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 $f_{O_2}$-$f_{H_2}$ 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 $f_{O_2}$-$f_{H_2}$ and H₂S (£3 mol%) at low $f_{O_2}$-high $f_{H_2}$. 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 $X_{CO_2} = 0.10$, which disagrees with observed fluid inclusion compositions. Methane was never a significant component at P-T-$f_{O_2}$-$f_{H_2}$ 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 $f_{H_2}$ 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 $f_{H_2}$ 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-Ilm-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 $f_{H_2}$ inside peak-metamorphic fluid inclusions with fluid in the surrounding rocks at 450 °C. Diffusive addition of H has profound effects on the P-V-X properties of the trapped fluid. Most importantly, the final composition of the fluid inclusions is $X_{H_2O} = 0.90$, $X_{CO_2} = 0.07$, $X_{CH_4} = 0.03$, and $X_{H_2S} = 0.001$, which compares favorably with the actual composition estimated from primary fluid inclusions ($X_{H_2O} = 0.93$, $X_{CO_2} = 0.03$, $X_{CH_4} = 0.04$, and $X_{H_2S} = 0.001$). 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 (Dii35-97
Hd42-Io02-02) 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

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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% gangue. 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, t alc, 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, metaconglomerate, and calc-silicate hornfels. The hornfels contains plagioclase, quartz, calcite, clinopyroxine, hornblende, garnet, and phengite, occurs as irregular podlike masses within metagraywacke, and may represent metamorphosed calcareous cretacions (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 Permain (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 H\text{2}, O\text{2}, S\text{2}, H\text{2}O, H\text{2}S, CO\text{2}, COS, CO, SO\text{2}, and CH\text{4}, which are related through the linearly independent reactions

\begin{align*}
C + O\text{2} & = CO\text{2} \\
CO + \frac{1}{2} O\text{2} & = CO\text{2} \\
H\text{2} + \frac{1}{2} O\text{2} & = H\text{2}O \\
CH\text{4} + 2O\text{2} & = CO\text{2} + 2H\text{2}O \\
\frac{1}{2}S\text{2} + O\text{2} & = SO\text{2} \\
CO + \frac{1}{2}S\text{2} & = COS \\
\frac{1}{2}S\text{2} + H\text{2}O & = H\text{2}S + \frac{1}{2}O\text{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\text{2}O, Burnham and Wall (1974) for CO\text{2}, Shaw and Wones (1964) for H\text{2} below 3 kbar, and from the reduced variable equations of Ryzhenko and Volkov (1971) for CO, CH\text{4}, SO\text{2}, CO\text{2}, and H\text{2}S and for H\text{2} above 3 kbar. Following Ohmoto and Kerrick (1977) \gamma_{S2} was assumed to be unity. Fugacities were then calculated from the equation

\[ (f_l)^{n_{int,r}} = X_i \gamma_i P_{\text{fluid}}. \]  

Fugacities for real mixing were calculated from the equation

\[ \ln(f_l) = \ln[V/(V - b_m)] + b_l/(V - b_m) - \left[ \frac{2}{\sum X_i a_i/(RT - b_m)} \ln[(V + b_m)/V] + (a_m b_l/(b_m RT)) \ln[(V + b_m)/V] - b_m/(b_m + V) - \ln(R/T) \right] \]  

(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\textsuperscript{-4} for all species.

Mineralogical constraints on fluid composition

Major components. The four reactions:

\begin{align*}
\text{Trem} + \text{Cc} + \text{Qtz} & = \text{Di} + \text{H}_2\text{O} + \text{CO}_2 \\
2\text{Zo} + \text{CO}_2 & = \text{Cc} + 3\text{An} + \text{H}_2\text{O} \\
\text{Musc} + \text{Cc} + \text{Qtz} & = \text{Ksp} + \text{An} + \text{H}_2\text{O} + \text{CO}_2 \\
\text{Rut} + \text{Cc} + \text{Qtz} & = \text{Titan} + \text{CO}_2
\end{align*}

