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Graphite precipitation in C–O–H fluid inclusions: closed system compositional and density changes, and thermobarometric implications

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Abstract Equilibrium C–O–H fluid speciation calculations predict that graphite will precipitate from initially graphite saturated fluid inclusions during cooling and exhumation of metamorphic rocks. In the case that no mass is gained or lost by the inclusions, the original X_{O} ratio $[\text{O}/(\text{O} + \text{H})]$ of the fluid phase must be maintained. Given this closed system constraint, the down-temperature progress of graphite precipitation can easily be monitored as a function of the variable X_{O} , and produces some effects that are of significance to fluid inclusion studies: 1. Variation of the $\text{H}_2\text{O}:\text{CO}_2:\text{CH}_4$ relationship in the graphite-saturated COH fluid, namely increase of $X_{\text{H}_2\text{O}}$ and decrease of the carbonic fraction; 2. Decrease of fluid density due to precipitation of graphite, which is denser than the residual fluid; 3. Alteration of the $\text{CO}_2:\text{CH}_4$ ratio of the fluid, depending on the initial O:H ratio of the fluid: for $X_{\text{O}} > 1/3$, fluids increase their $\text{CO}_2:\text{CH}_4$ ratio with decreasing temperature, and vice-versa. This implies that the $\text{CO}_2:\text{CH}_4$ ratio measured at room T will not represent the trapping value, which is in any case closer to unity. As a consequence of density reduction, isochores extrapolated from densities observed at room temperature do not pass through the pressure-temperature conditions at which the inclusion was trapped, with pressure underestimates of up to 2 kbar. Actual P - T trapping conditions are located along the equilibrium “bulk isochore” (curve of constant- X_{O} , constant-volume) of the fluid. Alteration of the $\text{CO}_2:\text{CH}_4$ ratio is a mechanism by which a CO_2 -rich or CH_4 -rich carbonic phase can be formed from aqueous fluids that are slightly off the neutral $X_{\text{O}} = 1/3$ value. Subsequent

segregation of this phase from the aqueous counterpart may account for the formation of pure CO_2 and CH_4 fluids in the upper crust.

Introduction

Commonly, fluid phase modelling in metamorphic systems is done in the carbon-oxygen-hydrogen (C–O–H) system, that includes the most abundant species observed in rocks and fluid inclusions: H_2O , CO_2 , CH_4 , H_2 , CO (French, 1966; Holloway, 1981).

Graphite or poorly ordered carbon is frequently observed in rocks from all metamorphic grades and even in silicate melts. The presence of graphite adds an important constraint on the thermodynamic behaviour of petrologic systems and indicates that in many cases metamorphic fluids are graphite saturated during both their generation and evolution, and at the times of their trapping as fluid inclusions. Graphite-fluid equilibrium has been inferred in many studies of C–O–H fluid inclusions (e.g. Ramboz et al. 1985; Thomas and Spooner 1988; Cathelineau et al. 1990; Duke et al. 1990; Frezzotti et al. 1994), especially in the presence of methane-bearing fluids (e.g. Alvarenga et al. 1990). In recent times, the importance of graphite-fluid equilibria has been strengthened by the increasingly reported occurrences of graphite in fluid inclusions, made possible by routine micro-Raman spectrometric analysis. Graphite occurs in natural fluid inclusions (e.g. Dubessy 1984; Guilhaumou et al. 1990; Huizenga and Touret 1993; Klemd et al. 1995) or was synthesized in C–O–H fluid inclusions in response to changes in pressure, temperature, f_{H_2} or f_{O_2} (Sterner and Bodnar 1984; Morgan et al. 1993). In several natural examples, graphite was not visible under the optical microscope, but could be detected by Raman analysis (Kerkhof et al. 1991; Wilmart et al. 1991); in other occasions,

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nucleation of graphite in the inclusions was induced by laser irradiation (Kerkhof et al. 1991).

If graphite is not trapped initially (i.e. is not a solid inclusion), the presence of graphite within fluid inclusions is often attributed to speciation reactions during cooling and decompression of C–O–H fluids; alternatively, diffusional loss or gain of components may also induce graphite precipitation (Morgan et al. 1993). The consequences of mass-conserving speciation reactions have been generally neglected or underestimated, and only a few workers (e.g. Kreulen 1987) have raised the question whether graphite-saturated C–O–H (GCOH) fluid inclusions really contain the metamorphic fluid present at trapping. This paper examines this problem, and presents a simple method of treating the limiting model of closed system behaviour for GCOH fluid inclusions. In particular, the possible effects (in part addressed by Dubessy 1984) of equilibrium speciation reactions on the density and composition of the fluid phase in inclusions during cooling and decompression are elucidated. Geologic implications of the compositional changes, particularly the thermobarometric use of fluid inclusion data and the generation of CO₂- and CH₄-rich fluids, are discussed by analysing the end-member model of fluids that are already graphite saturated at the time of entrapment.

