Fluid inclusion constraints on the uplift history of the metamorphosed massive sulphide deposits at Ducktown, Tennessee

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ABSTRACT Standard petrographic, microthermometric and Raman spectroscopic analyses of fluid inclusions from the metamorphosed massive sulphide deposits at Ducktown, Tennessee, indicate that fluids with a wide range of compositions in the C–O–H–N–S–salt system were involved in the syn- to post-metamorphic history of these deposits. Primary fluid inclusions from peak metamorphic clinopyroxene contain low-salinity, H₂O–CH₄ fluids and calcite, quartz and pyrrhotite daughter crystals. Many of these inclusions exhibit morphologies resembling those produced in laboratory experiments in which confining pressures significantly exceed the internal pressures of the inclusions. Secondary inclusions in metamorphic quartz from veins, pods, and host matrix record a complex uplift history involving a variety of fluids in the C–O–H–N–salt system. Early fluids were generated by local devolatilization reactions while later fluids were derived externally.

Isochores calculated for secondary inclusions in addition to the chronology of trapping and morphological features of primary and secondary fluid inclusions suggest an uplift path which was concave toward the temperature axis over the P–T range 6–3 kbar and 550–225°C. Immiscible H₂O–CH₄–N₂–NaCl fluids were trapped under lithostatic to hydrostatic pressure conditions at 3–0.5 kbar and 215 ± 20°C. Entrapment occurred during Alleghanian thrusting, and the fluids may have been derived by tectonically driven expulsion of pore fluids and thermal maturation of organic material in lower-plate sedimentary rocks which are thought to underlie the deposits. Episodic fracturing and concomitant pressure decreases in upper-plate rocks, which host the ore bodies, would have allowed these fluids to move upward and become immiscible. Post-Alleghanian uplift appears to have been temperature-convex.

Uplift rates of 0.10–0.05 mm year⁻¹ from middle Ordovician to middle Silurian – late Devonian, and 0.07–0.12 mm year⁻¹ from middle Silurian – late Devonian to late Permian are suggested by our uplift path and available geochronological data.

Key words: C–O–H–N–S fluids; Ducktown, Tennessee; fluid inclusions; metamorphosed massive sulphides; P–T–t paths.

INTRODUCTION
Metamorphosed pyrrhotite–pyrite-rich massive sulphide deposits, some of the largest and best studied of which are located at Ducktown, Tennessee, occur throughout the Appalachian–Caledonian orogen (Fig. 1). Despite the importance of these ores and their long history of exploitation, many questions remain unanswered regarding their origin and their behaviour during metamorphism, due in part to a lack of information regarding the temporal and spatial chemical evolution history of fluids attending burial, metamorphism and uplift of these deposits.

Fluid inclusions provide one of the best tools available for determining properties of fluids associated with various geological processes, and could provide valuable information on the nature of fluids attending the metamorphism at Ducktown and other massive sulphide deposits in the Appalachians. Studies of fluid inclusions may provide more detailed fluid composition data and may be more sensitive to temporal/spatial variations in fluid composition as compared with fluid compositions obtained from mineral equilibria calculations.

To date, no detailed fluid inclusion studies have been conducted on this important class of ore deposit. The Ducktown deposits provide an excellent opportunity for studying the fluids in metamorphosed massive sulphide ores because large fluid inclusions suitable for study are found in and around the ore bodies, and because several recent detailed geological and geochemical studies have provided a sound basis for understanding the relationship between the ores and adjacent rocks and for interpreting the fluid inclusion data. In this paper, data from fluid inclusions are combined with tectonic and geochronologi-
magnetite (Magee, 1968). Other reported metallic phases include galena, molybdenite, tetrahedrite, native bismuth, cubanite, stannite, bornite, rutile and ilmenite. Traces of gold and silver have been reported from assays but the mineralogical hosts for these metals remain unknown as no discrete precious-metal-bearing phase has ever been reported. Gangue minerals include tremolite–actinolite, cummingtonite, biotite, muscovite, stilpnomelane, chlorite, quartz, calcite, dolomite, rhodochrosite, talc, clinoopyroxene, plagioclase, garnet, epidote-group minerals, anhydrite and rhodonite. Detailed stratigraphical studies have been conducted by Emmons & Laney (1926), Magee (1968) and Holcombe (1973). The ore bodies are located within one to three stratigraphic horizons (Fig. 2) but are difficult to correlate due to the effects of deformation.

The host rocks are dominantly metagreywackes and quartz–mica schists with less abundant quartzite, metaclassic, and calc-silicate hornsfels. The hornfels, which contains plagioclase, quartz, calcite, clinopyroxene, hornblende, garnet and titanite, occurs as irregular pod-like masses within metagreywacke, and may represent metamorphosed calcareous concretions (Hadley & Goldsmith, 1963). In addition, several lithologies occur only near the ore bodies, including chlorite schist, muscovite schist, biotite schist, plagioclase-rich rock and spessartine-rich rock. Similar lithologies have been recorded near other metamorphosed massive sulphides (e.g. Gair & Slack, 1984) and have been interpreted as representing either metamorphosed volcaniclastics or metamorphosed equivalents of alteration zones and exhalites typically

data to establish an uplift path, place it into an absolute time framework and derive average uplift rates.

GEOLOGICAL 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 254,000 to 71,120,000 tonnes (182,880,000 tonnes in 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 sulphide and 35 vol.% gangue. The massive sulphide 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.%

![Fig. 1. Index map of the eastern USA showing the locations of stratiform massive sulphide ore deposits in the Appalachians. MS = Machias, PB = Pembroke, HS = Harborside, BH = Blackhawk, MN = Milan, EL = Elizabeth, DV = Davis, FV = Friedensville, TV = Timberville, MD = Mineral District, NC = New Canton, DW = Dillwyn, AV = Austinville, GL = Great Gossan Lead, OK = Ore Knob, EK = Elk Knob, ET = East Tennessee, CA = Carthage, CH = Chestatee, PY = Pyriton. Modified from Craig (1983).](image)

![Fig. 2. Detailed map of the Ducktown mining district showing the distribution of the ore bodies and mapable lithological units (adapted from Addy & Ypma, 1977).](image)
found around unmetamorphosed volcanogenic massive sulphide deposits (Henry et al., 1979; Gair & Slack, 1984).

The Ducktown ore bodies and their host rocks have undergone polyphase regional metamorphism associated with the closing of the Iapetus ocean beginning in middle to late Cambrian time (the Taconic orogeny) and culminating in continent-continent collision of North America with Africa during the Carboniferous and Permian (the Alleghanian orogeny; Hatcher, 1978). Holcombe (1973) recognized three major episodes of deformation, the last of which generated several structural features. Addy & Ypma (1977) have proposed five deformation events (F1-F5) and three episodes of metamorphism (M1-M3). The M1-F1 event, which reached garnet grade, occurred during the Taconic orogeny (c. 480 Ma). The M2 metamorphic event attained staurolite-kyanite grade and was interpreted by Addy & Ypma (1977) to have occurred after the Acadian orogeny (F2, 380-340 Ma). Most workers now believe that the thermal peak, hence F2, was attained during the Taconic and not the Acadian (Fullagar & Bottino, 1970; Butler, 1972; Dallmeyer, 1975a, b; Hatcher et al., 1980). It is probable that the M1-M2 events of Addy & Ypma (1977) represent a single prograde heating episode.

