Evidence for postentrapment diffusion of hydrogen into peak metamorphic fluid inclusions from the massive sulfide deposits at Ducktown, Tennessee

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ABSTRACT

The Ducktown, Tennessee, mining district contains some of the largest metamorphosed pyrrhotite-pyrite-rich massive sulfide bodies in the Appalachian-Caledonian orogen. The ore bodies attained middle amphibolite grade (525–550 °C, 6–7 kbar) during the Taconic orogeny (~480 Ma). Theoretical calculations of C-O-H-S fluid speciation suggest that H₂O and CO₂ generally comprised 94–100 mol% of the molecular species in the peak metamorphic fluid over the entire range of fO₂-fS₂ conditions indicated by silicate + sulfide + oxide ± graphite equilibria in the massive sulfide deposits and country rocks. Other significant species were CH₄ (~1 mol%) at low fO₂-fS₂ and H₂S (~3 mol%) at low fO₂-high fS₂. The fluid in equilibrium with rocks bearing primary H₂O-CH₄-NaCl fluid inclusions in peak-metamorphic clinopyroxene is calculated to be essentially H₂O-CO₂, with X₃CO₂ = 0.10, which disagrees with observed fluid inclusion compositions. Methane was never a significant component at P-T-fO₂-fS₂ conditions indicated by mineral assemblages in the pyroxene-bearing rocks; its presence in primary fluid inclusions suggests a much more reducing environment.

A model for the postentrapment behavior of hypothetical peak metamorphic fluid inclusions and their host rocks indicates that during the initial stages of uplift a modest fH₂ gradient between inclusions and grain boundary fluids would have been established if the oxidation state of the latter fluids was buffered by the local mineral assemblage (Py + Po + Mt). A larger fH₂ gradient (e.g., 30–15 bars at 550–400 °C) may have been established if fluid infiltrated the ore zones from the relatively reduced country rock (Po-IIm-graph). It is probable that H diffusion into primary fluid inclusions would have occurred under these conditions. An amount of H approximately equal to 12.5% of the total H originally present in the inclusions must be added to equilibrate fH₂ inside peak-metamorphic fluid inclusions with fluid in the surrounding rocks at 450 °C. Diffusive addition of H has profound effects on the P-T-X-X properties of the trapped fluid. Most importantly, the final composition of the fluid inclusions is X₃H₂O = 0.90, X₃CO₂ = 0.07, X₃CH₄ = 0.03, and X₃H₂S = 0.001, which compares favorably with the actual composition estimated from primary fluid inclusions (X₃H₂O = 0.93, X₃CO₂ = 0.03, X₃CH₄ = 0.04, and X₃H₂S = 0.001). Our model for H diffusion is consistent with observed δD values of primary fluid inclusions in pyroxene, which are 65% too low to have been in equilibrium with local hydrous mineral phases at the temperature of peak metamorphism and can be explained by diffusive addition of isotopically light H to the inclusions.

INTRODUCTION

A study of fluid inclusions from the metamorphosed massive sulfide deposits at Ducktown, Tennessee (Hall et al., 1991) indicates that fluids with a wide range of compositions in the C-O-H-S salt system were involved in the syn- to postmetamorphic history of these deposits. Data from secondary fluid inclusions in quartz combined with various mineralogical, geological, and geochronological constraints allow construction of a P-T-time path that documents early post-Taconic, temperature-concave uplift. The data also suggest that fluctuations in near-isothermal fluid pressure occurred during Alleghanian thrusting in response to episodic fracturing that allowed generation of pressures intermediate between lithostatic and hydrostatic.

Coarse grained (up to 10 cm) clinopyroxene (Di₃₅₋₄₅ Ho₀₋₁₂ Fo₇₋₁₃) is uncommon within the ore bodies and generally coexists with amphibole + calcite + quartz + pyrrhotite ± garnet ± pyrite ± magnetite ± anhydrite. The pyroxene invariably contains large (up to several hundred micrometers) primary fluid inclusions containing a low-salinity aqueous liquid, CH₄-rich vapor, and, at room temperature, daughter crystals of quartz, calcite, and in
some cases pyrrhotite. Similar, apparently primary inclusions are rarely observed in amphibole and garnet coexisting with pyroxene, although these are much smaller (<5 μm) and not suitable for detailed study. Reintegration of all fluid and solid components found in fluid inclusions in pyroxene into a homogeneous fluid, assuming that C in carbonate and S in pyrrhotite were present in the peak metamorphic fluid as CO₂ and H₂S, respectively, results in a normalized volatile composition of 93 mol% H₂O, 4 mol% CH₄, 3 mol% CO₂, and 0.1 mol% H₂S (Hall et al., 1991). In this paper, the volatile composition presented above is compared to calculations of C-O-H-S fluid speciation. A model for H diffusion into primary fluid inclusions is presented to explain the discrepancies between calculated and observed fluid compositions.