constraint \( X_{\text{CO}_2} \) within the ore bodies and country rocks, with the assumption that \( X_{\text{H}_2\text{O}} = X_{\text{CO}_2} = 1 \). As will be shown, this restriction is generally valid except at conditions of lowest \( f_{\text{O}_2} \), highest \( f_{\text{S}_2} \), or both indicated by sulfide + oxide + graphite equilibria at Ducktown. Figure 2 shows the projection of these devolatilization reactions onto \( T-X_{\text{CO}_2} \) space for \( P_{\text{fluid}} = 6 \text{ kbar} \) (see Nesbitt, 1979).

A lower limit for \( X_{\text{CO}_2} \) in the country rocks is provided by \( \text{Zo}(\text{Zo}) + \text{An} + \text{Cc} + \text{Qtz} \), typically found in nodules of calc-silicate hornfels within metagraywacke. This assemblage restricts \( X_{\text{CO}_2} \) 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 \( \text{Cc} + \)
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,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 between >0.10 and 0.35 within the country rocks.

In the ore zones, 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 NaCl equivalent and imply over 11 wt% total dissolved solids in the trapped fluid (Hall et al., 1991).

Estimates of $f_O$ and $f_S$. Conditions of $f_O$ and $f_S$ are reasonably well constrained by silicate + oxide + sulfide + graphite equilibria at Ducktown. By considering equilibria among mineral assemblages bearing Fe-Ti-Ca-C-

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**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 $f_O$-$f_S$ in the system Fe-Ti-O-S at 6 kbar and 550 °C. Also shown is the $f_O$ of the graphite maximum calculated from Equation 1, assuming maximum $X_{CO_2}$ of 1.0, 0.3, and 0.1. The $f_O$ of FMQ is shown for reference. A, B, and C refer to $f_O$-$f_S$ trends used to model fluid composition, where A is the trend suggested by Nesbitt and Kelly (1980). Data from Toulin 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 + graphilite 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 f₀₂ or f₂, delineated by Nesbitt and Kelly (1980), do suggest that in many cases no smooth trend of increasing f₂ and f₀₂ exists as the ore bodies are approached. Specifically, it appears that f₀₂ 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 f₀₂ conditions in these portions of the ore bodies. A similar conclusion was reached by Nesbitt (1982) while investigating state + oxide + silicate equilibria. He found that, in general, the X₂O₃ 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 f₂ toward the ore, but that a decrease in f₀₂ was required within the wallrocks and ore zones. The foregoing indicates that f₀₂ and f₂ were variable within ore zones and country rocks. This is consistent with our T-X₂O₃ 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 activity of C, consistent with the location of the graphite maximum at log f₀₂ 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 X₂O₃ near 0.3. Therefore, a better estimate of the graphite maximum is obtained by setting X₂O₃ equal to 0.3 and calculating f₀₂ from Reaction 1, which results in an estimated log f₀₂ = -21.0 (Fig. 3). At f₀₂ 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 activity of C, at 6 kbar, 550 °C, log f₀₂ = -20.0, and log f₂ = -3.0. X₂O₃ increases as f₀₂ increases at constant f₂ and, depending on the activity of C at any f₀₂, above the graphite maximum, the fluid composition varies from essentially pure H₂O to pure CO₂ at P-T-f₂ 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 X₂O₃ conditions (~0.10). When graphite is found with low X₂O₃ assemblages, it is generally secondary (i.e., precipitated by retrograde fluids). Primary graphite, present during peak metamorphism, does not occur rarely in the ore zones, but the accompanying silicate + oxide + sulfide assemblages are consistent with relatively low f₀₂, high X₂O₃ conditions (0.1 < X₂O₃ < 0.4).