A Barrovian sequence of metamorphic mineral assemblages was produced during the Taconic orogeny. The biotite isograd is located c. 9 km west of Ducktown (Carpenter, 1970), and grade increases progressively to the east through garnet, staurolite and kyanite isograds (Fig. 3). Maximum grade in the mine area is middle amphibolite facies and is characterized by the assemblage staurolite±kyanite. Mineral thermobarometers constrained P-T conditions of peak metamorphism to be 6 ± 1 kbar and 540 ± 40° C (Nesbitt & Essene, 1982). Brooker et al. (1987) used sphalerite geobarometry on sphalerite grains armoured by pyrite to obtain a pressure estimate of 6.8 ± 0.8 kbar. Oxygen isotope thermometry on concordant mineral triplets suggests maximum temperatures of 530 ± 20° C (Hall, 1989). The M3 event of Addy & Ypma (1977) was associated with Alleghanian brittle deformation (F3-F5, 320-270 Ma) and reached chlorite grade (Holcombe, 1973; Addy & Ypma, 1977).

In a regional tectonic sense, the Blue Ridge and Inner Piedmont Provinces form a large allochthon composed of a series of thrust sheets which have been transported up to several hundred kilometres to the northwest (Hatcher & Zietz, 1980). Individual thrust sheets were emplaced at different times throughout the Palaeozoic—generally displaying westward younging—and in part probably overlie relatively unmetamorphosed Cambrian-Ordovician platform carbonates and Carboniferous-Permian clastics whose lateral equivalents are exposed in the Valley and Ridge Province (Hatcher & Zietz, 1980; Secor et al., 1986).

**FLUID INCLUSIONS**

Samples were collected at 1.5-m intervals from five drill cores that penetrate the Cherokee ore body and adjacent wallrock. Samples were also collected from approximately 60 additional drill cores from the Cherokee, Calloway, Boyd and Mary-Polk ore bodies (Fig. 2). Hand samples were collected from the open pit operation of the Cherokee ore body.

Fluid inclusions in ore and host rocks were studied utilizing standard petrographic, microthermometric and Raman spectroscopic techniques. Microthermometric data were collected on a USGS-type gas-flow stage manufactured by Fluid Inc and calibrated at the triple point of CO₂ (-56.6° C), the triple point of H₂O (0.0° C) and the critical point of H₂O (374.1° C) with synthetic fluid inclusions (Sterner & Bodnar, 1984). From -198 to -56.6° C the accuracy is estimated to increase in a near-linear manner from ±1° C at -198° C to ±0.1° C at -56.6° C. The estimated accuracy is ±0.1° C from -56.6° C to 100° C and ±2° C at 374.1° C. Reproducibility is in all cases within the estimated accuracy of the temperature determination. Qualitative spectroscopic analyses of the constituent molecular fluid species within fluid inclusions were collected on an ISA U-1000 Raman microscope equipped with an Ar-ion laser of wavelength 514 nm. All fluid inclusion data are tabulated in Hall (1989).

![Fig. 3. Map showing the distribution of principal lithological units and isograds in the Ducktown area (adapted from Nesbitt, 1979).](image-url)
Primary fluid inclusions

Occurrence

Primary fluid inclusions occur in clinopyroxene and rarely in garnet and amphibole from the Cherokee, Culloway, Boyd and Mary-Polk ore bodies. Pyroxene is generally coarse grained (≤10 cm), and is frequently accompanied by amphibole (in part retrograde), calcite, quartz, pyrrhotite ± garnet ± pyrite ± magnetite ± anhydrite, and is texturally and chemically similar to metasomatic pyroxene found in skarn deposits (see Einaudi et al., 1981). The pyroxene is a diopside–hedenbergite–johannesenite solid solution with Di<sub>58</sub>–Hd<sub>24</sub>–Jo<sub>18</sub>.

Primary fluid inclusions in pyroxene are usually crystallographically controlled (Fig. 4a, d) and tend to be elongate along (001). Rods of amphibole commonly have been included during pyroxene growth and are orientated parallel to the z axis of pyroxene. In some cases the inclusions are trapped adjacent to these amphibole inclusions (Fig. 4b) or between two such crystals.

Some primary fluid inclusions are unusually large for metamorphic rocks, attaining sizes of several hundred micrometers; the average size is 20 μm. Many are highly irregular (Fig. 4c) and exhibit textures which resemble implosion haloes produced during experimental deformation of inclusions in quartz under conditions of external overpressure (Stoner & Bodnar, 1989). This texture is important in constraining the uplift path of the terrane and will be discussed further in a later section.

At room temperature these inclusions contain liquid and vapour, several birefringent daughter crystals and, in some cases, an opaque daughter phase (Fig. 4e). The birefringent daughter minerals were identified as calcite and quartz using Raman spectroscopy. The opaque daughter was identified as pyrrhotite with reflected-light microscopy and Raman spectroscopy. Pyrrhotite daughters are generally very small and equant and are usually only visible in relatively large inclusions. They are interpreted to be true daughters rather than accidental crystals trapped during formation of the fluid inclusions based on their consistent phase ratios when present. Pyrrhotite may be metastably absent from many of the smaller inclusions. With the exception of pyrrhotite, the phases present and solid phase ratios in primary inclusions are uniform; however, the liquid-to-vapour (L/V) ratio is variable. Textural and microthermometric data presented below suggest that variable L/V ratios are the result of re-equilibration of inclusion densities in response to differential pressure between inclusions and matrix during uplift.

Microthermometry

Microthermometry and Raman spectroscopy reveal that the fluid portion is aqueous with a salinity of about 3 wt% NaCl equivalent, and approximately 5 mol% CH₄. On warming frozen inclusions, the first phase transition observed is the homogenization of residual CH₄ [T<sub>CH₄</sub>(CH₄)] in the presence of clathrate + ice + hydrohalite ± other salts or salt hydrates. Homogenization is to liquid at −157 to −90°C and rarely to vapour at −90 to −83°C. T<sub>CH₄</sub>(CH₄), especially to vapour, is not observed in many inclusions because of optical limitations. The next phase change observed in

Fig. 4. Photomicrographs of primary fluid inclusions in clinopyroxene from Ducktown, Tennessee. Scale bars = 25 μm.

(a) Crystallographically controlled fluid inclusions. Arrow indicates z direction.
(b) Fluid inclusions trapped at the boundary between pyroxene, p, and crystallographically controlled amphibole, a, which was included during growth of clinopyroxene.
(c, d) Inclusions showing evidence for extensive re-equilibration. (e) Fluid inclusions containing pyrrhotite, po, daughters (opaque) in addition to calcite, cc, and quartz, qz, daughters, a low-salinity aqueous phase and CH₄-rich vapour.
a very few inclusions is eutectic melting at \(-22\) to \(-23^\circ\) C, near the eutectic in the system NaCl-KCl-H\(_2\)O \((-22.9^\circ\) C; Linke, 1965). This suggests that NaCl ± KCl are the dominant salt(s) dissolved in the aqueous phase. Much of the melt produced at the eutectic is immediately consumed by formation of additional clathrate; however, in some cases the initial melt is armoured from the vapour bubble (i.e. the source of CH\(_4\)) by existing clathrate. The melting of ice \(T_m(\text{ice})\) in the presence of clathrate, liquid and vapour occurs at \(-2.8\) to \(-0.9^\circ\) C and CH\(_4\) clathrate dissociates \(T_m(\text{clath})\) at 11.5-25.2^\circ\) C. The temperature of the latter phase change is sensitive to the phases present at \(T_m(\text{clath})\), the salt content of the inclusion, the presence of other volatiles such as CO\(_2\) and N\(_2\), and the internal pressure at \(T_m(\text{clath})\). An increase in salinity acts to depress \(T_m(\text{clath})\) at constant pressure (Kobayashi et al., 1951), whereas an increase in internal pressure results in elevation of \(T_m(\text{clath})\) (Deaton & Frost, 1946). Addition of CO\(_2\) to the CH\(_4\) clathrate structure causes elevation of \(T_m(\text{clath})\) at a given pressure (Unruh & Katz, 1949), while addition of N\(_2\) depresses \(T_m(\text{clath})\) (Deaton & Frost, 1946). Using 5 wt% NaCl as the estimated maximum salinity (based on \(T_m(\text{ice})\) in the presence of clathrate) and the data of Kobayashi et al. (1951), internal pressures of 0.2-0.6 kbar at \(T_m(\text{clath})\) are calculated.

