quartz segregations passed within error of the metamorphic $P-T$ conditions (Fig. 4). As shown in Table 1, the calculated compositions of the metamorphic fluids show them to be composed predominantly of H_2O, whereas
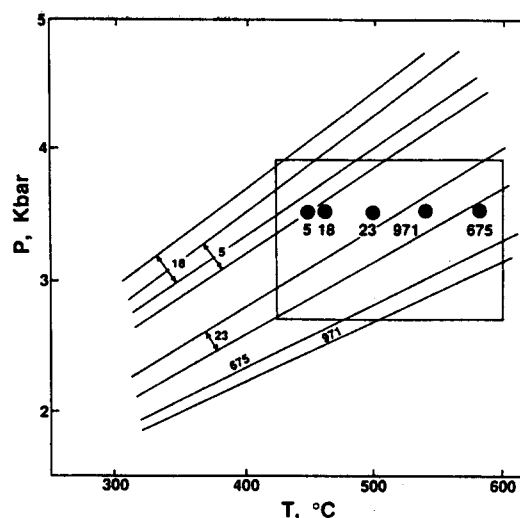

Fig. 4. The large circles represent $P-T$ conditions determined by Ferry (1986 and references therein) for the sample numbers indicated. The rectangular box includes the range of error for all the samples. The lines, also labeled by sample numbers, are for isochores for CO_2-rich fluid inclusions. For samples 5, 18 and 23, ranges of isochores for fluid inclusions in each sample are indicated by the double-headed arrows. For each sample, there is a progressive increase of equilibration temperatures, at a given pressure, for the fluid inclusions which correlate with the progressive increase of metamorphic temperatures determined by Ferry. Furthermore, the isochores pass through the uncertainty box for the $P-T$ conditions. The data indicate that the CO_2-rich inclusions could have been trapped at the conditions of metamorphism. Adapted from Sisson & Hollister (1990).

the fluid inclusion compositions are CO_2-rich. Arguments for several possible ways to interpret the results are given in Sisson & Hollister (1990). The crystal-plasticity model for selective leakage of H_2O posed here may also apply to some of the data from Maine.

Other support for leakage of H_2O from fluid inclusions during crystal-plastic deformation is found in the description of fluid inclusions in stromatic migmatite by Olsen (1987). She described CO_2-rich inclusions in the leucosomes with densities appropriate for the conditions of migmatization, although for those conditions only an H_2O-rich fluid could have been present along with partial melt. In the leucosome, she described polygonization of the boundaries of alkali feldspar grains which imply that they, and therefore the quartz in the leucosome, had experienced crystal-plastic deformation at high temperature. An interpretation of these data is

Table 1. CO_2 content of observed vs predicted fluid compositions

T (°C)	Observed*	Predicted+
450	0.7–1	0.14–0.16
450	1	0.14–0.16
460	1	0.26
460	1	<0.96
490	0.9–1	—
505	0.9–1	0.31
540	−0.05	0.23
550	0.67–1	0.2–0.38
550	0.4 –1	0.13
560	0.4 –1	0.17

*X_{CO_2} as observed in the earliest generation of fluid inclusions. From Sisson & Hollister (1990).

+X_{CO_2} as predicted by Ferry (1986, and references therein).

that during strain H_2O may have been drained from original inclusions containing H_2O and CO_2.

Olsen (1988) also described CO_2-rich fluid inclusions in the migmatite leucosomes which are much denser than would be appropriate for the $P-T$ conditions of migmatization. She noted that they occur along recognizable microshears which are associated with formation of retrograde hydrous phases. She suggested that the aqueous fluid which caused the alteration also locally caused hydrolytic weakening and, where the resulting microshears intersected pre-existing CO_2-rich inclusions, the quartz was able to ductilely contract around the CO_2-rich fluid inclusions until $P_i = P_c$. This explanation is similar to what I propose in calling upon hydrolytic weakening to produce a change of fluid inclusion volume. However, the original inclusions could have contained a mixed $CO_2 + H_2O$ fluid which lost H_2O during the shear strain that she described.

Strain-induced preferential loss of H_2O should lead to enrichment in all other components than CO_2 which do not contribute to dislocation creep. These would include $NaCl$ and $CaCl_2$ as well as CH_4 and N_2. Such a process should be considered as a possible explanation for the extremely concentrated brines reported from mylonitic quartz veins in a shear zone by Kirby *et al.* (1988). Some of the brines reported from metamorphic rocks discussed by Crawford *et al.* (1979a) may also have been enriched in salts by strain-induced leakage of H_2O.

CONCLUSIONS

Crystal-plastic strain in quartz, associated with hydrolytic weakening, is a physically viable mechanism for producing pure CO_2 fluid inclusions by removing H_2O from homogenous $CO_2 + H_2O$ inclusions. It should therefore be added to the list of other possible mechanisms for producing CO_2-rich inclusions discussed in Hollister (1988). If this mechanism can be confirmed, it would resolve the apparent conflict of why densities of CO_2-rich fluid inclusions can reflect metamorphic $P-T$ conditions whereas the compositions do not always reflect what is predicted for the peak metamorphic fluids. Using estimates of temperature of deformation, it may be possible to determine the total confining pressure during deformation from the density of the CO_2 fluid.

Clearly more work can and should be done to demonstrate by controlled field studies whether CO_2-rich fluid inclusions can originate in the way proposed, and it should be experimentally feasible to quantify the parameters controlling the process. The published data suggest that integrated deformation, metamorphism and fluid inclusion studies are needed in order to determine under what situations fluid inclusion densities can be used to constrain $P-T$ conditions of metamorphism, of deformation, or of both operating together.

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