Methane in fluid inclusions from granulites: A product of hydrogen diffusion?

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Abstract—Many fluid inclusion studies of granulite grade rocks reveal the presence of CO\(_2\)-rich inclusions that appear to have been trapped near the peak of metamorphism. Final melting temperatures of CO\(_2\) [\(Tm(CO_2)\)] reported for these inclusions are often below the CO\(_2\) triple point of \(-56.6^\circ C\), and some are below \(-60^\circ C\). This freezing-point lowering is usually attributed to the presence of a second volatile component, such as CH\(_4\), and the presence of CH\(_4\) has been confirmed in some cases by Raman or mass spectroscopy. A CO\(_2\) melting temperature near \(-56.6^\circ C\) is commonly offered as evidence that the inclusions contain "nearly pure CO\(_2\)". However, significant amounts of CH\(_4\) may be present but cause seemingly insignificant freezing point depressions.

C-O-H fluid speciation calculations for conditions representative of granulite facies metamorphism indicate that CH\(_4\) may comprise a significant portion of peak metamorphic fluids when graphite is present, but it is never a significant species in CO\(_2\)-rich fluids. In most cases the amount of CH\(_4\) should be virtually undetectable with microthermometric or spectroscopic techniques. Only in aqueous fluid inclusions can CO\(_2\) and CH\(_4\) both be significant species. Post-trapping speciation changes to fluid inclusions at constant mass cannot account for the reported compositions unless graphite precipitates in the inclusions. Thus, the observed compositions require post-trapping compositional changes due to loss or gain of components.

We have modeled variations in the fugacities of molecular fluid species in inclusion and matrix fluids during uplift from 6 kb and 800\(^\circ\)C, assuming hypothetical uplift pressure-temperature paths which are concave or convex toward the temperature axis (T-concave and T-convex, respectively). Our results suggest that for rocks buffered at \(fO_2\) within one log unit of the fayalite-magnetite-quartz equilibrium (FMQ \pm 1), most uplift paths result in external \(fH_2O\) overpressures of bars to tens of bars at temperatures \(\geq 400^\circ\)C. The highest overpressures are generated during T-concave uplift. Compositional changes resulting from equilibration of such gradients, via diffusive addition of hydrogen to peak metamorphic fluid inclusions and concomitant reduction of CO\(_2\) by conversion to CH\(_4\) and H\(_2\)O, are consistent with the compositions of fluid inclusions reported from granulite terranes.

Previous workers have postulated that CO\(_2\)-rich fluid inclusions in granulites could originate from post-trapping diffusive loss of H\(_2\)O from H\(_2\)O-CO\(_2\) inclusions in response to an \(fH_2O\) gradient between the inclusion and matrix fluids. The results of the present study suggest that for fluids buffered by FMQ \pm 1 this is possible only if (1) uplift is T-convex and the matrix fluid composition remains nearly constant, or (2) the matrix fluid evolves toward relatively H\(_2\)O-poor compositions. The latter could occur if influx of CO\(_2\)-rich fluids occurs during uplift.

INTRODUCTION

THE DISCOVERY of CO\(_2\)-rich fluid inclusions in granulites (TOURET, 1970, 1971; see also ROEDDER, 1984, pp. 375-380) has contributed significantly to models attempting to explain the origin of these rocks while at the same time presenting a conundrum. The presence of these inclusions coupled with mineral assemblages suggesting low water fugacities has been used to infer a CO\(_2\)-rich fluid phase during metamorphism. The origin(s) of these carbonic fluids are the subject of much debate. Mechanisms that have been proposed to explain the CO\(_2\)-rich fluids include (1) partitioning of the aqueous portion of the fluid into a partial melt, which is subsequently removed from the system leaving a CO\(_2\)-rich residual fluid (QUENSEL, 1951; McCARTHY, 1976; NESBITT, 1980), (2) influx of CO\(_2\)-rich fluids from an external source, such as the upper mantle (HARRIS et al., 1982), or from devolatilization of deeply subducted continental shelf sediments (HODGES et al., 1982; DRURY et al., 1984), mafic intrusions (TOURET, 1971; WELLS, 1979) or deeply buried carbonates (GLASSLEY, 1983), (3) scavenging of H\(_2\)O by retrograde hydration reactions (LAMB et al., 1987a; VAN REENEN and HOLLISTER, 1987), and (4) preferential loss of H\(_2\)O by diffusion out of fluid inclusions in response to differential pressure during uplift (ROEDDER, 1981). The first two mechanisms imply that the fluid inclusions are syn-metamorphic while the latter two hypotheses imply, respectively, that trapping of fluid inclusions post-dated metamorphism or that post-trapping compositional changes have altered the original inclusions. The distinction between syn- and post-metamorphic trapping of fluid inclusions is crucial to any model proposed for granulite formation. Unfortunately, most inclusions in granulites are texturally secondary. Inclusion paragenesis is based mainly on comparisons of inclusion compositions and densities with pressure, temperature, and fluid compositions indicated by mineral equilibria, although textural fea-

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tures such as cross-cutting inclusion planes may also be useful (TOURET, 1981; ROEDDER, 1984).