Continued heating above \(T_m(\text{clath})\) usually results in decrepitation, prior to liquid–vapour homogenization \(\{T_l(\text{L-V})\}\), at temperatures of 150-250\(^\circ\) C. Values of \(T_l(\text{L-V})\) that could be measured are 200-250\(^\circ\) C and correlate positively with inclusion size suggesting that re-equilibration toward lower densities has occurred during uplift. The positive correlation results from the fact that larger fluid inclusions re-equilibrate before smaller ones, and to a greater degree (Bodnar et al., 1989; Sterner & Bodnar, 1989). Recall that these same inclusions show textural evidence of earlier re-equilibration toward higher densities. There is no detectable dissolution of daughter minerals during heating to 250\(^\circ\) C.

**Bulk composition**

Daughter minerals can be re-integrated with fluid components to determine the bulk composition of primary fluid inclusions. On average, calcite, quartz and pyrrhotite daughters occupy 5, 1 and 0.1 vol% of the inclusion, respectively. As discussed above, microthermometry and Raman spectroscopy indicate that the fluid phase (excluding the daughter crystals) is adequately represented by the system H\(_2\)O-CH\(_4\)-NaCl. However, if the solid phases are re-integrated into a homogeneous fluid, assuming that carbonate existed in solution as Ca and CO\(_2\) and that pyrrhotite existed as Fe and H\(_2\)S, the estimated average composition of the peak metamorphic fluid is:

\[
\begin{align*}
X_{\text{H}_2\text{O}} &= 0.93, \quad \text{Ca} = 54,000 \text{ ppm}, \\
X_{\text{CH}_4} &= 0.04, \quad \text{NaCl} = 30,000 \text{ ppm}, \\
X_{\text{CO}_2} &= 0.03, \quad \text{SiO}_2 = 26,000 \text{ ppm}, \\
X_{\text{H}_2\text{S}} &= 1 \times 10^{-3}, \quad \text{Fe} = 3000 \text{ ppm},
\end{align*}
\]

where the volatile portion has been normalized to 100 mol% for comparison with fluid equilibria calculations. No attempt has been made to charge balance this composition due to the lack of information on the nature of ionic species in high-P-T metamorphic fluids, but there must have been appreciable dissolved carbonate or bicarbonate and perhaps chlorine to charge balance calcium and iron. The above calculation suggests that the amount of solids dissolved in the peak metamorphic fluid phase exceeded 11 wt%. Post-entrapment compositional changes resulting from re-equilibration of fluid constituents during closed-system cooling have been calculated using techniques outlined by Hall et al. (1991). These changes are negligible.

The normalized volatile portion of the calculated fluid composition exhibits important similarities and differences when compared to theoretical calculations of fluid speciation at elevated pressures and temperatures (Hall et al., 1991). In particular, the mole fractions of H\(_2\)O, H\(_2\)S and total carbonic species are consistent, but the CH\(_4\)/CO\(_2\) ratio is much greater in the fluid inclusions than in the calculated fluid. Methane appears to have been produced from CO\(_2\) in the inclusions by diffusive addition of hydrogen after inclusion formation, and the volatile portion of the original trapped fluid is inferred to have been largely H\(_2\)O + CO\(_2\) with 10 mol% CO\(_2\) (Hall et al., 1991).

Quartz, calcite and pyrrhotite daughter crystals probably precipitated in response to decreasing temperature. Calcite, which displays retrograde solubility in low-salinity, non-alkaline solutions, probably shows prograde solubility at elevated temperatures in saline fluids (Holland & Malinin, 1979) and at elevated P-T in pure H\(_2\)O (Walther, 1986). The resorbed appearance of most calcite daughter crystals suggests that they went through a solubility minimum. Available data suggest that a minimum in solubility as a function of temperature occurs near 500\(^\circ\) C at 3 kbar in pure H\(_2\)O solutions (Walther, 1986), although higher pressure data and data for salt ± CO\(_2\)-bearing solutions are not available.

**Secondary fluid inclusions in quartz**

**Immiscible H\(_2\)O-CH\(_4\)-N\(_2\)-NaCl inclusions**

The most common type of secondary fluid inclusions, which are found in metamorphic quartz from veins, pods and host matrix, contain H\(_2\)O-CH\(_4\)-N\(_2\)-NaCl fluids. These inclusions occur along recrystallized grain boundaries (Fig. 5a), healed intragranular and intergranular microfractures (Fig. 5b), microfractures surrounding hexagonal pyrrhotite inclusions (Fig. 5c) and, rarely, as isolated inclusions. All occurrences have indistinguishable compositions. Inclusions of this type which decorate grain boundaries (Fig. 5a) were trapped after grain-boundary cracking events, which also caused significant intergranular and intragranular fracturing (Fig. 5c). Not during the recrystallization of quartz that occurred during or soon after peak metamorphism. This is an important observation because it moves the time of trapping from early in the post-peak-metamorphic history, when rocks behaved in a ductile manner, to later in the uplift history during brittle deformation. Grain-boundary fluid inclusions in metamorphic rocks are often assumed to have been trapped during recrystallization, but rock mechanics studies have shown that grain-boundary cracking occurs before intragranular fracturing, in response to thermal expansion and elastic moduli mismatch between neighbouring grains (e.g. Fredrich & Wong, 1986). Fluids present during grain-boundary cracking events could be trapped along grain boundaries and then texturally appear to have been trapped during recrystallization. This may account for inclusions that are reported in some studies which appear to be texturally early but have compositional and density characteristics suggesting a late origin.

Microthermometry and Raman spectroscopy reveal two types of inclusions interpreted to represent the end-members of an immiscible fluid. The two inclusion types contain (i) CH\(_4\)-N\(_2\), with very little H\(_2\)O (optically indistinguishable) and (ii) H\(_2\)O-CH\(_4\)-NaCl with very little N\(_2\). At room temperature these appear, respectively, as a supercritical single phase CH\(_4\)-N\(_2\) inclusions, and two phase inclusions containing aqueous liquid and CH\(_4\)-rich vapour (Fig. 5d). One type is usually dominant in a given sample. In vapour-rich (CH\(_4\)-N\(_2\)) inclusions, \(T_l(\text{CH}_4)\) occurs at \(-82.2^\circ\) C (homogenization by critical behaviour) to \(-144^\circ\) C (homogenization to liquid). Homogenization is generally to liquid; however, a few inclusions homogenize to vapour at \(-83\) to \(-87^\circ\) C. No other phase changes were detected in CH\(_4\)-N\(_2\) inclusions, although we suspect that a very thin, aqueous film wets the wall of these inclusions. Homogenization by critical behaviour at \(-82.2^\circ\) C in one inclusion compares favourably with the critical temperature of pure CH\(_4\) (\(-82.6^\circ\) C). Similar inclusions from another sample exhibit critical behaviour at \(-88.6\) to \(-90.0^\circ\) C due to the effect of N\(_2\) as verified by Raman spectroscopy. Data compiled by van den Kerkhof (1988) indicate that c. 15 mol% N\(_2\) in CH\(_4\)-N\(_2\) inclusions
will produce a critical temperature near −90°C. The large range in $T_c$(CH₄), which implies an appreciable range in bulk density, is not the result of post-entrapment volume changes because there is no correlation between $T_c$(CH₄) and inclusion size.