**Geologic Setting**

The Ducktown mining district is located in the southeast corner of Tennessee in the Blue Ridge Province of the southern Appalachians (Fig. 1). Eight major ore bodies, ranging in size from 0.25 to 70 million tons (180 million tons total), are contained within the Late Precambrian Copperhill Formation of the Great Smoky Group within the Ocoee Series. The ore bodies vary from massive to disseminated but consist on average of 65 vol% massive sulfide and 35 vol% gange. The massive sulfide ranges from pyrrhotite rich to pyrite rich but consists in general of 60 vol% pyrrhotite, 30 vol% pyrite, 4 vol% chalcopyrite, 4 vol% sphalerite, and 2 vol% magnetite (Magee, 1968). Other reported metallic phases include galena, molybdenite, tetrahedrite, native bismuth, cubanite, stannite, bornite, rutile, and ilmenite. Traces of Au and Ag have been reported from assays, but the mineralogic hosts for these metals remain unknown, as no discrete phase containing precious metals has ever been reported. Gangue minerals include tremolite, actinolite, cummingtonite, biotite, muscovite, stilpnomelane, chlorite, quartz, calcite, dolomite, rhodochrosite, talc, clinopyroxene, plagioclase, garnet, epidote-group minerals, anhydrite, and rhodonite.

Detailed stratigraphic studies have been conducted by Emmons and Laney (1926), Magee (1968), and Holcombe (1973). The ore bodies are located within one to three stratigraphic horizons but are difficult to correlate because of the effects of deformation. The host rocks are dominantly metagraywackes and quartz-mica schists and minor quartzite, metaglomerate, and calc-silicate hornfels. The hornfels contains plagioclase, quartz, calcite, chlorite, hornblende, garnet, and sphene, occurs as irregular podlike masses within metagraywacke, and may represent metamorphosed calcareous concretions (Hadley and Goldsmith, 1963). In addition, several rock types occur only near the ore bodies, including chlorite schist, muscovite schist, biotite schist, plagioclase-rich rock, and spessartine-rich rock. Similar rock types have been recorded near other metamorphosed massive sulfides (e.g., Gair and Slack, 1984) and have been interpreted to represent either metamorphosed volcanioclastic rocks or metamorphosed equivalents of alteration zones and exhalites typically found around unmetamorphosed volcanogenic massive sulfide deposits (Henry et al., 1979; Gair and Slack, 1984).

The ore bodies were formed in a rift environment by a sea-floor hydrothermal system associated with the opening of Iapetus in the Late Precambrian (Mauger, 1972; Addy, 1973; Nesbitt, 1979). The deposit was metamorphosed and deformed during the Taconic (~480 Ma) and Alleghanian (~320-270 Ma) orogenies (Holcombe, 1973; Addy and Ypma, 1977). Peak metamorphism, characterized by the assemblage staurolite ± kyanite, occurred at 6-7 kbar and 525-550 °C (Nesbitt and Essene, 1982; Brooker et al., 1987; Hall et al., in preparation). Metamorphism and deformation document compressional tectonics associated with the closing of Iapetus, beginning in the Middle to Late Cambrian and culminating in con-
tinent-continent collision of North America and Africa during the Carboniferous and Permian (Hatcher, 1978).}

### C-O-H-S FLUID CALCULATIONS

#### Method

Speciation in the peak metamorphic fluids was calculated using the “equilibrium constant-mass balance” technique (French, 1966; Eugster and Skippen, 1967; Holloway, 1977; Ohmoto and Kerrick, 1977; Ferry and Baumgartner, 1987). The general procedure of Ohmoto and Kerrick (1977) was modified to allow for C activity less than 1 and for nonideal mixing in the fluid phase. In a homogeneous C-O-H-S fluid, five variables must be specified for the system to be invariant. However if graphite is present, then the system is invariant when four parameters are defined. By fixing the fluid pressure (\(P_{\text{fluid}}\)), temperature (\(T\)), oxygen fugacity (\(f_{\text{O}_2}\)), sulfur fugacity (\(f_{\text{S}_2}\)), and the activity of C (\(a_c\)), the system is completely constrained. We have assumed that the species present are \(\text{H}_2, \text{O}_2, \text{S}_2, \text{H}_2\text{O}, \text{H}_2\text{S}, \text{CO}_2, \text{CO}, \text{SO}_2, \text{and CH}_4\), which are related through the linearly independent reactions

\[
\begin{align*}
C + O_2 &= CO_2 \\
CO + \frac{1}{2}O_2 &= CO_2 \\
H_2 + \frac{1}{2}O_2 &= H_2O \\
CH_4 + 2O_2 &= CO_2 + 2H_2O \\
\frac{1}{2}S_2 + O_2 &= SO_2 \\
CO + \frac{1}{2}S_2 &= COS \\
\frac{1}{2}S_2 + H_2O &= H_2S + \frac{1}{2}O_2
\end{align*}
\]

and the constraint that

\[
\sum X_i = 1
\]

(see Table 1 for all notation).

Functions describing the equilibrium constants for reactions 1–7 are presented in Ohmoto and Kerrick (1977). Fugacity coefficients for ideal mixing were taken from Burnham et al. (1969) for \(H_2O\), Burnham and Wall (1974) for \(CO_2\), Shaw and Wones (1964) for \(H_2\) below 3 kbar, and from the reduced variable equations of Ryzhenko and Volkov (1971) for \(CO, CH_4, SO_2, COS, \text{and H}_2S\) and for \(H_2\) above 3 kbar. Following Ohmoto and Kerrick (1977) \(\gamma_S\) was assumed to be unity. Fugacities were then calculated from the equation

\[
Z_i = \frac{v_i X_i P_{\text{fluid}}}{\gamma_i}
\]

(9)

Fugacities for real mixing were calculated from the equation

\[
\ln(f_i) = \ln[\frac{V}{(V - b_m)}] + \frac{b_i}{V} \ln[\frac{V}{V - b_m}] + \frac{2 \sum x_{a_m} (RT)^{b_m}}{\gamma_i (V + b_m)} - \frac{(a_i b_i b_{m}^2 RT^2)}{\gamma_i (V + b_m)} - \frac{b_m (V + b_m)}{\gamma_i RT}
\]

(10)

(Flowers and Helgeson, 1983). The \(a\) and \(b\) terms were generated from the subroutine MRKMIX (Holloway, 1981). The general Redlich-Kwong equation was then solved explicitly for mean molar volume.