The approach taken here is the description of bulk fluid composition by the fluid composition variable

$$X_O (X_O = \frac{n_O}{n_O + n_H}),$$

where n denotes the number of

moles in the fluid), recently proposed for the study and description of petrologic problems involving C–O–H fluids (Connolly and Cesare 1993; Connolly 1995). The utility of this variable is that if a fluid inclusion and its daughter crystal(s) can be regarded as a closed isochoric system, then all the processes of re-equilibration must occur in a way such that the fluid phase maintains its original X_O .

Composition of GCOH metamorphic fluids

C–O–H fluids can be represented in a ternary composition diagram as illustrated in Fig. 1, where GCOH fluid compositions are located along the so-called "graphite saturation surface". The graphite saturation surface separates the two phase field of graphite + C–O–H fluid from the one-phase field of graphite-undersaturated C–O–H fluid. Previous workers have shown that under most geologically reasonable metamorphic conditions GCOH fluids are essentially mixtures of three species (H₂O, CO₂ and CH₄; H₂ and CO being negligible), and that considerable amounts of *both* CO₂ and CH₄ can only be present in H₂O-rich fluids (Lamb and Valley 1985). Given the low concentration of CO and H₂, it follows that X_{CO_2} approximates X_{CH_4} when X_{H_2O} reaches its max-

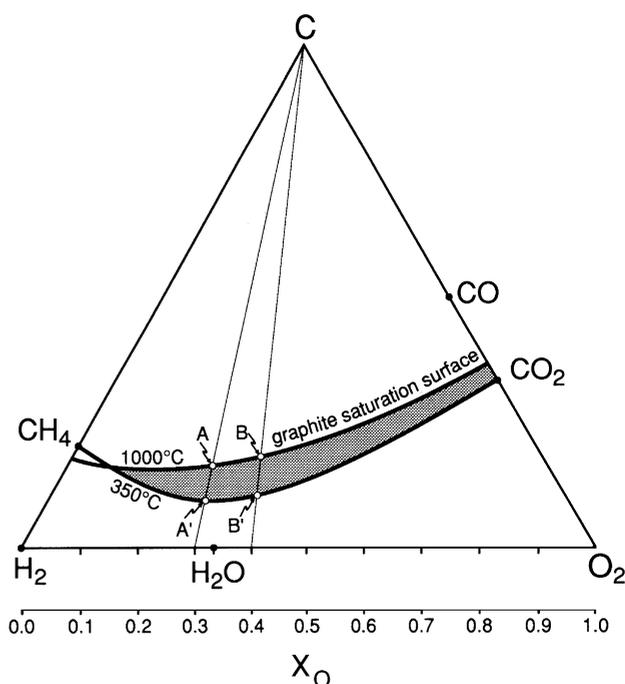


Fig. 1 Schematic C–O–H chemography with calculated graphite saturation curves at 1000°C (1 kbar) and 350°C (polybaric). Lines of constant $X_O = 0.3$ and 0.4 are also shown, with representative fluid compositions at trapping (A, B) and at room conditions (A', B'). Graphite-saturated (GCOH) fluid compositions are constrained to lie along the graphite saturation surface. Graphite-undersaturated (at 1000°C, 1 kbar) fluid compositions projecting within the shaded area will become saturated on cooling, and will precipitate graphite.

imum (i.e. at $X_O = 1/3$, Connolly and Cesare 1993; Connolly 1995).

The speciation of GCOH fluids can be calculated provided that P, T , and any additional property of the fluid is specified. Following the approach of French (1966), isobaric-isothermal C–O–H fluid speciation computations generally are done as a function of f_{O_2} (e.g. Ohmoto and Kerrick 1977; Lamb and Valley 1985), but the variable X_O , can be employed as an alternative constraint. In fact, because the graphite saturation surface is a single-valued function of X_O , this variable provides a better means of characterizing graphite-saturated fluid compositions (Connolly 1995). The advantage of the X_O variable is that it allows the fluid within an inclusion to modify its bulk composition by graphite precipitation (i.e. as in a closed system), since this process leaves the X_O of the fluid unchanged. If the fluid inclusion and its daughter crystal of graphite are assumed to constitute an isochoric system, then the equilibrium speciation of the fluid is uniquely determined for any specified X_O , and fluid density can be estimated from thermodynamic data. This approach is thus ideally suited for fluid inclusion studies, where isochoric-closed system behaviour is a fundamental premise in the retrieval of information about pressure, temperature and composition of metamorphic fluids at trapping. The X_O approach differs significantly from

previous treatments of post-trapping speciation modifications, that have made use of a constant or externally buffered f_{O_2} framework (e.g. Lamb et al. 1987; Hall and Bodnar 1990) and necessarily imply relevant mass changes within the inclusion.