A common problem encountered in these studies is that fluid inclusion densities are too high or too low to have resulted from trapping at inferred peak metamorphic P-T conditions. This may indicate trapping during uplift, i.e., following the peak of metamorphism. Alternatively, re-equilibration of inclusions to both higher and lower densities has been demonstrated during laboratory-simulated burial and uplift (STERNER and BODNAR, 1989). If the uplift path deviates significantly from being isochoric with respect to the densities of inclusions trapped at peak metamorphism, re-equilibration of fluid inclusions to lower or higher densities may occur. In these cases densities (or homogenization temperatures) could not be employed to determine whether the inclusions were trapped at peak metamorphic conditions.

Inconsistencies between fluid compositions implied by mineral equilibria and observed compositions of fluid inclusions are common. Often the fugacity of water implied by mineral equilibria, while low, is not zero and thus is at odds with apparently pure CO₂ fluid inclusions. LAMB et al. (1987b) have provided strong evidence that many CO₂-rich fluid inclusions within low /H₂O and /CO₂ mineral assemblages of the Adirondacks were not trapped during granulite-facies metamorphism. These authors favor a fluid absent model for metamorphism with subsequent trapping of CO₂-rich fluid inclusions during uplift. However, in other terranes (e.g., S. India; Scouri, Scotland; Bamble, S. Norway, and Buksefjorden, S.W. Greenland) the presence of CO₂-rich inclusions is consistent with trapping during metamorphism (NEWTON, 1986).

In this study we evaluate the methane content of CO₂-rich fluid inclusions in granulites and the /O₂ conditions implied by these inclusions. We have calculated the molecular speciation in a C-O-H fluid as a function of pressure, temperature, oxygen fugacity, and activity of carbon (P-T-fO₂-aC) and have compared these results with observed fluid inclusion compositions. Finally, we consider the possibility of post-entrapment compositional changes to fluid inclusions during uplift of granulite terranes as a mechanism to explain apparent inconsistencies between observed and calculated compositions.

**FLUID INCLUSIONS FROM GRANULITES**

A survey of the literature reveals that final melting temperatures of CO₂ [Tm(CO₂)] in fluid inclusions from granulites are often depressed below the triple point value for the pure CO₂ system (~56.6°C), indicating that other constituents are present. A cumulative histogram of Tm(CO₂) from 7 studies (Fig. 1) reveals values for Tm(CO₂) ranging from ~55.5°C to >-62.5°C with a mean near ~57.5°C. We do not claim that these studies are entirely representative of Tm(CO₂) from granulites; however, they do encompass ranges reported in other studies in which actual data is not tabulated (e.g., SCHREURS, 1984; KREULEN and SCHUILING, 1982; HANSEN et al., 1984). Furthermore, the presence of CH₄ has been mentioned in additional studies (e.g., PERCHUK et al., 1985; CHACKO et al., 1987; TOMILENKO and CHUPIN, 1983).

Some of the data included in Fig. 1 are from inclusions which have been interpreted to be secondary based on textural relationships and/or densities. However, as outlined earlier, these criteria are rarely unequivocal. Some might argue that the magnitude of the freezing-point depression shown on Fig. 1, which ranges from a few tenths of a degree to a few degrees Celsius, is not significant but, rather, reflects the accuracy of the measurement. In some cases this may be true. However, the reported accuracy and precision of the measurements is generally ±0.1°C to ±0.5°C and we accept these values as being correct.

Of the possible components that can cause depression of Tm(CO₂), methane and nitrogen are the most common. Methane has been detected during analysis of inclusions from granulites using Raman spectroscopy (RUDNICK et al., 1984; SCHREURS, 1984), mass spectrometry (TOMILENKO and CHUPIN, 1983), and gas chromatography (SWANENBERG, 1980; KREULEN and SCHUILING, 1982); however, in many studies such analyses have not been conducted and it is unresolved what additional component(s) are causing the depressions in Tm(CO₂), although CH₄ is a reasonable possibility.