To calculate the mixing terms \(a\) and \(b\), the mole fractions of the species must be known. These were obtained by assuming ideal mixing to calculate the initial real mixing fugacity coefficients and then, using the resulting mole fractions as the new mole fractions, to recalculate the real mixing fugacity coefficients. Convergence is reached in about six iterations. The criterion for convergence is that the relative variation in mole fraction between two successive iterations is less than \(10^{-4}\) for all species.

#### Mineralogical constraints on fluid composition

##### Major components.

The four reactions:

\[
\begin{align*}
\text{Trem} + Cc + Qtz &= \text{Di} + H_2O + CO_2 \\
2Zo + CO_2 &= Cc + 3An + H_2O \\
Musc + Cc + Qtz &= Ksp + An + H_2O + CO_2 \\
Rut + Cc + Qtz &= \text{Titan} + CO_2
\end{align*}
\]

(11) (12) (13) (14)

constraint \(X_{CO_2}\) within the ore bodies and country rocks, with the assumption that \(X_{H_2O} + X_{CO_2} = 1\). As will be shown, this restriction is generally valid except at conditions of lowest \(f_{CO_2}\), highest \(f_{S_2}\), or both indicated by sulfide + oxide + graphite equilibria at Ducktown. Figure 2 shows the projection of these devolatilization reactions onto \(T-X_{CO_2}\) space for \(P_{\text{fluid}} = 6\) kbar (see Nesbitt, 1979).

A lower limit for \(X_{CO_2}\) in the country rocks is provided by Zo(Czo) + An + Cc + Qtz, typically found in nodules of calc-silicate hornfels within metagraywacke. This assemblage restricts \(X_{CO_2}\) to approximately 0.10 at peak metamorphic conditions of \(550\) °C and \(6\) kbar (Fig. 2); however, in the metagraywackes and schists, which make up the bulk of the country rocks, the assemblage Cc +
An without epidote-group minerals suggests $X_{CO_2}$ greater than 0.10. An + Ksp + Musc + Cc + Qtz is common in the country rocks and restricts $X_{CO_2}$ to about 0.15 at 550 °C (Fig. 2). Assemblages indicative of 0.10 < $X_{CO_2}$ < 0.15 (e.g., An + Musc + Ksp + Qtz) and 0.15 < $X_{CO_2}$ < 0.85 (e.g., An + Musc + Cc + Qtz) are also present. Rut + Cc + Qtz is not observed in the country rocks and hence provides an upper limit of approximately 0.35 for $X_{CO_2}$ at 550 °C. No systematic spatial variations in the major fluid components H$_2$O and CO$_2$ were observed, as assemblages indicating relatively high $X_{CO_2}$ can be found a few meters from those indicating low $X_{CO_2}$. It appears that fluid composition was largely controlled by the local metamorphic mineral assemblage and that $X_{CO_2}$ varied between >0.10 and <0.35 within the country rocks.

In the ore zones, Di-Trem-Cc-Qtz restricts $X_{CO_2}$ to approximately 0.10 at 550 °C. In some samples, clinozoisite or zoisite and plagioclase coexist with the above assemblage, a further indication of an $X_{CO_2}$ near 0.10 (Fig. 2). In some rocks, amphibole is clearly retrograde, plagioclase is missing, and the stable peak metamorphic assemblage appears to have been Di + Cc + Qtz; thus, $X_{CO_2}$ varied to less than 0.10. In most of the calc-silicate rocks, the stable mineral assemblage is Trem + Cc + Qtz, implying $X_{CO_2}$ > 0.10. As in country rocks, samples from the ore zones contain mineral assemblages indicative of $X_{CO_2}$ conditions on either side of Equilibrium 13. In addition, Rut + Cc + Qtz is not uncommon, suggesting $X_{CO_2}$ in excess of 0.35. To summarize, $X_{CO_2}$ conditions in the ore zones appear to have varied from values less than 0.1 to values somewhat greater than 0.35. As in the country rocks, there is no discernible trend in fluid composition in the ore zones, and fluid composition appears to have been locally controlled. This is consistent with centimeter-scale variations in oxide + sulfide mineral assemblages that indicate small-scale variations in $f_{O_2}$ and $f_{S_2}$ (see below). Relatively high $X_{H_2O}$ conditions indicated by mineral assemblages in pyroxene-bearing samples are consistent with compositions of primary fluid inclusions found in pyroxene ($X_{H_2O} \approx 0.9-0.95$); however, as will be shown, we believe that the original compositions of these inclusions have been modified to slightly higher $X_{H_2O}$.

The addition of salt to fluid-mineral systems depresses the stability fields of mineral assemblages on the CO$_2$-bearing sides of Reactions 11–14 by increasing the activity of CO$_2$ in the fluid phase (Jacobs and Kerrick, 1981; Bowers and Helgeson, 1983). Thus, the maximum and minimum $X_{CO_2}$ conditions actually experienced by rocks at Ducktown may be significantly less than estimated above. The presence of appreciable amounts of dissolved constituents in peak metamorphic fluids is indicated by primary fluid inclusions in pyroxene, which contain 3 wt% NaCl equivalent and imply over 11 wt% total dissolved solids in the trapped fluid (Hall et al., 1991).