The equilibrium speciation and isochore calculations reported here were done as a function of X_{O} with the computer programs COHSRK, ISO, and SPECIES, recently included in the PERPLEX package (Connolly 1990, 1995); fugacities of pure H_2O , CO_2 , and CH_4 were computed from the HSMRK equation of state (Kerrick and Jacobs 1981; Jacobs and Kerrick 1981) and the fugacities and activities of all other species were computed from the MRK equation (deSantis et al. 1974; Holloway 1977). The MRK parameters are the same as in Connolly and Cesare (1993), and these authors provide a brief discussion of the accuracy of the selected equations of state.

To understand the effect of cooling (and related isochoric decompression) on GCOH fluid inclusions, consider a scenario in which a GCOH fluid is trapped at $T = 1000^\circ\text{C}$ and $P = 1$ kbar, and thereafter cooled to the "equilibration" temperature of 350°C , at which re-speciation ceases. The relative graphite saturation surfaces, calculated as a function of P , T , and X_{O} , are projected on the ternary C–O–H diagram of Fig. 1. Previous workers have generally concluded that equilibration in C–O–H inclusions ceases between 300°C and 400°C (Hall and Bodnar 1990; Dubessy 1984; Dubessy et al. 1989), and the temperature of 350°C is here chosen arbitrarily for purposes of illustration. Lower equilibration temperatures would not affect the position of the graphite saturation surface and fluid speciation as calculated at 350°C , except for the occurrence of immiscibility in the CO_2 – H_2O (Tödheide and Franck 1963) and CH_4 – H_2O (Larsen and Prausnitz, 1984) binaries. Decreasing temperature moves the graphite saturation surface so that for any initial fluid composition that lies at more carbon-rich composition than the CO_2 – H_2O and H_2O – CH_4 joins, equilibrium isochoric cooling invariably requires graphite precipitation (note, in Fig. 1, that this conclusion does not hold for $X_{\text{O}} < \approx 0.1$, conditions at which H_2 comprises a significant fraction of the fluid, so that fluid projection points lie below the H_2O – CH_4 join). As a consequence, although the following discussion and numeric examples refer to end-member fluids that are already graphite saturated (i.e. lie on the graphite saturation surface) at the time of trapping, re-speciation and graphite precipitation on cooling are predicted also for initially graphite undersaturated fluids. In fact, all the initial fluid compositions that project between the trapping and the equilibration graphite saturation surfaces (shaded area in Fig. 1) will become graphite saturated on cooling.

Fluids with initial compositions A and B in Fig. 1 will become depleted in carbon with cooling along lines of constant X_{O} , with final compositions A' and B' as

determined by the 350°C equilibration temperature. Unlike the 1000°C example, the 350°C graphite saturation surface shown in Fig. 1 is polybaric. This follows from the isochoric constraint adopted in the calculation: if fluid inclusions follow isochoric paths, P and T are dependent variables, and pressure values at constant T will differ for each GCOH fluid composition. The qualitative aspects of GCOH fluid behaviour are not affected by the extreme trapping conditions chosen in the example, and are of general applicability. However, in the analysis of real fluid inclusions, the equilibration temperature, and other non-equilibrium factors such as the degree of crystallinity of carbonaceous matter, are a source of uncertainty that must be borne in mind.

Several conclusions can be drawn from Fig. 1:

1. Peak metamorphic fluids are generally richer in carbonic species than equilibrated compositions at the same X_{O} (graphite saturation curve is closer to the C apex); e.g. in Fig. 1 for an $X_{\text{O}} = 1/3$ fluid, $X_{\text{H}_2\text{O}}$ is 0.35 at 1000°C , and increases to 0.67 at 350°C . Exceptions to this behaviour are represented by fluids that project below the H_2O – CH_4 joins, e.g. where H_2 is a significant species: as long as they do not contain N_2 (e.g. Moine et al., 1994) these fluids form at low- P , high- T conditions, and $X_{\text{O}} < 1/3$.
2. CO_2 -rich or CH_4 -rich GCOH fluids are generated for X_{O} approaching 1 or 0, respectively. As noted by Ohmoto and Kerrick (1977) and Kreulen (1987), the only conditions at which CO_2 and CH_4 can be present in comparable amounts is in GCOH fluids at X_{O} close to $1/3$, but in this case fluids are always H_2O -rich.
3. In a closed system, given that H_2O , CO_2 , and CH_4 are the only major species, the GCOH fluid equilibration during cooling can be described by the reaction: $\text{CH}_4 + \text{CO}_2 = 2\text{C} + 2\text{H}_2\text{O}$ (1). In the cases where CO and H_2 comprise a significant fraction of the fluid (e.g. at very low pressure and high temperature), these two species are added as reactants in (1).
4. Chemical evolution of GCOH fluids is constrained along a line of constant X_{O} for a closed system. This directly follows from reaction (1): since the only element removed from the fluid is carbon (to form graphite), the proportions of oxygen to hydrogen in the bulk fluid will not vary.