Figure 2 shows the CH₄ content of a binary CO₂-CH₄ inclusion as a function of Tm(CO₂). Because CH₄ is partitioned into the vapor phase, and Tm(CO₂) is a function only of the amount of CH₄ in the coexisting liquid phase (see BIRRIS, 1981), actual bulk inclusion compositions in the presence of a significant volume of vapor are more CH₄-rich than indicated by Tm(CO₂). For instance, for a Tm(CO₂) of ~57.5°C a bulk composition of approximately 6 mol% CH₄ is indicated if a negligible vol% vapor is present, while 9.5 mol% CH₄ is indicated if 50 vol% vapor coexists with liquid. Thus, even minor depressions of Tm(CO₂) below ~56.6 indicate that significant quantities of CH₄ may be present. A minimum of about one mol% CH₄ in a fluid inclusion cannot be detected microthermometrically due to the resolution limits of the
and the variance is reduced to 3. By specifying total fluid CO$_2$ ratio indicated by $T_m$(CO$_2$) will be unaffected. Similar quantities of H$_2$O in fluid inclusions identified for the system to be invariant. In the case of graphite clathrate (SEITZ and PASTERIS, 1989). In the absence of differential partitioning, H$_2$O merely acts as a diluent and the CH$_4$ is partitioned into the vapor phase. Data from VAN DEN KERKHOF (1988).

Likewise, Raman and infrared spectroscopy may fail to detect mol% H$_2$O may be undetectable by optical microscopy.

In the preceding discussion, the effect of an aqueous component on the CH$_4$ content indicated by $T_m$(CO$_2$) has been ignored. Due to its wetting characteristics, the aqueous phase forms a rim on the walls of the inclusions and up to 10–20 mol% H$_2$O may be undetectable by optical microscopy. Likewise, Raman and infrared spectroscopy may fail to detect similar quantities of H$_2$O in fluid inclusions (VRY et al., 1987).

If H$_2$O is present, clathrate hydrate should form upon cooling and CO$_2$ or CH$_4$ may be differentially partitioned into the clathrate (SEITZ and PASTERIS, 1989). In the absence of differential partitioning, H$_2$O merely acts as a diluent and the CO$_2$/CH$_4$ ratio indicated by $T_m$(CO$_2$) will be unaffected.

C-O-H FLUID SPECIATION

The speciation of C-O-H fluids at elevated P-T conditions has been calculated using the "equilibrium constants = mass balance" technique (FRENCH, 1966; EUGSTER and SKIPPEEN, 1967; OHMOTO and KERRICK, 1977; FERRY and BAUMGARTNER, 1987; HOLLOWAY, 1987). For a homogeneous C-O-H fluid in the system C-O-H the phase rule dictates that four variables can be independently and arbitrarily varied (within limits as indicated by the phase diagrams) without causing a phase change. Hence, four variables must be specified for the system to be invariant. In the case of graphite saturation two phases are present (graphite + C-O-H fluid) and the variance is reduced to 3. By specifying total fluid pressure ($P_{\text{fluid}}$), temperature (T), oxygen fugacity ($f_{O_2}$), and the activity of carbon ($a_c$), which is defined to be 1 at graphite saturation, the system is completely constrained. We have assumed that the only species present are H$_2$, O$_2$, H$_2$O, CO$_2$, CO, and CH$_4$. These are related through the linearly independent reactions

$$\begin{align*}
C + O_2 &= CO_2 \\
CO + \frac{1}{2}O_2 &= CO_2 \\
H_2 + \frac{1}{2}O_2 &= H_2O \\
CH_4 + 2O_2 &= CO_2 + 2H_2O
\end{align*}$$

and the constraint that

$$\sum x_i = 1 \tag{5}$$

where $x_i$ is the mole fraction of component $i$. The mole fractions of species are related to their fugacities through the equation

$$f_i|_{\text{fluid},T} = \Gamma_i x_i \gamma_i P_{\text{fluid}} \tag{6}$$

Fluid speciation was calculated using functions describing the equilibrium constants for reactions (1)–(4) presented in OHMOTO and KERRICK (1977). The procedure was modified to allow for nonideal mixing of fluid species and for carbon activities less than 1. For ideal mixing, fugacity coefficients for H$_2$O, CO$_2$, and H$_2$ below 3 kb were taken from BURNHAM et al. (1969), BURNHAM and WALL (unpubl. data), and SHAW and WONES (1964), respectively. Ideal mixing fugacity coefficients for CO, CH$_4$, and H$_2$ above 3 kb were calculated from the reduced variable equations of RYZHENKO and VOLKOV (1971). For nonideal mixing, fugacities were calculated from the equation

$$ln (f_i) = ln \left( \left[ \frac{V}{V(RT)} \right] a_i \right) + b_i \left( \frac{V}{V(RT)} \right)$$