**Estimates of $f_{O_2}$ and $f_{S_2}$**

Conditions of $f_{O_2}$ and $f_{S_2}$ are reasonably well constrained by silicate + oxide + sulfide + graphite equilibria at Ducktown. By considering equilibria among mineral assemblages bearing Fe-Ti-Ca-C-

**Fig. 2.** $T-X_{CO_2}$ relations calculated for $P_{fluid}$ of 6 kbar, illustrating $X_{CO_2}$-constraining equilibria pertinent to mineral assemblages at Ducktown. Modified after Nesbitt (1979). Original experimental data from Johannes and Orville (1972), Hewitt (1973), Slaughter et al. (1975), and Hunt and Kerrick (1977).

**Fig. 3.** Relations of $f_{O_2}$-$f_{S_2}$ in the system Fe-Ti-O-S at 6 kbar and 550 °C. Also shown is the $f_{O_2}$ of the graphite maximum calculated from Equation 1, assuming maximum $X_{CO_2}$ of 1.0, 0.3, and 0.1. The $f_{O_2}$ of FMQ is shown for reference. A, B, and C refer to $f_{O_2}$-$f_{S_2}$ trends used to model fluid composition, where A is the trend suggested by Nesbitt and Kelly (1980). Data from Toulmin and Barton (1964), Robie et al. (1978), and Barton and Skinner (1979).
menite contains an average of 2 mol% Fe₂O₃, 1 mol% MgO, and 1 mol% MnO. Pyrrhotite contains an average of 47.5 at.% Fe. The effects of solid solution have been ignored in constructing Figure 3.

Away from the ore bodies, within staurolite grade country rocks, the common sulfide + oxide + graphite assemblage is pyrrhotite + ilmenite + graphite; however, pyrrhotite + pyrite + ilmenite was also noted. As the ore bodies are approached, primary graphite disappears and rutile replaces ilmenite as the stable Ti-oxide phase. Within the ore bodies themselves, the common assemblages are Po ± Py ± Mt ± Rut. However, other apparently stable assemblages were noted, including Po + Rut + Graph, Po + Py + Graph, Po + Py + Rut + Graph, and Po + Py + Mt + Ilm. These assemblages, although not significantly extending the range of fₒ₂ or fₑ₂ delineated by Nesbitt and Kelly (1980), do suggest that in many cases no smooth trend of increasing fₒ₂ and fₑ₂ exists as the ore bodies are approached. Specifically, it appears that fₒ₂ remained low in much of the country rock and wallrock and attained values approaching pyrrhotite-pyrite-magnetite only in certain portions of the ore bodies. The presence of native bismuth in galena and the rare occurrence of primary graphite with calcite indicate low fₑ₂ conditions in these portions of the ore zones. A similar conclusion was reached by Nesbitt (1982) while investigating sulfide + silicate equilibria. He found that, in general, the Xₑ of biotite, garnet, staurolite, and chlorite decreased toward the ore and that the distribution and composition of these phases were consistent with a progressive increase in fₑ₂ toward the ore, but that a decrease in fₒ₂ was required within the wallrocks and ore zones.

The foregoing indicates that fₒ₂ and fₑ₂ were variable within ore zones and country rocks. This is consistent with our T-Xₑ analysis, which suggests that fluid composition was largely controlled by local lithologies.

Activity of C. In the country rocks, where graphite is common, the activity of C is defined to be unity. The general absence of primary graphite in the ore bodies and wallrock implies reduced aₑ, consistent with the location of the graphite maximum at log fₒ₂ of -20.5, as calculated from Reaction 1 at 6 kbar and 550 °C (Fig. 3). At the graphite maximum, the fluid is essentially pure CO₂, however, mineral assemblages in the country rocks fix maximum Xₐₑ near 0.3. Therefore, a better estimate of the graphite maximum is obtained by setting Xₐₑ equal to 0.3 and calculating fₒ₂ from Reaction 1, which results in an estimated log fₒ₂ = -21.0 (Fig. 3). At fₒ₂ conditions above that of the estimated graphite maximum, fluid composition is dependent on the activity of C. Figure 4 shows fluid composition as a function of aₑ at 6 kbar, 550 °C, log fₒ₂ = -20.0, and log fₑ₂ = -3.0. Xₐₑ increases as aₑ increases at constant fₒ₂, and depending on the activity of C at any fₒ₂ above the graphite maximum, the fluid composition varies from virtually pure H₂O to pure CO₂ at P-T-fₑ₂ conditions considered here (Fig. 4).