As previously mentioned, there is no systematic trend in X₂O₃ in the wallrocks or ore zones. Because the ranges of X₂O₃, recorded in the country rocks and ore zones are similar, we have arbitrarily chosen to model the activity of C along the f₀₂-f₂ trend of Nesbitt and Kelly (1980) (by 1) assuming a constant above the graphite maximum for X₂O₃ = 0.3 (log f₀₂ = -21.0) and is equal to 0.001, thereby producing a fluid with X₂O₃ = 0.10 at the f₀₂-f₂ conditions indicated by Py + Po + Mt and (2) assuming it varies above the graphite maximum for X₂O₃ = 0.1 (log f₀₂ = -21.4) in order to maintain an X₂O₃ of 0.1. The latter requires that a_c decreases fairly regularly from 1 at log f₀₂ 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 a_c 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 f₀₂-f₂ trend of Nesbitt and Kelly (1980) with a_c 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 f₀₂-f₂ end of the trend, CH₄ reaches 1 mol%, but the lower limit of f₀₂ is not well constrained by the oxide + sulfide mineral assemblages, and significantly larger proportions of CH₄ are possible at lower f₀₂.
(e.g., 7 mol% CH₄ at log fₒ₂ = -23.0, log fₛ₂ = -6.5). However, if Xₑ₃ were ≥0.1 everywhere, as suggested by silicate mineral assemblages, the minimum log fₒ₂ would be -21.4 and the maximum Xₑ₄ would be less than 1 mol%. Above the graphite maximum, H₂O and CO₂ dominate, and the ratio of these two species is completely dependent on the value chosen for aₑ. If aₑ is constant at 0.001 (Fig. 5A), then the fluid varies from pure H₂O just above the graphite maximum to H₂O + CO₂ with Xₑ₃ = 0.1 at the Po-Py-Mt buffer. At higher fₒ₂-fₛ₂ conditions, Xₑ₃, Xₑ₄, and Xₑ₅ decrease; Xₑ₃, Xₑ₇, Xₑ₉, and Xₑ₁₀ increase; and Xₑ₅ remains relatively constant (Fig. 5A). If Xₑ₃ is constant at 0.1 along the same trend (i.e., model 2 for aₑ), Xₑ₃, Xₑ₇, Xₑ₉, and Xₑ₁₀ remain approximately constant; Xₑ₄, Xₑ₇, and Xₑ₅ decrease; and Xₑ₁₀ increases (Fig. 5B). While fluid composition is reasonably well constrained at both ends of trend A (Fig. 3), it is poorly constrained in the middle because of uncertainties associated with aₑ. Nevertheless, the calculations do imply that the peak metamorphic fluid was essentially a binary H₂O-CO₂ mixture above the graphite maximum, along the fₒ₂-fₛ₂ trend of Nesbitt and Kelly (1980).

As previously mentioned, mineral assemblages suggest that in some areas fₒ₂-fₛ₂ conditions deviated significantly from trend A; specifically, low fₒ₂-high fₛ₂ conditions prevailed in some rocks (trend B, Fig. 3). The apparent equilibrium assemblage Po + Py + Graph + Titan is observed infrequently within the wallrocks, constraining log fₒ₂ to be -2.7 and log fₛ₂ to be as low as -22 (Fig. 3). At these conditions, the metamorphic fluid is composed of approximately 90 mol% H₂O, 7 mol% H₂S, 2.5 mol% CO₂, and 0.5 mol% CH₄. Fluid composition was calculated assuming constant log fₒ₂ = -21.0 (Xₑ₃ = 0.3) and variable log fₛ₂ between -6.5 and -2.7 (trend B, Fig. 3). Results, presented in Figure 6, indicate that as fₛ₂ increases, CH₄ is replaced by H₂S as the third most abundant species, but that everywhere along trend B Xₑ₇ increases. Mole fractions of all S species increase as fₛ₂ increases. Mole fractions of other species do not change appreciably.