On heating liquid-rich inclusions, the first phase change observed is eutectic melting in the presence of clathrate, ice, hydrohalite(?) and CH₄-rich vapour. Eutectic temperatures are generally −22 to −23°C, suggesting that NaCl ± KCl are the dominant salts in solution. Ice melts at −5 to −11°C in the presence of clathrate, liquid and vapour, and clathrate melts at 6–14°C in the presence of liquid and vapour. $T_c$(ice) in the presence of clathrate provides a maximum salinity estimate of 8–15 wt% NaCl equivalent for these inclusions (Hall et al., 1988). It is likely that true salinities are closer to 5–10 wt% NaCl equivalent, although these cannot be determined microthermometrically. The data of Kobayashi et al. (1951) suggest internal pressures of 65–200 bar at $T_c$(clath) for H₂O–CH₄–NaCl fluids containing 5–10 wt% NaCl. True internal pressures may be slightly higher as these inclusions contain up to several mol% N₂ (Deaton & Frost, 1946).

Fig. 5. Photomicrographs of secondary fluid inclusions in quartz found at Ducktown. Scale bars = 25 μm. (a) H₂O–CH₄–N₂–NaCl inclusions occurring along grain boundaries between recrystallized quartz. (b) H₂O–CH₄–N₂–NaCl inclusions occurring along healed intragranular and intergranular microfractures. (c) H₂O–CH₄–N₂–NaCl inclusions along radial microfractures associated with secondary inclusions of pyrrhotite, po. (d) Coexisting liquid-rich and vapour-rich H₂O–CH₄–N₂–NaCl inclusions. (e) H₂O–CO₂–NaCl inclusions along transgranular fractures. (f) Randomly orientated H₂O–CO₂–NaCl inclusions. (g) Low-salinity, one-phase aqueous inclusions occurring as an isolated group. (h) Low-salinity, one-phase aqueous inclusions along intergranular fractures. (i) Low-salinity, one-phase aqueous inclusions showing ‘sheared’ terminations on negative crystals. (j) Halite-bearing inclusions along healed fractures. (k) Late-stage CaCl₂–MgCl₂–NaCl–H₂O inclusions.
Total homogenization of liquid-rich inclusions occurs at temperatures of 200–265°C (average of 215°C). However, many inclusions decrepitate at temperatures of 130–230°C, prior to homogenization. The higher homogenization temperatures were obtained on inclusions that partially decrepitated during heating. True homogenization temperatures are interpreted to be 215 ± 20°C.

A group of variable-sized, liquid-rich inclusions was monitored during heating in order to estimate their internal pressures at decrepitation and hence provide constraints on the location of their isotherm in P–T space. The volume of each inclusion (modelled as spheres or prolate spheroids) was recorded as was the clathrate dissociation temperature. Inclusions were heated slowly in 25°C increments and then cooled slowly to room temperature between each heating step. \( T_d \) (clath) was remeasured for each inclusion after each heating increment. As \( T_d \) (clath) is sensitive to changes in internal pressure, it provides an indication of volume changes due to decrepitation. The equation of Bodnar et al. (1998), which relates inclusion size or volume to internal pressure at decrepitation, was used to estimate the internal pressure at the decrepitation temperature \( \Delta T_d \), the latter being defined as the midpoint of the heating increment that caused a decrease in \( T_d \) (clath). A negative correlation between \( T_d \) and inclusion volume was recorded (Fig. 6), and internal pressures of 1.5–2.5 kbar at \( T_d \) (160–250°C) were calculated. Interpolation to \( T_d \) (215°C) suggests an internal pressure of c. 2.3 kbar at \( T_d \) for this group of inclusions.

Evidence for simultaneous trapping of immiscible fluids is rarely unequivocal in metamorphic rocks. Nevertheless, we feel that reasonably good evidence does exist in this case, including:

1. Common occurrence of vapour-rich CH4–N2 (H2O) and liquid-rich H2O–CH4–N2 salt (\( \Delta N_2 \)) inclusions together in a single sample. Both types exist in similar textural settings;
2. Inclusion planes which are dominated by one end-member, but which contain the other end-member (Fig. 5d). Mixed inclusions are common near inclusions containing the subordinate end-member;
3. When the two types of inclusions coexist, those representing the vapour-rich end-member are often larger than those representing the liquid-rich end-member, perhaps reflecting the minimum stable vapour bubble size that may exist. Similar behaviour was reported by Bodnar et al. (1985) for the system H2O–NaCl;
4. Phase ratios and compositions that are qualitatively consistent with those expected for immiscible fluids in the system.

Inclusions containing H2O–CO2–salt (\( \Delta N_2 \)) were found only in samples of quartzite from wallrock collected from the open pit work of the Cherokee ore body. The inclusions occur along transgranular fractures (Fig. 5e), along grain boundaries, and in random orientations (Fig. 5f). They contain an aqueous liquid and CO2-rich liquid at room temperature. Raman analyses indicate that detectable amounts of CH4 and N2 are present in the CO2-rich phase of some of these inclusions.

Carbon dioxide melts at -36.6 to -58.9°C in the presence of clathrate, ice, CO2-rich vapour, CO2-rich liquid and hydrohalite (?). These temperatures are consistent with Raman data and suggest 5–15 mol% CH4 + N2 in the CO2-rich phase liquid (van den Kerkhof, 1988). Apparent eutectic melting of the aqueous phase occurs at 20.5 ± 2°C, suggesting NaCl ± KCl as the dominant salt(s) in solution. It should be noted that this is not a true eutectic because CO2 is in excess, and thus the aqueous melt produced should immediately combine with liquid CO2 to form more clathrate. In reality, however, the melt is effectively isolated from liquid CO2, which is armoured by clathrate, allowing a metastable eutectic, applicable to the aqueous portion of the inclusion, to be measured. Ice melts in the presence of clathrate, liquid CO2 and CO2-rich vapour at -5.5 to -8.7°C, and CO2-rich clathrate dissociates at 7.1 to 8.8°C. Carbon dioxide liquid–vapour homogenization to the liquid occurs at -2.2 to 21.7°C. Smaller inclusions display total homogenization at 250–292°C and larger inclusions decrepitate over the range 180–260°C. Frequently, an orientated array of microfractures develops during decrepitation and it is probable that some of the inclusions with the highest \( T_d \) partially decrepitated or stretched during heating, as was verified in some cases by re-measuring \( T_d \) (CO2) before and after measuring \( T_d \). Homogenization temperatures of the smallest inclusions (c. 250°C) are believed to be the most realistic because nearly all large inclusions partially decrepitate before 200°C as evidenced by the following decrepitation study.

The decrepitation behaviour of these inclusions was studied using the technique outlined in the previous section and substituting \( T_d \) (CO2) for \( T_d \) (clath) as the discriminator for density changes. \( T_d \) was found to be inversely proportional to the inclusion volume (Fig. 7) and application of the equation of Bodnar et al. (1988) suggests internal pressures of 3.0 kbar at \( T_d \) (250°C). Although \( T_d \) (CO2) implies a range in CO2 densities from 0.76 to 0.94 cm3 at a given volume versus \( T_d \) (CO2) shows no trend (Fig. 8). Hence, except in a few cases where inclusions have obviously decrepitated, there is no evidence to support extensive re-equilibration of these fluid inclusions during uplift. Density variations with a given fracture plane are minimal.