(FLowers and HELGESON, 1983), where $V$ is the mean molar volume of the fluid mixture, $a$ and $b$ are empirical coefficients of the Redlich-Kwong equation of state, subscript $m$ refers to the fluid mixture, subscripts $i$ and $j$ refer to individual fluid components, subscript $ij$ refers to interaction between unlike molecules $i$ and $j$, and $R$ is the gas constant. The terms $a$ and $b$ were calculated using the subroutine MKRMIx (HOLLOWAY, 1981). The general Redlich-Kwong equation was then solved explicitly for mean molar volume. In order to calculate the mixing terms the mole fractions of the species must be known. These were obtained by iteration: Ideal mixing was initially assumed to calculate the nonideal mixing fugacity coefficients. The resulting mole fractions then became the new mole fractions to re-calculate the nonideal mixing fugacity coefficients. Using this procedure convergence was usually achieved in about six iterations. The criterion for

**Figure 2.** Final melting temperature of solid CO$_2$ [$T_m$(CO$_2$)] and corresponding bulk mol% methane in CO$_2$-CH$_4$ fluid inclusions for negligible (~0 vol%) and 50 vol% vapor present at $T_m$(CO$_2$). $T_m$(CO$_2$) is insensitive to the amount of vapor present but the bulk mol% methane for a given $T_m$(CO$_2$) will vary from the limiting value at ~0 vol vapor to some higher value as the vol% vapor increases because CH$_4$ is partitioned into the vapor phase. Data from VAN DEN KERKHOF (1988).
convergence is that the relative variation in mole fraction between two successive iterations is less than $10^{-4}$ for all species, by the relation

$$\text{abs}(x^t_i - x^{t-1}_i) / x^t_i < 10^{-4} \quad (9),$$

where $k$ is the iteration number.

Mineral thermobarometry generally indicates pressures of 6–9 kb and temperatures of 700–1000°C for granulite facies metamorphism (Bohlen, 1987; Valley, 1987). Although granulites show a wide range of oxidation states from graphite-bearing varieties to varieties containing hematite (Newton, 1986), most oxygen fugacities indicated by coexisting magnetite-ilmenite solid solutions or orthopyroxene-bearing assemblages suggest /O₂ within 1 to 2 log units of the fayalite-magnetite-quartz equilibrium (FMQ ± 1–2) (e.g., Rollinson, 1980; Perkins et al., 1982; Hansen et al., 1984; Lamb and Valley, 1984; Schreurs and Westra, 1986; Weber and Barbee, 1986). We have calculated C-O-H fluid speciation over the P-T range 1–8 kb and 400–800°C at three /O₂ conditions: FMQ + 1, FMQ and FMQ − 1. We have contoured isopleths of constant mol% CO₂ and CH₄ in P-T space at these three /O₂ conditions (Fig. 3, a–f) because we are concerned with speciation among the carbonic species. At temperatures below the graphite maximum (graphite stable region), $a_ν = 1$. At temperatures above the graphite maximum, $a_ν$ is defined as 0.6 for /O₂ = FMQ and 0.06 for /O₂ = FMQ + 1. These values of $a_ν$ were chosen in order to generate low water fugacities at P-T conditions of granulite-facies metamorphism. Over the P-T-/O₂ conditions considered here the fluid can be adequately modeled as a mixture of the three species CO₂, CH₄, and H₂O, all other species combined generally comprising less than 1 mol% of the fluid. Thus, the balance of the fluid not contoured in Fig. 3 is composed essentially of H₂O. It is evident from Fig. 3 that at granulite pressures and temperatures the fluid phase should be dominantly a binary CO₂-H₂O fluid, except at low /O₂ where CH₄ may comprise several mol% of the fluid (Fig. 3f). The presence of primary graphite in some granulites (Hollister and Burress, 1976; Rudnick et al., 1984; Chacko et al., 1987) is consistent with metamorphism at /O₂ conditions at or below FMQ. Above the graphite maximum, the fluid phase may vary from essentially pure H₂O to pure CO₂, depending on the activity of carbon. One trend which is clear from Fig. 3 is that methane should never be a significant species in H₂O-poor fluids at any P-/O₂ conditions of granulite facies metamorphism. In general, CO₂ and CH₄ can both be significant species only in fluids which contain appreciable H₂O, and then only at relatively low P-/O₂ (e.g., Fig. 3 e–f).

Methane contents at reasonable granulite P-/O₂ conditions should not exceed ~0.2 mol% in CO₂-rich fluids and should reach this value only when graphite is present. Above the graphite maximum methane contents are uniformly low (<0.01 mol%). The small quantity of CH₄ predicted at granulite-facies metamorphic conditions would be undetectable in fluid inclusions with current microthermometric and spectroscopic techniques.

These results are consistent with those of other workers (e.g., Lamb and Valley 1985; Lamb et al., 1987b) who have used similar calculations to show that CO₂-rich inclusions containing appreciable CH₄ are incompatible with estimated P-T-/O₂ conditions of granulite facies metamorphism. It has been suggested in these studies that leakage, re-equilibration or late-stage trapping, even for those aberrant inclusions that “appear to be primary” (Lamb and Valley, 1985), may explain the discrepancies. However, the details of these mechanisms, or direct evidence for a particular one, have not been presented.