Within the ore zones, the most oxidized mineral assemblages (i.e., those containing Py + Po + Mt) invariably indicate the lowest Xₐₑ conditions (≤0.10). When graphite is found with low Xₐₑ assemblages, it is always secondary (i.e., precipitated by retrograde fluids). Primary graphite, present during peak metamorphism, does occur rarely in the ore zones, but the accompanying silicate + oxide + sulfide assemblages are consistent with relatively low fₒ₂, high Xₐₑ conditions (0.1 < Xₐₑ < 0.4). As previously mentioned, there is no systematic trend in Xₐₑ in the wallrocks or ore zones. Because the ranges of Xₐₑ recorded in the country rocks and ore zones are similar, we have arbitrarily chosen to model the activity of C along the fₒ₂-fₑ₂ trend of Nesbitt and Kelly (1980) by (1) assuming it is constant above the graphite maximum for Xₐₑ = 0.3 (log fₒ₂ = -21.0) and is equal to 0.001, thereby producing a fluid with Xₐₑ = 0.10 at the fₒ₂-fₑ₂ conditions indicated by Py + Po + Mt and (2) assuming it varies above the graphite maximum for Xₐₑ = 0.1 (log fₒ₂ = -21.4) in order to maintain an Xₐₑ of 0.1. The latter requires that aₑ decreases fairly regularly from 1 at log fₒ₂ of -21.4 to 0.001 at Py + Po + Mt. Considering the nonsystematic local control of fluid composition within the country rocks and ore zones, it is improbable that aₑ varied smoothly from country rock to ore zones but rather oscillated in response to the same local controls of fluid composition.

Results

Fluid speciation was calculated for points along the suggested fₒ₂-fₑ₂ trend of Nesbitt and Kelly (1980) with aₑ modeled as described above (Fig. 5). Results indicate that H₂O and CO₂ were generally the dominant molecular species, comprising 94–100 mol% of the peak metamorphic fluid. At the low fₒ₂-fₑ₂ end of the trend, CH₄ reaches 1 mol%, but the lower limit of fₒ₂ is not well constrained by the oxide + sulfate mineral assemblages, and significantly larger proportions of CH₄ are possible at lower fₒ₂.
Fig. 5. $X_i-f_{O_2}$ relations calculated for 6 kbar and 550 °C with $f_{O_2}$ and $f_{S_2}$ constrained by trend A (Fig. 3). (A) The $a_c = 0.001$ above log $f_{O_2}$ of -20.96, which produces a maximum $X_{CO_2}$ of 0.3. (B) $X_{CO_2} = 0.10$ ($a_c = 1 - 0.001$). The graphite maximum is located at $f_{O_2} = -21.35$, which corresponds to a $X_{CO_2}$ of 0.1.

Fig. 6. $X_i-f_{S_2}$ relations calculated for 6 kbar and 550 °C with $f_{S_2}$ constant at -20.96 (trend B, Fig. 3). An $f_{S_2}$ of -20.96 corresponds to an $X_{CO_2}$ of 0.3.

(mol%, 7 mol% CH$_4$ at log $f_{O_2} = -23.0$, log $f_{S_2} = -6.5$). However, if $X_{CO_2}$ were $\approx 0.1$ everywhere, as suggested by silicate mineral assemblages, the minimum log $f_{O_2}$ would be -21.4 and the maximum $X_{CH_4}$ would be less than 1 mol%. Above the graphite maximum, H$_2$O and CO$_2$ dominate, and the ratio of these two species is completely dependent on the value chosen for $a_c$. If $a_c$ is constant at 0.001 (Fig. 5A), then the fluid varies from pure H$_2$O just above the graphite maximum to H$_2$O + CO$_2$ with $X_{CO_2} = 0.1$ at the Po-Py-Mt buffer. At higher $f_{O_2}$, $f_{S_2}$ conditions, $X_{H_2O}$, $X_{CH_4}$, and $X_{CO_2}$ decrease; $X_{CO_2}$, $X_{CO}$, $X_{SO_2}$, and $X_{CO}$ increase; and $X_{H_2S}$ remains relatively constant (Fig. 5A). If $X_{CO_2}$ is constant at 0.1 along the same trend (i.e., model 2 for $a_c$), $X_{H_2O}$, $X_{CO_2}$, $X_{CH_4}$, and $X_{CO}$ remain approxi-
fluid at low $f_{O_2}$; $X_{H_{2}SO_4}$ increases and mole fractions of all other species decrease as log $f_{O_2}$ increases (Fig. 7).

**Comparison of calculated fluid compositions with primary fluid inclusions**

Comparison of calculated peak metamorphic fluid compositions, constrained by mineral assemblages coexisting with clinopyroxene, with the estimated compositions of primary fluid inclusions in clinopyroxene indicates significant similarities and differences (Table 2). Both compositions imply that $H_2O$ was the dominant molecular fluid species during peak metamorphism and that $CO_{2}$ was a significant species as well. Also, both predict comparable quantities of $H_{2}S$. However, the calculated composition suggests that $CH_{4}$ was present in negligible amounts, whereas observed compositions of primary fluid inclusions show that $CH_{4}$ is present in proportions subequal to or greater than $CO_{2}$. To reconcile the calculated-speciation with fluid-inclusion data would require extremely reducing conditions during trapping, specifically, log $f_{O_2}$ of $\sim$ -22.8 and log $f_{O_3}$ of $\leq$ -6.5; in other words, conditions within the stability fields of Po + IIm + Graph or Po + Rut + Graph (Fig. 3) are required. This is inconsistent with the equilibrium mineral assemblages coexisting with pyroxene containing primary fluid inclusions that indicate trapping at log $f_{O_2}$ near -18.3 and log $f_{O_3}$ near -2.7 (i.e., defined by Py + Po + Mt). The discrepancy cannot be explained by any reasonable errors in the determination of $P$-$T$-$f_{O_2}$-$f_{O_3}$-dC conditions attending pyroxene growth. Furthermore, reasonable errors in the thermodynamic data used to calculate $X_{CH_4}$ cannot account for the inconsistency. Specifically, varying all fugacity coefficients involved in Reaction 14 by 20% in a direction to maximize $X_{CH_4}$ increases $X_{CH_4}$ by less than half an order of magnitude. A 100% error in all fugacity coefficients or an error in log $K$ for Reaction 4 of 7 orders of magnitude is required to bring observed and calculated methane concentrations into agreement.