Salinities of 2.4–5.6 wt% NaCl equivalent were estimated for these inclusions using the method of Collins (1979) and the equation of Bazzu et al. (1979). This assumes that the system is adequately represented as H2O–CO2–NaCl. Raman analyses and microthermometry indicate that 5–15 mol% CH4 + N2 may be present in the non-aqueous portion of the inclusions, which translates to roughly 0.5–2 mol% of the total inclusion (XCO2 is calculated to be 0.10–0.15). By considering clathrate melting data of Deaton & Frost (1946) and Unruh & Katz (1949) and liquid–vapour equilibrium data for CO2–CH4 and CO2–N2 mixtures compiled by van den Kerkhof (1988) it is apparent that
one or both terminations of the negative crystal. After
decrystallization these inclusions are two-phase liquid+vapour at
room temperature, and subsequent freezing tests give vapour-
present ice melting temperatures of 0.0 to −5.8 °C, corresponding
to an NaCl equivalent salinity of 0–6 wt% (Hall et al., 1988).
Reliable eutectic temperatures could not be measured for these
inclusions. Single-phase inclusions decrepitate over the range
225–300 °C; application of the equation of Bodnar et al. (1988)
implies internal pressures of c. 2.5–3.5 kbar at \( T_e \). Many of these
inclusions have apparently decrepitated during uplift and are now
two-phase with widely varying L/V ratios, or are empty. Crushing
tests and Raman analyses revealed no non-condensable gas
species.

**Three-phase, brine + vapour + halite inclusions**

Three-phase, brine + vapour + halite inclusions occur along
healed fractures in deformed quartz veins in country-rock schists
and metagreywackes (Fig. 5j). Many show evidence of necking
down and display inconsistent L/V ratios; some lack a vapour
phase altogether. The inclusions do not freeze even when held at
liquid nitrogen temperatures for several minutes. Halite
dissolution temperatures range from 198 to 202 °C, corresponding
to an equivalent salinity of 32.5 wt% NaCl (Sterner et al., 1988).
Inclusions showing no evidence of necking down homogenize to
the liquid at 160–190 °C. Crushing tests and Raman analyses
revealed no non-condensable gases.

**CaCl\(_2\) ± MgCl\(_2\)-rich inclusions**

CaCl\(_2\) ± MgCl\(_2\)-rich inclusions generally are large and irregularly
shaped, and are usually associated with late-stage microfractures
in quartz and calcite (Fig. 5k). They are characterized by very low
initial melting temperatures (−30 to −70 °C) and low final melting
temperatures of ice (−9.1 to −43 °C). Individual planes of
inclusions display much narrower \( T_m − T_e \) variations than the total
measured range. A positive correlation between apparent eutectic
temperature and final melting temperature was noted in some
samples. Because it is difficult to detect first melting in fluid
inclusions unless significant quantities of melt are produced at the
eutectic (i.e. the bulk composition of the inclusion is close to the
eutectic composition), the lowest temperature apparent eutectic
may be most accurate. Apparent eutectics below −57 °C (the
eutectic temperature in the system CaCl\(_2\)-MgCl\(_2\)-NaCl-H\(_2\)O;
Linke, 1965) may indicate additional components are present.
However, initial melting temperatures as low as −80 °C were
observed by Davis et al. (1990) in synthetic NaCl–CaCl\(_2\)–H\(_2\)O and
NaCl–MgCl\(_2\)–H\(_2\)O inclusions grown in halite. These authors have
attributed initial melting temperatures below those of the stable
eutectics of these systems (−35 & −52 °C, respectively) to the
melting of metastable magnesium and/or calcium salt hydrates.

Most CaCl\(_2\)–MgCl\(_2\)-rich inclusions in Ducktown rocks are
one-phase liquids or have very low homogenization temperatures
(<100 °C). However, in one sample homogenization temperatures
of 175–265 °C were recorded on small inclusions, whereas larger
inclusions had still higher \( T_h \). In this sample a positive correlation
recorded between inclusion size and \( T_h \) suggests that the inclusions
partially decrepitated during uplift. We believe that the true
homogenization temperatures for these inclusions are probably
<75 °C. Leakage and partial decrepitation appears to have been
intensified by the large size and poorly formed nature of these
inclusions. Given the compositional and density variations within
this type it is likely that several generations of fluids are
represented.

**Chronology of entrapment**

Fluid inclusions from Ducktown document a complex,
post-metamorphic uplift history involving a variety of
fluids. The densities, textures and chronology of entrapment of the inclusions provide significant constraints on possible uplift paths. Not all fluid inclusion types are found at all sample localities, suggesting that fluid flow was not pervasive or that fluid composition was locally controlled. This is consistent with stable isotope data, which record minimal post-metamorphic exchange and imply low integrated fluid-to-rock ratios (D. Hall et al., unpublished data). The restriction of some fluid types to certain areas (e.g. halite-bearing inclusions only in deformed quartz veins) implies that they may have been derived locally or channelled through favourable horizons.

Primary fluid inclusions located in pyroxene from ore zones were trapped during peak metamorphism since the host was present and equilibrated at peak metamorphic conditions (Addy & Ypma, 1977; Nesbitt, 1979, 1982). These inclusions would record the compositional and volumetric properties of the peak metamorphic fluid present in oxidized and sulphidized portions of the ore zones (i.e. at \( f_{O2} - f_{S2} \) conditions near the Py-Po-Mt buffer) provided that no post-trapping changes in density or composition have occurred. Density variations in primary fluid inclusions have already been noted, however, and are interpreted as resulting from re-equilibration in response to differential pressures between host and inclusions during uplift. Unfortunately, these inclusions re-equilibrated compositionally as well, in response to \( f_{H2} \) gradients established during the early uplift history of the terrane (Hall et al., 1991).

It is inferred, from textural evidence and cross-cutting relationships, that low-salinity, one-phase inclusions record the next oldest fluid. Their deformed nature coupled with their textural maturity (i.e. negative crystal morphology), common evidence for movement of inclusions away from the original fracture plane in response to strain in the host quartz (Roedder, 1971), evidence for partial decrepitation or stretching, and their occurrence as isolated patches in the cores of recrystallized quartz suggest that they were trapped prior to the end of peak metamorphism.

The next oldest fluid is recorded as \( CO_2-H_2O-NaCl \) inclusions in wallrock quartzite. These show moderate textural maturity, little or no evidence of movement from original planes, and relatively little evidence for re-equilibration of inclusion densities during uplift. The \( CO_2-H_2O-NaCl \) inclusions were trapped before immiscible \( H_2O-CH_4-N_2-NaCl \) inclusions because the homogenization temperatures and pressures of the former, which represent minimum formation conditions, are higher than the trapping temperatures and pressures of the latter (see below).

Immiscible \( H_2O-CH_4-N_2-NaCl \) inclusions are the next fluid recorded and provide a tight constraint on the uplift path because the \( P-T \) conditions of homogenization are the trapping conditions (3-0.5 kbar, 215 ± 20°C as inferred from intersections of \( T_h \) for liquid-rich inclusions with calculated isochores for coexisting vapour-rich inclusions). This event appears to have been the most pervasive because this type of inclusion is the most commonly encountered. However, these inclusions are much more abundant in and near the ore bodies which may have acted as conduits for fluid flow during uplift. This inclusion type is also present in minor amounts throughout the host rocks and in biotite-granite rocks to the west of Ducktown.