Results described above present us with a dilemma. Fluid calculations predict that CO₂-rich inclusions from granulites should contain only trace quantities of CH₄, while fluid inclusions reported from some granulites commonly contain greater than 6 mol% CH₄. Assuming that our calculations adequately model fluid speciation at conditions of granulite-facies metamorphism, then either the inclusions were not trapped at peak metamorphism or they have undergone post-trapping compositional changes. Our calculations suggest that the observed fluid compositions require trapping at low P and /O₂ and fairly high T (e.g., 0.2 kb, FMQ-1 and 700°C; Fig. 3e–f) during uplift. Such inclusions would have low densities and their isochors would not pass through peak metamorphic conditions.

**POST-TRAPPING CHANGES IN FLUID COMPOSITION**

**Closed system**

One possible explanation for the discrepancy between calculated and observed fluid compositions is that compositions recorded in fluid inclusions at room temperature are *not* representative of fluid compositions originally trapped, owing to post-trapping re-equilibration among fluid species during cooling. We have calculated speciation changes in model fluid inclusions trapped at various P-T-/O₂ conditions using methods outlined by Holloway (1981) and Dubessy (1984).

A fluid inclusion is assumed to contain a fluid of known composition and molar volume at some initial P-T condition (e.g., of trapping or observation). By specifying an arbitrary inclusion volume at this P-T and assuming the system remains isovolumetric, or by correcting for thermal expansion and compressibility of the host, the new composition, molar volume, and internal pressure of the fluid inclusion at some final temperature may be calculated. This is accomplished via the functions describing equilibrium constants for reactions (2)–(4) (Ohmoto and Kerrick, 1977). Equ. (3), and the additional mass balance constraints

$$\Sigma n_i C = \Sigma n_i C$$

$$\Sigma n_i O = \Sigma n_i O$$

$$\Sigma n_i H = \Sigma n_i H$$

where $n_i$ and $n_i$ are the initial and final moles, respectively, of carbon, oxygen, or hydrogen in the inclusion. Fugacity coefficients for H₂, O₂, H₂O, CO₂, CO, and CH₄ are calculated using Holloway's (1981) program MRKMIX. The new P-V-X properties of the inclusion are obtained at the new temperature by simultaneously solving six equations (3 describing fluid speciation and 3 describing mass balance) using New-
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Mole % CO₂  Mole % CH₄

**FIG. 3.** P-T projections contoured for isopleths of mol% CO₂ (a, c, and e) and CH₄ (b, d, and f), at fO₂ defined by fayalite-magnetite-quartz ± 1 log unit (FMQ ± 1). The activity of carbon is defined as 1 below (low T side) the graphite maximum (gr) and is arbitrarily defined to be 0.6 and 0.06 above the graphite maximum for FMQ and FMQ + 1, respectively.

A temperature of 400°C was chosen as the minimum temperature for our calculations for three reasons. Firstly, this is the lower temperature limit of Holloway's equation for aqueous fluids. Secondly, it is questionable if chemical equilibrium is attained among carbonic fluid species at temperatures much below 400°C (SACKETT and CHUNG, 1979; HARTING and MAASS, 1980; ZIEGENBEIN and JOHANNES, 1980). Thirdly, limiting our calculations to >400°C allowed us to neglect the effects of fluid immiscibility over the P-T conditions considered here.

Figure 4 shows the speciation changes generated upon cooling a fluid inclusion, which was trapped at 6 kb, 800°C and fO₂ = FMQ, to 400°C. At the time of entrapment, the inclusion contains 83.6 mol% CO₂, 15.4 mol% H₂O, 0.006 mol% CH₄, 0.9 mol% CO, and 0.05 mol% H₂. At 400°C the inclusion composition has changed to 84.7 mol% CO₂, 15.1 mol% H₂O, 0.2 mol% CH₄, 0.01 mol% CO, and 0.006 mol% H₂. While the amounts of the major components CO₂ and H₂O remain nearly constant, the concentrations of minor components including CH₄ change significantly. Although the mole fraction of methane has increased over one order of magnitude, the final concentration is still below the detection limit of microthermometry and probably other spectroscopic techniques as well. Our calculations for other trap-
ping conditions suggest that post-trapping, closed system speciation changes may produce maximum CH₄ contents of perhaps 1 mol%, which is insufficient to account for phase relations described from natural fluid inclusions from granulites.