Many mineral assemblages imply buffering of fₛ₂ by Py + Po at log fₒ₂ conditions between -21.0 (assuming a maximum Xₑ₃ of 0.3 and aₑ = 1) and -18.3 (Py + Po + Mt). As mentioned above, mineral assemblages in ore zones indicating the lowest fₒ₂ also imply the highest Xₑ₇. Fluid compositions calculated along this trend (C in Fig. 3) are presented in Figure 7 and assume a linear decrease in Xₑ₃ from 0.3 at log fₒ₂ = -21.0 to 0.1 at log fₒ₂ = -18.3. H₂S may have comprised up to 3 mol% of the
fluid at low $f_{O_2}$; $X_{H_2O}$ 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 $H_2S$. 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 $\log f_{O_2}$ of $\leq$ 6.5; in other words, conditions within the stability fields of $Po$ + Ilm + 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 $\log f_{O_2}$ near 2.7 (i.e., defined by $Py$ + $Po$ + Mt). The discrepancy cannot be explained by any reasonable errors in the determination of $P-T-f_{O_2}-f_{H_2S}$ 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 Ohmoto and Kerrick, 1977), Equation 8, and the additional mass balance equations

\[
\sum n_C = \sum n_C \quad (15)
\]
\[
\sum n_O = \sum n_O \quad (16)
\]
\[
\sum n_H = \sum n_H \quad (17)
\]
\[
\sum n_S = \sum n_S \quad (18)
\]

Fugacity coefficients for the ten species considered are computed from Holloway’s (1981) program MRKMIX, and the new $P-V-X$ 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

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<th>Table 2. Observed and calculated fluid compositions</th>
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<td>Observed</td>
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<tr>
<td>$X_{H_2O}$ = 0.93</td>
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<tr>
<td>$X_{CO_2}$ = 0.04</td>
</tr>
<tr>
<td>$X_{H_2}$ = 0.03</td>
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<tr>
<td>$X_{H_2S}$ = 0.001</td>
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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 appli-
cable 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, S2, H2, SO2, and CH4 vary up
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 un-
dersaturated with respect to graphite during cooling be-
cause graphite was not detected petrographically or
during Raman analyses. If graphite were to precipitate in
the fluid inclusions during cooling, then significant CH4 may
be produced at low temperatures and pressures. Although
\(X_{CH4}\) 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

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 com-
position of primary peak metamorphic fluid inclusions at
Ducktown.

H diffusion

Several phenomena reported in the fluid inclusion liter-
are have been attributed to the effects of diffusion.
Daughter minerals such as hematite, anhydrite, and chal-
copyrite, 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 Skin-
ner, 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 dif-
sion in wet quartz and berlinite (AIPO4) 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 gran-
ulites 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 \(f^*\) gradient between the host (or that
imposed by the fluid circulating through the rock) and
the fluid inside the inclusion. These gradients may be-
come appreciable during cooling and decompression. Dif-
sion 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 \(f^*\) 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 dif-
sion depends on the P-T-time path as well as the com-
positions of the inclusion and matrix fluid and crystal
chemistry.

We have calculated the changes in the \(f^*\) in the matrix
fluid and in model peak-metamorphic fluid inclusions
during uplift. The inclusions trapped the fluid composi-
tion calculated for 6 kbar, 550 °C, log \(f^*_O = -18.3\), log \(f^*_S = -2.7\), and \(a_c = 0.001\) (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

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**Fig. 8.** \(X-T\) relations showing closed system speciation changes obtained by trapping a peak metamorphic fluid at 6
kbar, 550 °C, log \(f^*_O = -18.3\), log \(f^*_S = -2.7\), and \(a_c = 0.001\) and cooling it at constant volume to 400 °C.
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., $P_{\text{ext}} > P_{\text{in}}$) 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 $f_{\text{H}_2}$ gradient established during the postmetamorphic history is presented in Figure 10. For these calculations it is assumed that the matrix fluid composition (i.e., $f_{\text{H}_2}$ and $f_{\text{H}_2}$) is buffered by Py-Po-Mt. Two $f_{\text{H}_2}$-$T$ curves were calculated for the matrix, one with $a_{\text{c}}$ constant at 0.001 (matrix 1; Fig. 10) and the other with $a_{\text{c}}$ varying from 0.001 at 6 kbar and 550 °C to 0.159 at 5 kbar and 400 °C, so that $X_{\text{CO}_2}$ is constant at 0.10 (matrix 2; Fig. 10). These calculations indicate that $f_{\text{H}_2}$ 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 $f_{\text{H}_2}$ gradient may have been established during uplift, and this gradient theoretically could have promoted H diffusion into primary fluid inclusions.