Three-phase \( NaCl-H_2O \) inclusions appear to have been trapped at relatively low \( P-T \) conditions. There is substantial evidence for necking in many of these texturally immature inclusions. Their occurrence only in deformed (and presumably early) quartz veins in host-rock schists and metagreywackes is somewhat problematic as late-stage fluids might be expected to be more pervasive. Textural evidence, however, suggests that they are contemporaneous with or post-date immiscible fluids.

The youngest fluid inclusions are one-phase, texturally immature \( CaCl_2-MgCl_2-NaCl-H_2O \) inclusions. These are located in poorly healed fractures which cross-cut all other inclusion types and were probably trapped very late in the uplift history from low-\( T \) (<75°C) fluids.

### Uplift History

Representative isochors for the above inclusion types were calculated from available experimental and theoretical data (Fig. 9). Where possible we have indicated the total uncertainty associated with the individual isochors, which arises from determination of the \( P-V-T \) properties of the fluids (i.e. experimental \( P-V-T \) measurements or equations of state) and from the observed range in densities and compositions for a given inclusion type that cannot be attributed to post-entrapment changes.

The composition of the peak metamorphic fluid present at 6 kbar, 550°C and \( f_{O2} - f_{S2} - a_C \) conditions indicated by sulphide-oxide-silicate assemblages in pyroxene-bearing rocks (pyroxene ± amphibole + calcite + quartz + pyrite + pyrrhotite + magnetite) is calculated to be 90 mol% \( H_2O \), 10 mol% \( CO_2 \) and 0.1 mol% \( H_2S \). A theoretical isochore for inclusions which trapped this fluid was obtained by calculating the \( P-V-X \) changes to the trapped fluid during cooling at constant volume (isochore 1, Fig. 9; see Hall et al., 1991, for method). This theoretical isochore was included in order to explain textures observed in primary fluid inclusions in pyroxene. The range of actual isochors for the fluid portion of primary inclusions is shown as well, but this is not very useful since post-entrapment density and compositional modifications have occurred. In particular, primary inclusions show textural evidence of having increased their densities in the early stages of uplift, changed composition through addition of hydrogen (resulting in increased density as well), and then decreased their densities via stretching in the late stages of uplift. These modifications, coupled with the probable decrease in density caused by precipitation of daughter minerals, render actual isochors essentially meaningless.

The isochore for low-salinity (3 ± 3 wt% \( NaCl \) equivalent), one-phase inclusions was extrapolated from the data of Potter & Brown (1977) coupled with the decrepitation behaviour of these inclusions (isochore 2, Fig. 9). The isochore for \( CO_2-H_2O-NaCl \) inclusions
Fig. 9. Isochores for fluid inclusion types observed at Ducktown, and a proposed \( P-T-t \) path. Crosses represent estimated uncertainties in isochore locations. Isochores are enumerated chronologically with (1) corresponding to the earliest inclusions. (1) Calculated isochore for the peak metamorphic fluid based on COHS fluid speciation calculations (see Hall et al., 1991). The actual range of isochores for primary fluid inclusions in pyroxene is shown by inclined dashed lines. (2) Low-salinity, one-phase inclusions. (3) \( H_2O-CO_2-NaCl \) inclusions. (4A) One of several isochores representing the liquid-rich, aqueous end-member of immiscible \( H_2O-CH_4-N_2-NaCl \) fluids. (4C) Vapour-rich, \( CH_4-N_2 \)-rich, low-density end-member of immiscible \( H_2O-CH_4-N_2-NaCl \) fluids, which coexist with 4A inclusions and contain approximately 15 mol\% \( N_2 \). Isochores 4B and 4D show the range in density observed for vapour-rich end-members of immiscible fluids. Vertical dashed lines indicate the temperature window of entrainment of immiscible \( H_2O-CH_4-N_2-NaCl \) fluids. (5) Halite-bearing inclusions. (6) \( CaCl_2-MgCl_2-NaCl-H_2O \) inclusions. The vertical bar marked \( P_{\text{fluid}} \) indicates variable fluid pressures recorded during entrainment of immiscible \( H_2O-CH_4-N_2-NaCl \) fluids. At this time, rock pressure followed the path labelled \( P_{\text{rock}} \). NE, BCR and H are \( P-T \) conditions of peak metamorphism from Nesbitt & Essene (1982) (patterned box), pressure conditions from Brooker et al. (1987) and temperature conditions from Hall (1989), respectively.

(isochore 3, Fig. 9) was calculated from the decrepitation behaviour of the inclusions, and methods of Brown & Lamb (1989). The two techniques produce similar isochores, which lends support to the decrepitation method for delineating isochores of inclusions which either decrepitate prior to homogenization (Hall & Bodnar, 1986) or for which \( P-V-T \) data are not available.

Isochores representing the observed range in density of the vapour-rich end-member of immiscible \( H_2O-CH_4-N_2-NaCl \) inclusions (isochores 4B–4D, Fig. 9) were calculated from \( CH_4 \) density data of Kleinrahm & Wagner (1986), \( CH_4-N_2 \) densities from van den Kerkhoff (1988) and a modified version of Holloway's (1981) program ISOCHEM. The single isochore for the high-density (aqueous) end-member shown (isochore 4A, Fig. 9) was calculated from the decrepitation behaviour of one group of inclusions coexisting with vapour-rich inclusions (isochore 4C). The intersection of these two isochores, representing coexisting liquid and vapour phases of the immiscible fluid, defines a point on the solvsus, which was at c. 200°C and 2.1 kbar for these inclusions (Fig. 9). This is consistent with trapping temperatures of 210°C indicated by \( T_b \) of the liquid-rich inclusions. Density variations in \( CH_4-N_2 \) inclusions suggest that immiscible fluids were trapped over a range of pressures (3–0.5 kbar), but homogenization temperatures (trapping temperatures) of coexisting liquid-rich inclusions imply entrainment over a limited temperature range (215 ± 20°C). It is emphasized that the single isochore shown for liquid-rich inclusions (isochore 4A) is one of many which exist and, when combined with coexisting vapour-rich inclusions, define a vertical belt of immiscible fluid entrapped on Fig. 9. This configuration is possible because isoplethal solvi in the \( H_2O-CH_4 \) system, and presumably in the \( H_2O-CH_4-NaCl \) system, are steep in \( P-T \) space above 0.5 kbar (Welsh, 1973).

The isochore for halite-bearing inclusions (isochore 5, Fig. 9) was estimated from the solubility data of Sterner et al. (1988), the volumetric data of Bodnar (1985) and data compiled by Potter & Brown (1977). They were modelled based on NaCl equivalent salinities derived from \( T_m \) (halite), but a reliable eutectic temperature could not be measured for these inclusions thus verifying NaCl as the dominant salt. Finally, the isochore for one-phase \( CaCl_2-MgCl_2-NaCl-H_2O \) inclusions (isochore 6, Fig. 9)
was approximated from data compiled by Potter & Brown (1977) assuming the inclusions behave as 25wt% NaCl solutions.