The preceding calculations assumed that graphite does not precipitate in the inclusions during cooling. If graphite were to precipitate, significant quantities of CH₄ may be produced at low temperatures and pressures (Fig. 3; see also DUBESSY, 1984). Graphite-bearing inclusions are not uncommon in granulites (TOURET, 1985; VRY and BROWN, 1987) and often contain detectable to significant quantities of CH₄. Graphite-bearing inclusions sometimes contain more CH₄ than apparently coeval graphite-absent inclusions, and it is likely that the methane contents of graphite-bearing inclusions (and the implied fO₂ conditions) are not representative of the values at trapping. In the absence of graphite precipitation, however, the presence of detectable methane is inconsistent with predicted fluid compositions. We are left with the hypothesis that the inclusions have changed bulk composition due to preferential loss or gain of fluid components and not by closed system changes in speciation during cooling.

Open system

Recent studies (e.g., PASTERIS and WANAMAKER, 1988; STERNER et al., 1988, HALL et al., 1989a, b) have shown that fluid inclusions can change composition at elevated temperatures and pressures during laboratory experiments. The mechanisms of exchange, the conditions under which these changes occur, and the actual species which are diffusing have not been fully investigated, but it is clear that fugacity gradients between inclusion fluids and matrix fluids play a key role in the process. In order to investigate the possibility that high methane contents in granulite fluid inclusions result from inward hydrogen diffusion and conversion of CO₂ to CH₄ + H₂O via the reaction

$$\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O} \quad (13)$$

we have modeled the variations in fluid composition in the host rock (e.g., grain boundary fluids) and fluid inclusions during uplift assuming the granulite host is continuously buffered by FMQ + 1, FMQ or FMQ - 1. During uplift the host rock fluid composition will be a function of the uplift path, and several different P-T-time paths have been proposed for granulites (Fig. 5). Two endmember types of uplift paths are noted, one which is concave toward the temperature axis (hereafter referred to as T-concave uplift) and one which is convex toward the temperature axis (hereafter referred to as T-convex uplift). From these we constructed two hypothetical paths from peak metamorphic conditions of 6 kb and 800°C (Fig. 6) and then calculated matrix fluid compositions along these paths assuming that the fO₂ of the fluid is buffered by FMQ + 1, FMQ or FMQ - 1.

The variation in /H₂ during T-concave and T-convex uplift is shown in Fig. 7. Also shown are the /H₂ variations in a model fluid inclusion trapped at 6 kb and 800°C during cooling at constant volume. The graphite maximum is shown schematically by vertical dashed lines; due to the pressure dependence of the graphite maximum it intersects the two uplift paths at different temperatures. The activity of carbon
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FIG. 7. Variation in $f_{\text{H}_2}$ in matrix (host) fluids and a model fluid inclusion as a function of temperature at FMQ + 1 (a), FMQ (b) and FMQ - 1 (c). Pressures along the T-concave and T-convex host uplift paths are constrained from Fig. 6. The internal pressure of the fluid inclusion is dictated by the $P$-$V$-$T$-$X$ properties of the trapped fluid and the assumption that the inclusion maintains a constant volume. The maximum stability of graphite along a particular $f_{\text{O}_2}$ buffer is shown schematically by vertical lines in a and b, where the dashed line corresponds to T-concave uplift and the dotted line corresponds to T-convex uplift. Above the graphite maximum the activity of carbon is defined to be 0.04 in a and 0.4 in b. Graphite is stable over all P-T considered in Fig. 7c and the activity of carbon is defined as 1.

During both T-concave and T-convex uplift significant $f_{\text{H}_2}$ overpressures may be generated by matrix fluids. Maximum $f_{\text{H}_2}$ gradients between inclusion and matrix range from 5 to 25 bars for T-concave uplift, depending on $f_{\text{O}_2}$ (Fig. 7). The higher $f_{\text{H}_2}$ attained in the matrix fluid during T-concave uplift is due to the higher total fluid pressure (Fig. 6). Given the high diffusion rates of hydrogen through quartz at elevated temperatures (KATS, 1962; KATS et al., 1962; KRONENBERG et al., 1986), it is unlikely that $f_{\text{H}_2}$ gradients of the magnitudes indicated in Fig. 7 could be maintained for geologic time, and it is probable that at least partial re-equilibration would occur via hydrogen transport into fluid inclusions. For instance, the diffusion coefficient for hydrogen in $\beta$-quartz at 800°C is $2 \times 10^{-11}$ m²/sec (KRONENBERG et al., 1986). This corresponds to about 0.07 mm/hr. The average path length for diffusion of hydrogen from grain boundaries into fluid inclusions is on the order of 1 mm. Thus, within a few hours inclusions can be in hydrogen communication with matrix fluids, and over geologic time significant amounts of hydrogen could enter the fluid inclusions.