The difference in $f_{\text{H}_2}$ 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 + Ilm + 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 $f_{\text{O}_2}$ (pyroxene-bearing) portions of the ore bodies after peak metamorphism. The $f_{\text{H}_2}$ gradient resulting from infiltration of a fluid with $f_{\text{O}_2}$ buffered by FMQ and $f_{\text{H}_2}$ buffered by pyrrhotite with $X_{\text{FeS}} = 0.95$, relative to FeS-S, is shown in Figure 11. If this fluid comes into diffusive communication with primary fluid inclusions, a $f_{\text{H}_2}$ 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-$f_{\text{O}_2}$, low-$f_{\text{H}_2}$ 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-$f_{\text{O}_2}$-low-$f_{\text{H}_2}$ fluids after metamorphism. Given the rapid rate of H diffusion through minerals (e.g., Kronenberg et al., 1986), the calculated $f_{\text{H}_2}$ 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 $f_{\text{H}_2}$ 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 $f_{\text{H}_2}$ gradient. If the matrix fluid is buffered by FMQ, how-
Fig. 11. Relationships for $f_{H_2}-T$ calculated for matrix fluids and a hypothetical peak metamorphic fluid inclusion. Conditions are the same for the inclusion as in Figure 10. Here, the $f_{O_2}$ of the matrix fluid is buffered by FMQ and $f_{CO_2}$ is buffered by Po with $X_{FMQ} = 0.95$.

However, an amount of H approximately equivalent to 12.5 mol% of the H originally present in the inclusion must diffuse into the fluid inclusion to equilibrate $f_{H_2}$. Diffusion of this much H into a fluid inclusion has 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 reequilibrated 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 $f_{H_2}$ in the inclusions by reducing the total pressure, perhaps resulting in further H diffusion to equilibrate $f_{H_2}$. 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 Suzuoki and Epstein (1976) and Graham et al. (1987). Furthermore, coexisting minerals give nearly identical $\delta D_{H_2O}$ 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 diff-
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 (ΔH₂O-H₂ = 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 ΔH₂O-H₂. Mass balance calculations using a ΔH₂O-H₂ 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 fCH₄/fCO₂ 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, 10⁻² mol% CH₄, 10 mol% CO₂, and 0.1 mol% H₂S. Methane was not a significant component of peak metamorphic fluids in ore 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 fCH₄, approximately 3 log units below oxidized portions of ore zones. If such an fCH₄ 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.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the Tennessee Chemical Company for permission to obtain and study samples from the Ducktown ore bodies. We thank mine geologist Charles Acker for his aid and helpful discussions, Bruce Nesbitt for lending us the thin section suite from his dissertation research, and Todd Solberg for help with electron microprobe analyses. Some of the computer programs used in this study were developed with the assistance of Bob Downs, John Doyle, and Mike Sterner. Additional discussions with Mike Sterner and Mathew Nyman were invaluable. Early reviews by Dave Hewitt, Don Rimstidt, and Dave Wesolowski are much appreciated. Insightful reviews by Terry Bowers and Bruce Nesbitt significantly improved the final presentation. This study was supported by grants from the Earth Sciences division of the National Science Foundation (NSF grant EAR-8614095), the American Chemical Society Petroleum Research Fund (grant 18861-G2), and by funds from the Department of the Interior's Mining and Mineral Resources Research Institute program administered by the Bureau of Mines under allotment grants G1164151, G1174151, and G1184151.

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MANUSCRIPT RECEIVED December 15, 1989
MANUSCRIPT ACCEPTED April 16, 1991