An uplift path consistent with the chronology and \( P-V-T-X \) properties of fluid inclusions at Ducktown is shown in Fig. 9, and was constructed using the following constraints:

1. Peak metamorphism occurred near 6 kbar and 550°C.

2. Entrapment of low-salinity, single-phase inclusions occurred prior to entrapment of \( CO_2-H_2O-NaCl \) inclusions. The latter must have formed at \( P-T \) conditions above c. 250°C and c. 3.2 kbar (the \( P-T \) at homogenization). Note that while isochores 1 and 2 and 2 and 3 are essentially indistinguishable within the given uncertainties, 1 and 3 are not and suggest temperature-concave uplift.

3. Imbition haloes around peak metamorphic inclusions in pyroxene (Fig. 4c) imply that they were subjected to confining pressures at least 1 kbar above internal pressures during uplift. This requires an early uplift path which is temperature-concave, consistent with the chronology of inclusions represented by isochores 1-3. It could be argued that actual isochores of peak metamorphic inclusions have higher densities because of this post-entrapment overpressuring event. As discussed earlier, however, other post-entrapment compositional and density changes to these inclusions have also occurred.

4. Entrapment of immiscible \( H_2O-CH_4-N_2-NaCl \) fluids occurred over a \( P-T \) range of 3-0.5 kbar and 215 ± 20°C. There is no correlation among the relative ages of individual planes of these inclusions and their densities (inferred trapping pressures), which implies oscillatory pressure fluctuations under nearly isothermal conditions. We interpret this pattern as documenting transitory pressure regimes which varied from lithostatic to near hydrostatic; thus, the \( P-T-t \) path of the rock is different from that of the fluid at this point (Fig. 9). Observed partial decrepitation of some inclusions probably occurred during hydrostatic periods. If the lowest density \( CH_4-N_2 \) inclusions and NaCl-bearing inclusions were trapped under hydrostatic conditions, rock pressure must have dropped to at least 2 kbar, and perhaps as low as 1.4 kbar (0.5 kbar hydrostatic), in the 215 ± 20°C temperature window. This requires a relatively isothermal jog in the uplift path (Fig. 9), and, subsequently, temperature-convex uplift to surface conditions. Isothermal uplift at this point is supported by the post-Alleghanian uplift model of Jamieson & Beaumont (1988), which suggests that some 5 km of erosion has occurred in the Ducktown area since the end of the Alleghanian orogeny. This translates to c. 1.4 kbar of lithostatic pressure at temperatures of perhaps 150–200°C, because the Alleghanian orogeny reached chlorite grade at Ducktown. Immiscible fluids are trapped along Alleghanian-age brittle deformation features, and are thus interpreted to have formed during Alleghanian thrusting; pressure variations are envisioned to have been controlled by faulting. Halite-bearing inclusions were probably trapped at \( P-T \) conditions similar to low-density immiscible fluids since they post-date coexisting \( CH_4-N_2 \) inclusions and have minimum trapping temperatures of 165–190°C.

The uplift path for Ducktown rocks differs from those modelled by some workers for similar tectonic settings (e.g. Albarede, 1976; England & Richardson, 1977; Oxburgh & England, 1980; England & Thompson, 1984) or implied by some fluid inclusion studies (e.g. Hollister et al., 1979; Schreurs, 1984; Droop, 1985; Selverstone & Spear, 1985; Casquet, 1986; Santosh, 1987). In most terranes, fluid inclusions suggest that a period of near-isothermal decompression occurs after peak metamorphism, subsequently requiring a substantial amount of cooling at low pressures and implying high near-surface geothermal gradients (e.g. > 100°C km⁻¹, assuming lithostatic pressure). Isothermal decompression, which is also predicted by thermal models of overthrust orogenic zones, has been interpreted as resulting from exhumation of tectonically thickened crust in such environments, or, alternatively, as related to post-peak metamorphic extension and rapid crustal thinning in an extensional regime (Harris & Holland, 1984; Santosh, 1987; Selverstone, 1988).

Despite the abundance of profiles that are convex toward the temperature axis, those suggestive of relatively constant decrease in pressure and temperature (Rudnick et al., 1984) or near-isobaric cooling (Swanenberg, 1980; Bohlen, 1987; Henson & Warren, 1987; Sisson et al., 1989) have also been described, based on evidence from both fluid inclusions and metamorphic mineral assemblages. The latter profiles, generally recorded in granulite terranes, are usually attributed to development of a thermal dome resulting from magmatically heated crust (Bohlen, 1987; Henson & Warren, 1987), although extensional tectonism has been suggested as a mechanism as well (Harley, 1987) and Spear (1989) suggests that near-isobaric cooling paths can be recorded in the lower parts of upper plates of thrust sheets.

The Ducktown ore bodies are located in a subsidiary thrust sheet of the Blue Ridge–Inner Piedmont allochthon (Hatcher & Zietz, 1980), bounded by the Alleghanian-age Great Smoky thrust to the west and the Taconic-age Hayesville thrust to the east (Fig. 3). According to cross-sections presented by Hatcher (1978) the package of Ocoee sediments hosting the ore bodies was overthrust during the Taconic by laterally equivalent sedimentary rocks and continental basement, which was moving westward along the Hayesville thrust. During Alleghanian thrusting, the ore bodies were in turn thrust over relatively unmetamorphosed Cambrian–Ordovician platform carbonates and perhaps Carboniferous–Permian clastics along the Great Smoky fault.

According to calculations of England & Thompson (1984), \( P-T-t \) paths of crust thickened by rapid emplacement of a single thrust sheet are characterized by isobaric heating at peak pressure followed by thermal relaxation along a temperature-convex uplift path. Spear (1989) suggests that \( P-T-t \) data from lower plates of
thrust sheets should record nearly isothermal compression while upper plates should record nearly isobaric cooling.

Using the above relationships a burial/uplift path has been constructed which, although entirely speculative, is consistent with available tectonic data (Fig. 10). We present this figure only as a suggestion of the general P–T path the rocks may have followed and what sort of path they might expect to be recorded in an ideal fluid inclusion record. The Ducktown ore bodies, which were formed as syndepositional sea-floor sulphides (probably in an environment similar to that of the present-day Red Sea brine pools) may have been buried beneath as much as 15–17 km of overburden prior to the Taconic (Hatcher, 1978; Glover et al., 1983). This suggests that the ore bodies underwent burial metamorphism at 4–4.5 kbar and 350–400°C prior to deformation, assuming lithostatic pressure and an average geothermal gradient. Deformation associated with the Taconic orogeny thickened the crust to approximately 22 km in the area of the ore bodies perhaps resulting in isothermal compression followed by isobaric heating to peak metamorphic conditions (6 kbar, 550°C). The uplift path initially may have been temperature-convex, as predicted by the model of England and co-workers, and may have become relatively isobaric during Alleghanian overthrusting of Ducktown rocks (Fig. 10). Subsequent thermal relaxation or a phase of rapid uplift may have produced an isothermal jog in the uplift path followed by post-tectonic cooling along a local geotherm.

The conjectural burial/uplift path shown in Fig. 10 is obviously much more complex than that constructed from fluid inclusion data, and the inclusions do not record the pre-peak metamorphic history of the area. The simplest post-peak metamorphic uplift path derived from fluid inclusions is temperature-concave at least to c. 200°C and c. 3 kbar. We cannot, however, rule out the possibility that initial uplift was temperature-convex (as suggested by the model of England & Thompson, 1984), became isobaric and eventually temperature-concave as in Fig. 10, as long as this occurred prior to entrapment of fluids represented by isochores 2 and 3, and occurred at fairly high P–T so that implosion haloes in primary fluid inclusions could form. This would preclude this alternative path being related to Alleghanian thrusting. At 215 ± 20°C the P–T path of the rock deviates significantly from that of the fluid and fluid pressures as low as 0.5 kbar are recorded. As discussed above, lithostatic pressure appears to have dropped abruptly at this point, producing a near-isothermal leg in the P–T path of the rock followed by temperature-convex uplift to the surface.