Point 2 deserves further comment. Many fluid inclusion studies report the presence of water-free CO_2 – CH_4 mixtures (e.g. Cathelineau et al. 1990; Kerkhof et al. 1991; Török 1992), but only a few authors (e.g. Lamb and Valley 1985; Kreulen 1987; Cesare and Hollister, 1995) have noted the metastability of such fluid compositions at any P – T conditions. Furthermore, most of the proposed explanations to such metastability seem hardly acceptable. Any loss or gain of material to change fluid composition (e.g. Duke et al. 1990) cannot explain such paradox if equilibrium conditions are maintained; neither can, as in the case of migmatitic rocks described by Hollister (1988) and

Whitney (1992), the mechanism of selective partitioning of H_2O in a melt: the presumed residual CO_2-CH_4 fluid must react to $H_2O +$ graphite until either equilibrium is reached with water saturation of the melt, or one reactant is consumed. As a consequence, dehydration melting in presence of graphite leaves the graphite content of the rock virtually unchanged. Given that any equilibrium behaviour is unsuited, the only plausible mechanisms for producing CO_2-CH_4 fluids are non-equilibrium processes, if graphite fails either to nucleate or grow. Failure in the nucleation of graphite was also proposed by Bergman and Dubessy (1984) for fluid inclusions in the system C–O. Since graphite nucleation requires a high activation energy (Ziegenbein and Johannes 1980; Mathez and Delaney 1981), such processes are likely to occur at low temperature. Only in this case can H_2O fractionation of both miscible and unmixed fluids (by leakage, diffusion, or crystal-plastic deformation) explain the formation of metastable CO_2-CH_4 mixtures.

Changes of $H_2O-CO_2-CH_4$ relationships

Given that fluid inclusion properties are studied at room $P-T$ conditions after they have undergone post-entrapment cooling (and decompression), the fluid we are observing is likely to have re-equilibrated. It follows that GCOH fluid composition has changed from the “primary” peak graphite saturation curve to the assumed equilibration temperature ($350^\circ C$).

Two primary GCOH bulk fluid compositions (A and B in Fig. 1), with X_O respectively 0.3 and 0.4 (on opposite sides of the neutral composition $X_O = 1/3$) have been chosen for explanation of post-entrapment compositional changes. On cooling and decompression the bulk fluid compositions move along lines of constant X_O until equilibration compositions are reached (A' and B'); with further cooling, the fluid within inclusions is only permitted to modify its internal pressure, but no chemical changes take place. Primary GCOH fluid inclusions do not necessarily contain graphite as solid inclusions at the time of their trapping, so the calculation assumes graphite is initially absent. Fluid speciation at the four points is reported in Table 1. As noted by Dubessy (1984), the largest compositional changes occur in GCOH fluids with X_O close to $1/3$.

Isochorically equilibrated, low-T GCOH fluid is always richer in water than equivalent “peak” fluid. This is a result of the down- T progress of $H_2O +$ graphite producing reactions of the type (1). Simultaneously, the carbonic fraction ($CO_2 + CH_4$) is diminished, and graphite precipitates in the inclusion: in the favourable cases where it forms either a well-shaped daughter crystal or a thin film coating the walls and causing the darkening of the inclusion, graphite presence can be optically detected by careful petrogra-

Table 1 Speciation (mol%) of the GCOH fluid phase, and graphite precipitated (vol.% of the inclusion), at trapping and equilibration conditions of Fig. 1 (points A, A', B and B'), Fig 2a (C and C'), 2b (D and D'), and 2c (E and E').

Id	$P(\text{bar})$	$T(^{\circ}C)$	X_O	H_2O	CO_2	CO	CH_4	H_2	Graphite
A	1000	1000	0.3	0.345	0.163	0.129	0.224	0.139	0
A'	285	350	0.3	0.671	0.126	0.000	0.201	0.002	1.0
B	1000	1000	0.4	0.345	0.243	0.158	0.143	0.111	0
B'	281	350	0.4	0.658	0.241	0.000	0.098	0.001	1.1
C	7000	800	0.379	0.812	0.140	0.002	0.040	0.005	0
C'	1408	350	0.379	0.898	0.100	0.000	0.001	0.000	1.6
D	7000	800	0.333	0.829	0.082	0.002	0.080	0.007	0
D'	714	350	0.333	0.979	0.010	0.000	0.010	0.000	2.8
E	7000	800	0.29	0.791	0.051	0.002	0.147	0.009	0
E'	1424	350	0.29	0.896	0.002	0.000	0.102	0.000	1.8

phy (Dubessy 1984); otherwise, micro-Raman spectroscopy is required.