Hydrogen diffusion into CO$_2$-$\text{H}_2$O fluid inclusions and concomitant reduction of CO$_2$ to CH$_4$ (+H$_2$O) via reaction (13) has been verified experimentally (HALL et al., 1989b). Fluid inclusions containing 50 mol% CO$_2$ were synthesized in Brazilian quartz at 825°C and 3 kb. The inclusions were then re-equilibrated for 15 days at 650–825°C and 1.5 kb at $f_{\text{H}_2}$ conditions defined by the graphite-methane buffer (~100–250 bars). Preliminary results indicate that inclusions with initial $T_m$(CO$_2$) = -56.6 ± 0.1°C now have $T_m$(CO$_2$) as low as -65.4°C. Raman spectroscopic analysis indicated only the presence of CO$_2$ (+H$_2$O) in the original inclusions, whereas large quantities of CH$_4$ and detectable H$_2$ were present, in addition to CO$_2$ and H$_2$O, in re-equilibrated inclusions. Perhaps the most significant aspect of these results is that hydrogen diffusion into fluid inclusions occurred in spite of the 0.825–1.5 kb internal overpressures during re-equilibration. This observation indicates that it is the fugacity of hydrogen and not the total pressure that is driving diffusion.

We have modeled the effects of hydrogen diffusion on the P-V-X properties of a CO-H fluid inclusion trapped at 6 kb, 800°C, and FMQ. The procedure used to calculate closed system speciation changes was modified to allow for changes in total hydrogen content. Addition of an arbitrary amount of hydrogen to a fluid inclusion is assumed to occur at a given temperature and the equilibrium speciation is recalculated based on the modified bulk composition of the inclusion. Figure 8 shows the effect of addition of hydrogen on the $f_{\text{H}_2}$ inside the fluid inclusion assuming addition occurs at 450°C or 550°C. The percentage of hydrogen which is added to the inclusion (Fig. 8) is relative to the amount of total hydrogen originally present in the inclusion (i.e., $2n$H = 2nH$_2$O + 2nH$_2$ + 4nCH$_4$), so that 100% diffusion corresponds to adding an amount of hydrogen equal to the total amount originally present. Because the original inclusion was relatively hydrogen-poor (i.e., 0.3 moles H per mole of fluid, compared to 1.84 moles O per mole of fluid) a small amount of hydrogen diffusion contributes significantly to the total hydrogen content. It should be emphasized that these calculations do not incorporate any diffusion coefficients and that instantaneous additions of the given amounts of hydrogen are assumed.

As expected, $f_{\text{H}_2}$ inside the inclusion increases as progressively more hydrogen is added to the inclusion. At 550°C
the initial $f_{H_2}$ inside the inclusion is 4 bars while that of the matrix, assuming T-convex uplift, is 13 bars (Fig. 7b). If hydrogen diffusion were allowed to progress to completion (i.e., to the point where the $f_{H_2}$ inside the inclusion equals 13 bars), 175% of the total hydrogen originally present in the inclusion (i.e., contributed from the species H$_2$O, CH$_4$, and H$_2$) is assumed to be in equilibrium.

The mole fraction of CO$_2$ decreases while those of CH$_4$ and H$_2$O increase (Fig. 9). After 175% hydrogen addition, the amount required to equilibrate inclusion and matrix $f_{H_2}$ during T-convex uplift to 550°C, the $f_{H_2}$ in the matrix would be 25 bars and 275% hydrogen must be added to equilibrate $f_{H_2}$ (Fig. 7b; Fig. 8).

Speciation changes resulting from hydrogen diffusion are significant. Figure 9 shows the variation in mol% CO$_2$, H$_2$O, and CH$_4$ during progressive hydrogen diffusion at 550°C. Addition of hydrogen causes reduction of CO$_2$ to CH$_4$ via reaction (13). The mole fraction of CO$_2$ decreases while those of CH$_4$ and H$_2$O increase.

Effectively constant, such as would occur if uplift followed one of the isopleths of CO$_2$ shown in Fig. 3. In this case the ratios of various species are similar inside and outside the inclusion. Methane concentrations on the order of 5-10 mol% may be produced in inclusions which contained negligible CH$_4$ at the time of entrapment. These concentrations are consistent with Tm(CO$_2$) of granulite fluid inclusions (ROEDDER, 1981). The driving force for such diffusion is an $f_{H_2O}$ gradient between inclusion and matrix. This mechanism has been shown to be experimentally viable at granulate temperatures for saline synthetic fluid inclusions in Brazilian quartz (STERNER et al., 1988; HALL et al., 1989a), and thus might be expected in similar geologic environments.

We have plotted the variation in $f_{H_2O}$ of matrix fluids during T-convex and T-concave uplift, and the $f_{H_2O}$ inside our model fluid inclusion trapped at 6 kb, 800°C, FMQ, and $a_k = 0.4$ to test this possibility (Fig. 10). Pressure-temperature conditions in the host rock during uplift are the same as in Fig. 7. Compositions more H$_2$O-rich can be generated by specifying $a_k < 0.4$, in which case the $f_{H_2O}$ at trapping would be greater than that shown in Fig. 10 and the loci of $f_{H_2O}$ in the inclusion during uplift would be translated to higher values.