Pyrrhotite daughters occur in only $\sim$20% of the inclusions studied. They are generally confined to larger inclusions, which suggests that pyrrhotite may be metastably absent from the smaller inclusions. There is no measurable difference in the proportions of major fluid components (e.g., CH$_4$) between pyrrhotite-bearing and pyrrhotite-absent inclusions, suggesting that elevated CH$_4$ contents cannot be ascribed to the tendency for pyrrhotite to maintain reducing conditions within the inclusions.

**POSTENTRAPMENT CHANGES IN FLUID COMPOSITION**

**Closed system**

A mechanism that could account for the disparity between calculated and observed fluid compositions is continued reequilibration of the trapped molecular species in C-O-H-S fluid inclusions during cooling, resulting in a speciation that is substantially different at room temperature than at the conditions of trapping. The change in speciation during cooling of a hypothetical C-O-H-S fluid inclusion can be calculated using methods outlined by Holloway (1981) and Dubessy (1984).

In this procedure, an 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 pressure and temperature and assuming the system remains at constant volume, or by correcting for thermal expansion and compressibility of the host mineral, the new composition, molar volume, and internal pressure of the fluid inclusion can be calculated at a specified temperature. The solution requires the functions describing equilibrium constants for Reactions 2–7 (compiled by Ohimoto and Kerrick, 1977), Equation 8, and the additional mass balance equations

\[ \sum n_C = \sum n_C \]  \hspace{1cm} (15)

\[ \sum n_O = \sum n_O \]  \hspace{1cm} (16)

\[ \sum n_H = \sum n_H \]  \hspace{1cm} (17)

\[ \sum n_S = \sum n_S \]  \hspace{1cm} (18)

Fugacity coefficients for the ten species considered are computed from Holloway’s (1981) program MRKMIX, and the new $P$-$T$-$X$ properties of the inclusion are calculated by simultaneously solving the ten equations (six describing fluid speciation and four describing mass balance) using Newton’s method for nonlinear equations.
(Burden and Faires, 1985). The criterion for convergence is the same as for our previous calculations.

Closed system speciation changes that result when the calculated peak metamorphic fluid is trapped and cooled to 400 °C are shown in Figure 8. A minimum temperature of 400 °C was chosen for several reasons. Holloway's modified Redlich-Kwong equation of state is only applicable above 400 °C for aqueous fluids. Furthermore, the kinetics of exchange among carbonic fluid species and graphite are very sluggish below 400 °C (Sackett and Chung, 1979; Harting and Maass, 1980; Ziegenbein and Johannes, 1980). Finally, the positions of the solvi of C-O-H-S fluids are unknown but, in general, probably lie at temperatures below the critical point of H₂O. Thus, a minimum temperature of 400 °C restricts calculations to the single fluid phase region.

The major components of the peak metamorphic fluid, namely H₂O and CO₂, vary insignificantly during cooling, but the minor species O₂, S, H₂, SO₂, and CH₄ vary up to several orders of magnitude (Fig. 8). This agrees with the conclusion of Dubessy (1984) that it is not possible to render a major fluid component minor or vice versa in the absence of a daughter precipitate, such as graphite, or a mechanism that preferentially removes one or more fluid components. The fluid was assumed to remain undersaturated with respect to graphite during cooling because graphite was not detected petrographically or during Raman analyses. If graphite were to precipitate in the fluid during cooling, then significant CH₄ may be produced at low temperatures and pressures. Although XCH₄ does increase significantly during cooling, the initial quantity of this species is so small (10⁻⁷ mol%) that an increase of several orders of magnitude leaves CH₄ below detection by any microthermometric or spectroscopic technique.

We conclude that postentrapment compositional changes in a fluid inclusion that remains a closed system cannot explain the disparity between the calculated peak metamorphic fluid composition and the observed composition of primary peak metamorphic fluid inclusions at Ducktown.

H diffusion

Several phenomena reported in the fluid inclusion literature have been attributed to the effects of diffusion. Daughter minerals such as hematite, anhydrite, and chloropyrite, which do not dissolve upon heating, may have precipitated in response to changes in oxidation state or pH resulting from diffusive loss of H (Roedder and Skinner, 1968; Roedder, 1981). Tiny, ubiquitous fluid inclusions in quartz from high grade metamorphic rocks may form by diffusive exsolution of H₂O from the quartz structure during cooling and decompression (White, 1973; Wilkins and Barkas, 1978); H₂O precipitation and diffusion in wet quartz and berthierite (AlPO₄) during annealing has been documented (Cordier et al., 1988). Similarly, Sterner et al. (1988) and Hall et al. (1989a) have shown that preferential loss of H₂O from NaCl-KCl-H₂O fluid inclusions in quartz can occur in response to differential pressure between inclusion and matrix. Pasteris and Wanamaker (1988) were able to diffuse O into and out of CO₂-rich inclusions in olivine at 1000-1400 °C, and Hall et al. (1989b) have documented H gain by CO₂-H₂O fluid inclusions in quartz and reduction of CO₂ to CH₄ + H₂O at temperatures as low as 650 °C. Diffusive loss of H₂O from C-O-H inclusions has been suggested as a possible explanation for nearly pure CO₂ inclusions in granulites and other high-grade rocks (Roedder, 1981), and diffusive gain of H and reduction of CO₂ may explain the occurrence of appreciable CH₄ in fluid inclusions from some granulites (Hall and Bodnar, 1989).