If GCOH fluid inclusions re-equilibrate under decreasing $P-T$, their composition, as deduced by microthermometry and/or analysed by Raman spectrometry, will not be equal to that of the fluid present at trapping. The first result of re-speciation on cooling is the underestimation of the primary carbonic fraction, which might have been much more abundant at the time of metamorphism and trapping (Table 1 and Fig. 2). Besides the different bulk carbon content of the fluid, which diminishes as a result of graphite formation, also the $H_2O-CO_2-CH_4$ relationships can radically change (see below). Reconstruction of the trapping bulk fluid composition and speciation would require knowledge of the X_O of the fluid and $P-T$ of trapping. Both parameters are very difficult to estimate: the first because of the large uncertainty in determining the H_2O content of the inclusion; the second because $P-T$ values are generally unknown.

Changes of density and isochoric systems: bulk isochores

One of the main purposes of fluid inclusion studies is evaluation of the $P-T$ conditions of fluid entrapment, that relies on the possibility that fluid inclusions may contain the metamorphic fluid present at the time of trapping. The theoretical basis of fluid inclusion thermobarometric methods, as well as assumptions and problems related to this research, are treated by Roedder and Bodnar (1980) and Roedder (1984, cap. 9). Trapping $P-T$ conditions are generally obtained by assuming inclusions to be constant-volume constant-mass systems and by determining the isochoric $P-T$ curve of the fluid (isochore), that represents the locus of the possible $P-T$ values at which the inclusion has formed. Independent knowledge of either P or T at trapping defines the second parameter.

Even if the constant-mass and constant-volume frame is maintained, the chemical changes GCOH fluid inclusions undergo by decreasing $P-T$ conditions have

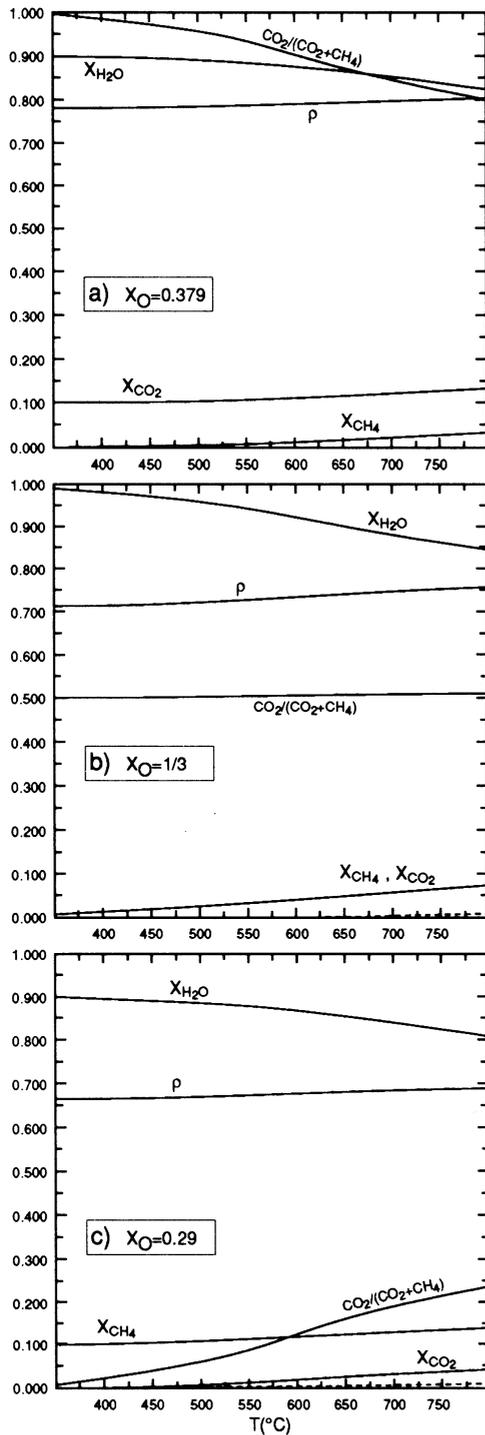


Fig. 2 Chemical and density changes at constant volume of GCOH fluids trapped at 7 kbar, 800° C, with starting X_O value of 0.379 (a), 1/3 (b), 0.29 (c)

important consequences on the possibility of using room P - T compositional data for obtaining meaningful isochores. In fact, equilibrium re-speciation of GCOH fluids determines significant variations in the relative abundance of the fluid species, as well as density changes. The increase of H_2O content is caused by