**Timing and sources of fluids**

Dallmeyer (1975a) determined 40Ar/39Ar incremental gas release ages of 424 and 435 ± 15 Ma for two biotite samples collected near the margin of the Cherokee ore body and 372 ± 15 Ma for a single sample collected near the centre of the ore body. These were interpreted to be cooling ages rather than ages of peak metamorphism, the latter of which is placed at c. 480 Ma on the basis of Rb–Sr work by Fullagar & Bottino (1970) and other geochronological data and geological arguments (Butler, 1972; Dallmeyer, 1975b). An estimate of 320°C for the Ar closure temperature for Ducktown biotite was calculated from Dodson’s (1973) equation, incorporating parameters and methods discussed by McDougall & Harrison (1988). Using this information in conjunction with our uplift path (Fig. 9) we conclude that c. 430–370 Ma ago Ducktown ore bodies were experiencing P–T conditions of c. 320°C and 4.5 kbar. Given that peak metamorphism (6 kbar, 550°C) occurred at c. 480 Ma, we calculate an average uplift rate of 0.10 or 0.05 mm year−1 from middle Ordovician to middle Silurian or late Devonian, depending on which retention age is used. The younger cooling age, recorded by biotite in the ore zone, implies either that the ore body cooled more slowly than the host rocks or that the interior of the ore body was subjected to a later thermal event, both of which imply different P–T paths for ore bodies and host rocks. As was previously mentioned, the abundance of fluid inclusions within the ore bodies as compared to the host rocks suggests that the ore bodies may have been channels for fluid flow during uplift. This presumably resulted from rheological contrasts between the sulphide bodies and surrounding silicate rocks, which allowed development of fractures near ore bodies. It is possible that these fluids caused Ar to be lost from biotite in the ore zones. This hypothesis is consistent with the Rb–Sr work of Fullagar & Bottino (1970), who report that samples away from the ore zones approximate an isochron corresponding to 475 Ma, which is interpreted to be the age of peak metamorphism, but that samples collected near the ore bodies suggest significantly younger ages. These authors interpreted the younger ages to have resulted from loss of radiogenic and common Sr from the ore zones.

An additional constraint on uplift comes from a model presented by Jamieson & Beaumont (1988), which suggests that some 5 km of erosion has occurred at
Ducktown since the end of the Alleghanian (270 Ma). This implies an average uplift rate of 0.07 or 0.12 mm year⁻¹ from middle Silurian or late Devonian to late Permian. The calculated average uplift rate from 270 Ma to the present is 0.02 mm year⁻¹.

Age–uplift relationships presented above suggest that low-salinity, one-phase aqueous inclusions were trapped during the late Taconian, and that H₂O–CO₂–NaCl inclusions were trapped after the Taconian but prior to the Alleghanian. Immiscible H₂O–CH₄–N₂–NaCl inclusions and halite-bearing inclusions are Alleghanian in age, and CaCl₂–MgCl₂–NaCl–H₂O inclusions are post-Alleghanian.

Although the sources of the fluids represented by secondary fluid inclusions are in most cases unknown, some generalizations can be made based on the P–T–t relationships established above. The localized distribution of early fluids (e.g. primary fluid inclusions and low-salinity, one-phase and H₂O–CO₂–NaCl secondary inclusions) and the pervasive nature of later fluids (e.g. immiscible H₂O–CH₄–N₂–NaCl and CaCl₂–MgCl₂–NaCl–H₂O inclusions) suggests that early fluids were derived by local devolatilization reactions and later fluids were derived externally.

The composition of H₂O–CO₂–NaCl inclusions, which also contain minor CH₄, combined with inferred trapping conditions near 5.5 kbar and about 425°C (Fig. 9) implies fₒ₂ conditions approximately one log unit above the fayalite–magnetite–quartz (FMQ) buffer. The oxidation state of this fluid is consistent with local derivation from rocks near the ore bodies. The ore bodies were buffered at fₒ₂ conditions ranging from FMQ to three log units above FMQ at conditions of peak metamorphism, while distal host rocks were buffered at fₒ₂ conditions ranging from FMQ to approximately one log unit below FMQ (Nesbitt & Kelly, 1980; Hall et al., 1991).

The compositions of H₂O–CH₄–N₂–NaCl fluids suggest derivation from reduced lithologies buffered at fₒ₂ conditions significantly below FMQ. These fluids may have formed by expulsion of pore fluids and thermal maturation of organic material during thrusting of Ducktown ore bodies over unmetamorphosed Palaeozoic carbonates and clastic rocks. Episodic fracturing and concomitant pressure decreases apparently allowed these fluids to “boil” and circulate upward from the underlying sediments. Methane-bearing fluids of possible Alleghanian age are also found in ore bodies of the Great Gossan Lead, Virginia (Fig. 1) (D. Hall, unpublished data) and within the Tallulah Falls dome, in NE Georgia (Oakes et al., 1987). Hearn et al. (1987) document regional-scale, Alleghanian-age brine migration in the central and southern Appalachians.

SUMMARY

Primary fluid inclusions trapped in peak metamorphic clinopyroxene contain H₂O–CH₄–NaCl fluids with c. 5 mol% CH₄ and 3 wt% NaCl, and daughter crystals of calcite, quartz and pyrrhotite. Calculated bulk compositions suggest that 11 wt% total dissolved solids were present in the peak metamorphic fluids which formed pyroxene in the ore zones. Textural and density relationships indicate that some of these inclusions underwent density increases during early uplift and then density decreases later in the uplift history. Additionally, comparison of calculated and observed fluid compositions suggest that hydrogen diffused into these inclusions converting CO₂ to CH₄ + H₂O (Hall et al., 1991).

Secondary fluid inclusions in quartz from the ore zones and country rocks document a complex uplift history involving a variety of fluids in the system C–O–H–N–salt. These are, from oldest to youngest, low-salinity, one-phase inclusions, CO₂–H₂O–NaCl inclusions, immiscible H₂O–CH₄–N₂–NaCl inclusions, halite-bearing NaCl–H₂O inclusions and CaCl₂–MgCl₂–NaCl–H₂O inclusions. Early fluids were formed by local devolatilization reactions while late fluids were more pervasive and were externally derived. The ore zones appear to have acted as conduits for fluid flow during the later stages of uplift.

Fluid inclusion P–V–T properties, textures and chronology of entrapment suggest that uplift was temperature-concave from approximately 6 kbar and 550°C to about 3 kbar and 200°C. Over the narrow temperature range 215 ± 20°C, lithostatic pressure decreased from 3.5 to as low as 1.4 kbar and fluid pressure varied from lithostatic to nearly hydrostatic. This trend is interpreted to document episodic pressure release in response to fracturing associated with Alleghanian thrusting. NaCl–H₂O fluids and immiscible H₂O–CH₄–N₂–NaCl fluids trapped during this stage have characteristics of basal brines, and may have originated through tectonic expulsion of pore fluids and thermally matured organic material from relatively unmetamorphosed rocks exposed in the Valley and Ridge Province to the west and proposed to underlie Ducktown rocks. The latest stages of uplift appear to have been temperature-convex. Integration of our uplift path with available geochronologic data implies average uplift rates of 0.10–0.05 mm year⁻¹ from 480 Ma to 427–372 Ma and 0.07–0.12 mm year⁻¹ from 424–372 Ma to 250 Ma.

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