The driving force for H diffusion out of or into a fluid inclusion is the fH₂ gradient between the host (or that imposed by the fluid circulating through the rock) and the fluid inside the inclusion. These gradients may become appreciable during cooling and decompression. Diffusion rates of H through minerals are sufficiently rapid above 600 °C (Kats, 1962; Kats et al., 1962; Kronenberg et al., 1986) that over geologic time appreciable gradients in fH₂ could not be maintained. It is unclear however what the effective blocking temperature is for H diffusion over geologic time. The extent or importance of H diffusion depends on the P-T-time path as well as the compositions of the inclusion and matrix fluid and crystal chemistry.

We have calculated the changes in the fH₂ in the matrix fluid and in model peak-metamorphic fluid inclusions during uplift. The inclusions trapped the fluid composition calculated for 6 kbar, 550 °C, log fO₂ = -18.3, log fS = -2.7, and aC = 0.001 (Table 2). The uplift path chosen for the matrix was constrained by paragenetic and microthermometric data from secondary fluid inclusions in quartz (Hall et al., 1991) and is slightly concave toward the temperature axis (Fig. 9) over the temperature range.

![Figure 8](image-url)
considered here (550–400 °C). The pseudoisochore calculated by cooling the peak metamorphic fluid at constant volume, but taking into account P-V-T variations due to speciation changes, indicates that the hypothetical inclusions are underpressured (i.e., $P_{ex} > P_{in}$) during uplift (Fig. 9). At 400 °C, the pressure differential is about 750 bars. It is significant that many primary fluid inclusions in pyroxene from Ducktown exhibit textures resembling implosion halos produced in synthetic fluid inclusions by Sterner and Bodnar (1989) during laboratory experiments where confining pressures exceeded internal pressures of the fluid inclusions (Hall et al., 1991).

The $f_{H_2}$ gradient established during the postmetamorphic history is presented in Figure 10. For these calculations it is assumed that the matrix fluid composition (i.e., $f_{O_2}$ and $f_{H_2}$) is buffered by Py-Po-Mt. Two $f_{H_2}$-T curves were calculated for the matrix, one with $a_c$ constant at 0.001 (matrix 1; Fig. 10) and the other with $a_c$ varying from 0.001 at 6 kbar and 550 °C to 0.139 at 5 kbar and 400 °C, so that $X_{CO_2}$ is constant at 0.10 (matrix 2; Fig. 10). These calculations indicate that $f_{H_2}$ in the matrix is greater than that in the fluid inclusion; in fact, it is four times that in the inclusion at 450 °C, although both fugacities are low and the gradient is only approximately 0.3 bars (Fig. 10). Thus, a small $f_{H_2}$ gradient may have been established during uplift, and this gradient theoretically could have promoted H diffusion into primary fluid inclusions.

The difference in $f_{H_2}$ between matrix and inclusion is magnified by an order of magnitude if the fluid in “H communication” with primary fluid inclusions is not controlled by Py + Po + Mt but by a more reduced assemblage, such as Po + Ill + Graph or FMQ. This may have occurred if fluid in equilibrium with the bulk of the host metagraywackes and quartz-mica schists, or reduced portions of ore zones, infiltrated high $f_{O_2}$ (pyroxene-bearing) portions of the ore bodies after peak metamorphism. The $f_{H_2}$ gradient resulting from infiltration of a fluid with $f_{O_2}$ buffered by FMQ and $f_{H_2}$ buffered by pyrrhotite with $X_{FeS} = 0.95$, relative to FeS-Si, is shown in Figure 11. If this fluid comes into diffusive communication with primary fluid inclusions, a $f_{H_2}$ gradient of 15–30 bars will result, again promoting H diffusion into primary fluid inclusions. Secondary fluid inclusions in quartz document influx of post-peak metamorphic fluids into ore zones from external sources; at least one such fluid was responsible for precipitation of secondary graphite and replacement of sulfides by graphite in ore zones. The observed replacement of magnetite and pyrite by pyrrhotite may be evidence for influx of low-$f_{O_2}$, low-$f_{H_2}$ fluids as well. The ore bodies are relatively small geochemical anomalies contained within a large volume of relatively reduced metasedimentary rocks. As such, it is expected that the ore bodies were exposed to low-$f_{O_2}$-$f_{H_2}$ fluids after metamorphism. Given the rapid rate of H diffusion through minerals (e.g., Kronenberg et al., 1986), the calculated $f_{H_2}$ gradient between inclusions and externally derived grain boundary fluids could induce addition of H to fluid inclusions in a geologically short time.

We have calculated the amount of H diffusion necessary to eliminate the $f_{H_2}$ gradient between inclusions and matrix at 450 °C. If the matrix fluid is buffered by Py + Po + Mt, diffusion of much less than 0.1 mol% of the total H originally present in the inclusion will negate the $f_{H_2}$ gradient. If the matrix fluid is buffered by FMQ, how-
ever, even though only a small amount of H is present in the fluid, diffusion of H into a fluid inclusion can have significant effects on the P-V-X properties. The mole fraction of methane increases over 7 orders of magnitude from $10^{-9}$ to 0.03; the fluid is essentially 90 mol% H$_2$O, 7 mol% CO$_2$, and 3 mol% CH$_4$ after diffusion of 12.5 mol% H (Fig. 12). Methane becomes an important component, which may be detectable during routine microthermometric studies and spectroscopically. Furthermore, the above fluid composition compares favorably with the actual composition estimated for primary fluid inclusions (Table 2).