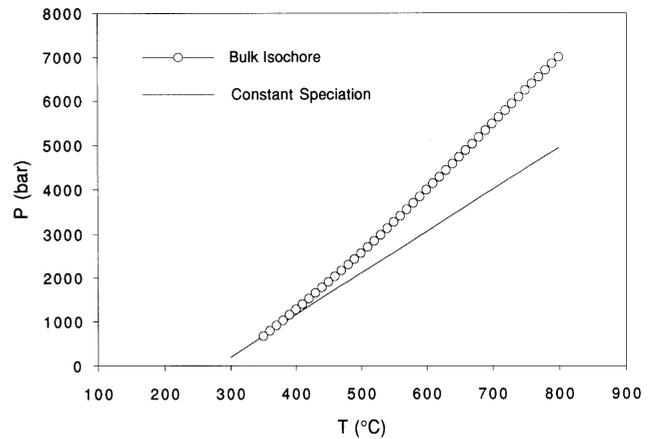


Fig. 3 Bulk isochore and constant-speciation isochore for an $X_O = 1/3$ fluid trapped at 800° C, 7 kbar. The constant-speciation isochore is back-calculated assuming the re-equilibration process stops below 350° C. The displacement between the isochores is maximized for the $X_O = 1/3$ composition

graphite precipitation, which has the counteracting effects of diminishing the effective volume occupied by the fluid and decreasing the mass of the fluid as well. Since the density of graphite is higher than that of the bulk fluid the net result will be a slight decrease of the fluid density (see also Dubessy, 1984).

Density and speciation changes have been calculated for three representative GCOH fluid compositions (Fig. 2), trapped at typical granulite-facies conditions of 800° C and 7 kbar. Density changes are apparently minimal, generally less than 0.04 g/cm³. The effects of increasing H_2O content and decreasing density of the fluid determine the impossibility for the fluid to follow a constant-density, constant-composition isochoric path. Hence, during cooling, the P - T conditions representative of a certain GCOH fluid will have to change continuously to:

1. A different set of isochores, for the continuously H_2O richer composition;
2. A new isochore in each set, pertinent to the continuously decreasing density.

Increasing H_2O content steepens the slope of isochores, whereas decreasing density has the opposite effect. It turns out that the process is dominated by the changes of density that move fluid compositions along isochores with progressively flatter slope.

However, as noted before, variations of density and abundance of species occur under constant X_O values, so that instead of calculating continuously changing arrays of isochores for a starting composition, fluid behaviour can be described more elegantly by the constant X_O "bulk isochore" (Fig. 3). This curve defines conditions of constant volume for the system that comprises the fluid plus its graphite daughter crystal(s). The bulk isochore of Fig. 3 is calculated assuming that after cooling below 350° C there isn't any re-speciation or

further density changes. Fluid will then follow the “constant-speciation” isochore, which corresponds to the isochore that can be calculated from the room properties of the fluid. The constant-speciation isochore, and the bulk isochore for the same fluid intersect at the equilibration temperature of 350° C, but have different P - T slopes, the bulk isochore being steeper. Thus, the constant-speciation isochore extrapolated to $T > 350^\circ\text{C}$ does not pass through the real P - T trapping conditions, which are instead located along the “bulk isochore”. Improper use of the constant-speciation isochore causes pressure to be underestimated (in the present example by about 2 kbar), or alternatively, overestimation of temperature (by about 200° C). These errors are directly proportional to the trapping temperature, and are maximized for $X_O = 1/3$ fluids.

Changes in the CO_2/CH_4 ratio of the carbonic fraction

An important consequence of constant-mass fluid re-speciation upon cooling is the change of CO_2/CH_4 ratio of the carbonic fraction, as can be monitored on a C–O–H diagram, if X_O and $\text{CO}_2/(\text{CH}_4 + \text{CO}_2)$ isopleths are drawn on it (Fig. 4): the former isopleths radiate from the C apex, whereas the latter converge to the position of H_2O ($X_O = 1/3$) on the H–O side.

During cooling to the equilibration temperature of 350° C, GCOH fluids will follow X_O isopleths, moving towards the CO_2 – H_2O or CH_4 – H_2O binaries and intersecting $\text{CO}_2/(\text{CH}_4 + \text{CO}_2)$ isopleths. If the initial