Over much of the uplift history $f_{H_2O}$ is higher in the matrix than in the inclusion, particularly during T-concave uplift. Thus, H$_2$O would be expected to diffuse into, and not out of, fluid inclusions during uplift. Exceptions occur if the uplift is strongly T-convex and the fluid composition remains relatively constant, such as would occur if uplift followed one of the isopleths of CO$_2$ shown in Fig. 3. In this case the ratios of various species are similar inside and outside the inclusion but the total pressure, hence $f_{H_2O}$, inside the inclusion is

**DIFFUSION OF H$_2$O**

Preferential diffusive loss of H$_2$O from CO$_2$-H$_2$O inclusions has been postulated to explain the occurrence of nearly pure CO$_2$ inclusions in granulites (ROEDDER, 1981). The driving force for such diffusion is an $f_{H_2O}$ gradient between inclusion and matrix. This mechanism has been shown to be experimentally viable at granulate temperatures for saline synthetic fluid inclusions in Brazilian quartz (STERNER et al., 1988; HALL et al., 1989a), and thus might be expected in similar geologic environments. We have plotted the variation in $f_{H_2O}$ of matrix fluids during T-convex and T-concave uplift, and the $f_{H_2O}$ inside our model fluid inclusion trapped at 6 kb, 800°C, $f_0_2 = FMQ$, and $a_k = 0.4$ to test this possibility (Fig. 10). Pressure-temperature conditions in the host rock during uplift are the same as in Fig. 7. Compositions more H$_2$O-rich can be generated by specifying $a_k < 0.4$, in which case the $f_{H_2O}$ at trapping would be greater than that shown in Fig. 10 and the loci of $f_{H_2O}$ in the inclusion during uplift would be translated to higher values.

Over much of the uplift history $f_{H_2O}$ is higher in the matrix than in the inclusion, particularly during T-concave uplift. Thus, H$_2$O would be expected to diffuse into, and not out of, fluid inclusions during uplift. Exceptions occur if the uplift is strongly T-convex and the fluid composition remains relatively constant, such as would occur if uplift followed one of the isopleths of CO$_2$ shown in Fig. 3. In this case the ratios of various species are similar inside and outside the inclusion but the total pressure, hence $f_{H_2O}$, inside the inclusion is

![Figure 8. Variation in $f_{H_2}$ in a model fluid inclusion trapped at 6 kb, 800°C, FMQ, and $a_k = 0.4$ and subsequently cooled to 550°C or 450°C, at which point hydrogen is added to the inclusion. The percent of hydrogen added is referenced to the total amount of hydrogen originally contained in the inclusion (i.e., contributed from the species H$_2$O, CH$_4$, and H$_2$) (D. L. Hall and R. J. Bodnar).](image)

![Figure 9. Variation in mol% CO$_2$, H$_2$O, and CH$_4$ during hydrogen diffusion at 550°C under the same conditions described in Fig. 8.](image)
higher than outside. Diffusion of water out of fluid inclusions is also feasible if matrix fluids evolve toward more H₂O-poor compositions during uplift. This may occur if fluids undersaturated with respect to graphite become saturated, perhaps due to influx of CO₂-rich fluids from an external source. In graphite-saturated fluids near the graphite maximum, the fluid is essentially pure CO₂ (Fig. 3). Secondary graphite is sometimes found in granite terranes, suggesting that graphite saturation was reached in matrix fluids during uplift of these areas. Thus, CO₂-rich fluids may be present in the matrix after peak metamorphism, consistent with the proposed paragenesis for these inclusions in some terranes (LAMB et al., 1987b).

CONCLUSIONS

Calculations of fluid speciation for P-T/0₂-a, conditions consistent with granite facies metamorphism predict that methane contents should be uniformly low in CO₂-rich fluids. Despite this result, many fluid inclusions which have apparently been trapped during or shortly after granite-facies metamorphism contain on the order of 6 to 10 mol% methane relative to CO₂ + CH₄. Post-entrapment, closed system speciation changes in fluid inclusions do not produce detectable amounts of CH₄ unless graphite precipitates within the inclusions, and even then the amounts produced may be small.

Modeling of uplift paths which are concave (T-concave) and convex (T-convex) toward the temperature axis suggests that decompression and cooling from conditions of granite facies metamorphism may result in H₂O gradients between inclusion and matrix fluids during uplift of these areas. Thus, CO₂-rich fluids may be present in the matrix after peak metamorphism, consistent with the proposed paragenesis for these inclusions in some terranes (LAMB et al., 1987b).

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