After diffusion of 12.5% H, the molar volume of the fluid has decreased from 22.8 to 21.6 cm$^3$ and the internal pressure has increased from 4.8 to 6.4 kbar. Because the matrix is at about 5.5 kbar at 450°C (Fig. 9), H diffusion results in approximately 900 bars of internal overpressure inside the inclusions, which may be enough to cause the inclusions to stretch (Sterner and Bodnar, 1989). Variable liquid-vapor ratios have been observed in primary fluid inclusions in pyroxene, and clathrate-dissociation temperatures suggest a range of internal pressures at room temperature, perhaps resulting from equilibration toward lower densities during uplift (Hall et al., 1991). It is important to emphasize that, in the absence of H diffusion, the primary inclusions should be underpressured during uplift and may tend toward higher densities (Fig. 9). Although the appearance of the inclusions may be qualitatively similar, in the latter case the lowest rather than highest density inclusions would most closely approximate the original isochore, and a negative rather than positive correlation between inclusion size and homogenization temperature should be observed. As previously mentioned, textures indicating internal underpressuring have been noted in primary fluid inclusions (Hall et al., 1991), but it is suggested that inclusions were initially underpressured and then recrystallized to higher densities prior to the H diffusion event, which may have subsequently caused stretching. If the inclusions were to begin stretching during H diffusion, the effect would be to reduce the $f_{H2}$ in the inclusions by reducing the total pressure, perhaps resulting in further H diffusion to equilibrate $f_{H2}$. This in turn would result in higher CH$_4$/CO$_2$ in the final inclusion fluid.

Values for δD of primary fluid inclusions

C, H, and O isotope analyses were collected from CH$_4$, H$_2$O, and CO$_2$ liberated from primary fluid inclusions in pyroxene (Hall et al., in preparation) (analyses by Isotope Specialists Inc.). Calculated bulk δD values for these inclusions range from $-96$ to $-104$ per mil SMOW. The δD values of the peak metamorphic (530°C) fluid implied by the H isotope compositions of Ducktown biotite, muscovite, and chlorite analyzed by Addy and Ypma (1977) are $-33$ to $-42$ per mil, according to the fractionation factors of Suzuki and Epstein (1976) and Graham et al. (1987). Furthermore, coexisting minerals give nearly identical δD$_{H2O}$ values, consistent with equilibration of H isotopes at peak metamorphic temperatures with little retrograde exchange.

Bulk δD values obtained from primary fluid inclusions are thus significantly lower than the estimated δD of H$_2$O in equilibrium with local hydrous phases during peak metamorphism. Because the fluid present in primary fluid inclusions was produced by local devolatilization reactions such as Equation 11, it should be in isotopic equilibrium with local hydrous minerals. Low δD primary fluid inclusions are consistent with the proposed H dif-
fusion model since molecular H diffusing into these inclusions would have very low δD values with respect to those of the aqueous grain boundary source fluids. Fractionation of H isotopes between H and H₂O in the source aqueous solution may have been as high as that for H₂ gas in equilibrium with H₂O vapor (ΔδD,H₂O = 360‰ at 450 °C, Bottinga, 1969). During diffusion, additional fractionation would result from the faster rate of diffusion of H relative to D; thus, the net fractionation between H reaching the inclusion and H₂O in the parent solution may have been significantly greater than ΔδD,H₂O. Mass balance calculations using a ΔδD,H₂O of 360 per mil indicate that 16–18% of the H present in these inclusions would have to be added during diffusion. This value compares favorably with the calculated 12.5% necessary to effect the required compositional changes to the fluid inclusions.

CONCLUSIONS

Primary fluid inclusions in pyroxene, which formed at peak metamorphic conditions of 6 kbar and 550 °C with fO₂ = fO₂ values buffered near Py-Po-Mt, contain a normalized volatile composition of 93 mol% H₂O, 4 mol% CH₄, 3 mol% CO₂, and 0.1 mol% H₂S. Fluid speciation calculations and silicate mineral assemblages suggest that the trapped fluid should consist of 90 mol% H₂O, 10–7 mol% CH₄, 10 mol% CO₂, and 0.1 mol% H₂S. Methane was not a significant component of peak metamorphic fluids in some zones.

Postentrapment speciation changes can account for the discrepancy in the CH₄/CO₂ ratio if the inclusions behaved as open systems and H diffused into the inclusions causing reduction of CO₂ to CH₄. This has been shown to be feasible if fluids in equilibrium with the bulk of the country rocks infiltrated the ore zones after peak metamorphism, because country rock fluids are buffered at fO₂ approximately 3 log units below oxidized portions of ore zones. If such an fO₂ gradient was established between inclusions and grain boundary fluids, diffusion of H into primary fluid inclusions may have occurred.

Values for δD of primary fluid inclusions are 65 per mil lower than equilibrium values at peak metamorphism. H diffusion would drastically lower the bulk δD of the inclusions by addition of isotopically light H. Mass balance calculations suggest that the amount of H necessary to lower δD will also result in sufficient compositional changes to reconcile calculated and observed fluid compositions. Hence, H diffusion is presently the best explanation for discrepancies between calculated and observed fluid compositions in primary fluid inclusions from Ducktown.

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