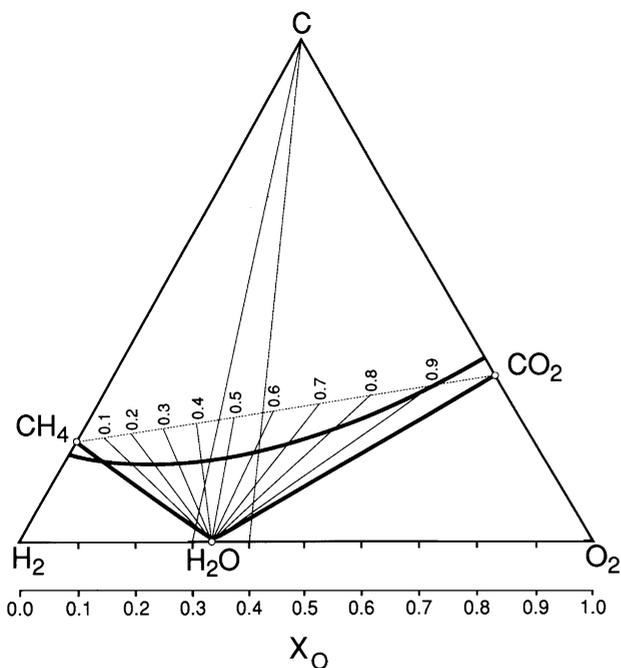


Fig. 4 C–O–H chemography representing the effects of closed system re-equilibration on $\text{CO}_2/(\text{CO}_2 + \text{CH}_4)$ fluid ratio. Labels along the CO_2 – CH_4 join indicate values of $\text{CO}_2/(\text{CO}_2 + \text{CH}_4)$ isopleths

X_O is different from 1/3 [equivalent to $\text{CO}_2/(\text{CH}_4 + \text{CO}_2) = 0.5$], this will cause the carbonic fraction to become progressively enriched in CO_2 or CH_4 , depending if X_O is respectively more or less than 1/3. From this analysis it is evident that:

1. The $\text{CO}_2/(\text{CH}_4 + \text{CO}_2)$ in the carbonic fraction, measured at room conditions, is generally different from the actual value during trapping. It will only match the trapping value in the limiting case that the X_O of the fluid is 1/3.
2. Down-temperature re-equilibration tends to move $\text{CO}_2/(\text{CH}_4 + \text{CO}_2)$ values away from the value of 0.5. Hence, room-temperature investigation will always underestimate the less abundant carbonic species.
3. Eventually, the less abundant carbonic species (those on the opposite side of the $X_O = 1/3$ line) will be reduced to undetectable concentrations, so that fluids originally trapped as CO_2 – CH_4 – H_2O ternaries will be regarded as essentially CO_2 – H_2O or CH_4 – H_2O binary mixtures.

The same conclusions are seen in Fig. 2. The $\text{CO}_2/(\text{CH}_4 + \text{CO}_2)$ value of a fluid with $X_O = 1/3$ remains constant at 0.5, whereas it moves either to 1 or 0 for the X_O values of 0.379 and 0.29, respectively. Such X_O values have been chosen to produce a room- T carbonic fraction of 10 mol% CO_2 or CH_4 .

Consider the GCOH fluid with $X_O = 0.379$: its composition at the elevated P - T trapping conditions (right-hand side in Fig. 2a) is $X_{\text{H}_2\text{O}} = 0.812$, $X_{\text{CO}_2} = 0.140$, $X_{\text{CH}_4} = 0.040$. The trapping methane content of the carbonic fraction (more than 20%, giving a $\text{CO}_2/(\text{CH}_4 + \text{CO}_2)$ value of about 0.80) could be detected easily by microthermometry, due to a depression of the CO_2 melting temperature to less than about -61°C (if the carbonic fraction homogenizes to the liquid; Thiéry et al. 1994). After cooling below 350° C (left-hand side in Fig. 2a), fluid has re-speciated to graphite and a binary 90% H_2O –10% CO_2 fluid. The $\text{CO}_2/(\text{CH}_4 + \text{CO}_2)$ ratio of the carbonic fraction has changed to essentially 1, so that the amount of methane in the room- T fluid is undetectable and the carbonic fraction is effectively pure CO_2 .

Decreasing temperature below about 350° C also causes the unmixing of fluids, as a consequence of the appearance of the fluid phase solvi in this P - T region. If brittle deformation and microfracturing, or ductile recrystallization of the mineral host takes place, unmixed GCOH fluids will eventually be reworked (Johnson and Hollister 1995), with the separation of an aqueous fluid from a carbonic phase that will comprise either CO_2 or CH_4 . In the case of $X_O = 0.379$, low-temperature unmixing could then form almost pure CO_2 fluids. If the trapping X_O was less than 1/3, the same mechanism could produce pure CH_4 fluids. Such a process may account for the genesis of nearly pure CO_2 and CH_4 fluids from starting H_2O -rich compositions. Mass balance constraints limit the effectiveness of the process, so that the unmixed carbonic fluid will be

much less abundant than the H₂O-rich counterpart. Carbonic fractions of 10 mol% of the bulk fluid can nonetheless be formed (Fig. 2).

Summary and conclusions

Graphite is predicted to precipitate in initially graphite saturated C–O–H fluid inclusions as a result of cooling of host rocks under equilibrium; this is most likely to take place when fluid trapping occurs under relatively high temperature (above upper-greenschist facies), so that the slow kinetics of graphite nucleation are overcome.

Continuous changes in composition occur in the fluid as graphite forms: unless X_O is either 0 or 1, fluids evolve to higher H₂O fractions and lower carbonic content. At the same time the density of the residual fluid decreases and the CH₄/CO₂ ratio of the carbonic fraction varies, with the tendency to diminish the amount of the less abundant species until it is eventually exhausted. Such an evolution may account for the presence of graphite-bearing, H₂O–CO₂ or H₂O–CH₄ (e.g. Guilhaumou et al. 1990) binary fluids.

The GCOH fluid compositions determined by microthermometry and/or Raman spectroscopy may not be representative of the composition of fluid at trapping. If graphite has formed during equilibration, primary fluids were more carbonic and had a CH₄/CO₂ ratio closer to unity. The primary CH₄/CO₂ ratio (*not* the primary fluid density) will be preserved only in the limiting case of $X_O = 1/3$.

Density decrease of GCOH fluids evolving towards room- P - T conditions prevents use of constant-speciation isochores, as calculated from microthermometric study, to determine the P - T values at trapping. Given that re-speciation does not alter the X_O of the fluid, the actual P - T path of the inclusion fluid is truly represented by the constant- X_O “bulk isochore”. In the case that graphite is present within inclusions, extrapolation of the constant-speciation isochore for thermobarometric purpose may result in pressure underestimates of up to 2 kbar. However, the practical use of the bulk isochore to retrieve real trapping P - T conditions is very difficult, because of the uncertainty in the temperature at which fluid re-equilibration stops.

Low-temperature unmixing of fluids composed of H₂O and a carbonic fraction that has evolved to either CO₂- or CH₄-rich values, can account for the presence of virtually pure CO₂ (e.g. Johnson and Hollister 1995) or CH₄ fluids (e.g. Alvarenga et al. 1990; Poutiainen 1990) in the upper crust. This would occur if there was selective escape of the H₂O fraction either by wicking (Craw and Norris 1993) or by crystal-plastic deformation (e.g. Hollister 1990; Bakker and Jansen 1994). Equilibrium evolution of GCOH fluids can generally account for formation of small quantities of CO₂- or CH₄-rich fluids, but coupling the unmixing of re-

speciated GCOH fluids with diffusion in or out of inclusions (e.g. hydrogen diffusion, Roedder and Skinner 1968; Hall and Bodnar 1990), might extremely increase the ability of the process.

Equilibrium behaviour of GCOH inclusions does not permit the stability of H₂O-free CO₂–CH₄ mixtures, as often reported; these metastable fluids must form by disequilibrium processes at low-temperature conditions, when graphite nucleation is more likely to be inhibited. It must be noted, however, that in many natural occurrences (e.g. Cathelineau et al. 1990; Török 1992), the size of the CO₂–CH₄ inclusions is very small (5–8 µm) so that the possibility of optically invisible H₂O coating inclusion walls has to be considered.

The main question arising from the foregoing conclusion concerns the applicability of the model, and how commonly graphite occurs within C–O–H fluid inclusions. Many inclusions containing fluids shown or assumed to have been in equilibrium with graphite at the time of their trapping are graphite-free. In this case, the absence of graphite indicates metastability of the fluid in the inclusions, which is probably related to kinetic barriers to the nucleation and precipitation of graphite. The observed nucleation of graphite under laser irradiation (Kerkhof et al. 1991; Klemd et al. 1995) supports the idea that metastability of C–O–H fluids is a common geological phenomenon. However, the number of studies that report the presence of graphite within fluid inclusions is large and rapidly increasing. Furthermore, the fact that graphite is often undetectable optically, and that very low amounts are predicted to precipitate during equilibration (1–3 vol.%, Table 1), implies that its presence can be confirmed, or ruled out, only by Raman spectroscopy. This suggests that in many cases (more than we are actually aware of) post-entrapment fluid re-equilibration did occur, and that the compositional and density changes here described are relevant during geologic processes.

This study shows that graphite presence is a critical parameter for the understanding of C–O–H fluid inclusions, and should be looked for carefully, even in the absence of optical evidence. In the case that fluids have re-equilibrated during cooling and exhumation, and graphite precipitated within the inclusions, the validity of the extrapolation of room temperature V - X properties to estimate trapping P - T - X conditions must be tested carefully. The presented approach does not address the possible effects of non-equilibrium speciation (see Connolly 1995 for discussion) or open system fluid modifications such as leakage and diffusion in and out of the inclusion, but it is the writer's opinion that these latter must necessarily be analysed after the first order, closed system, phenomena discussed here. Although they add complexity in the interpretation of fluid inclusion data, the consequences of both closed and open system modifications that may occur after fluid entrapment can in many cases be appreciated, and eventually modelled. In this perspective it is important to compare

the results of careful petrography and the examination of morphological and chemical inhomogeneities within sets of inclusions of the same generation.

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