FLUID INCLUSION EVIDENCE FOR A SUPERCritical MAGMATIC FLUID, MODIFIED BY WALL-ROCK INTERACTION AND MIXING WITH METEORIC WATERS

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ABSTRACT

Supercritical fluids derived from magmas may have different cooling paths depending on the confining pressures. Shallowly emplaced magmas generate supercritical fluids, which, during cooling form hypersaline fluid and vapor. Supercritical fluid derived from deeper emplaced magmas does not undergo phase separation and the fluids cool below the solvus curve to form a single aqueous-dominated phase. This paper presents an example of the latter in which a magmatically-derived fluid entered a metal deposit. The magmatic fluid was trapped as quartz-hosted fluid inclusions at ~8 km depth. Abundant primary fluid inclusions are trapped within vein and ore quartz.

Fluid inclusion microthermometry, gas analysis using a quadrupole mass spectrometer, and bulk crush leach methods were applied to establish the fluid chemistry trapped within these inclusions. Microthermometry shows that the source fluids have salinities that range from 6-10 eq. wt. % NaCl. Conditions during trapping were around 300°C and 2 kbar pressure, corresponding to ~8 km depth under lithostatic conditions. Gas analysis results show that ore fluids have up to 8 mol. % CO₂ for individual crushes whereas the average is 5-6 mol. % CO₂. Methane is typically 0.5-1 mol. % and CO₂/CH₄ is generally 10. Ratios of N₂/Ar range from 400-5000, which, are typical magmatic numbers. The H₂S content averages 0.013 mol. % whereas some analyses gave values up to 0.03 mol. %.

Fluids that have reacted with the carbonate host rocks exhibit changes to the fluid chemistry typified by the reaction:

\[ \text{H}_2\text{CO}_3 + \text{CaCO}_3 = \text{Ca}^{2+} + 2\text{HCO}_3^- \]

Microthermometry measurements show an increase in salinity >20 eq. wt. % NaCl, driven by the addition of Ca²⁺. Ratios of Ca/Na measured show that Ca>Na and that a “missing” component (assumed to be bicarbonate) is highest in Ca-rich samples. Gas analysis shows that CO₂ and H₂S vary systematically as CO₂ decreases one order of magnitude, the concentration of H₂S decreases more than two orders of magnitude. This variation in CO₂ and H₂S is attributed to wall-rock reactions wherein CO₂ dissolves limestone and H₂S reacts with iron liberated from carbonate to form pyrite. Gold solubility in the ore fluid is calculated at ~200 ppb whereas fluids that have reacted with the wall rocks have a maximum gold solubility <2 ppb.

Calcite was deposited after quartz. Fluid inclusion barometry indicates that subsequent to gold mineralization there was a change from lithostatic to hydrostatic conditions. Microthermometry shows that the calcite inclusion salinity is ~3 eq. wt. % NaCl. Gas analysis confirms that fluid gas content decreased by one order of magnitude and the N₂/Ar ratio decreased to <100. The data indicate that the late calcite was deposited by an inflow of cooler, dilute meteoric waters presumably as a consequence of fracturing and pressure drop. Calcite deposition is consistent with fluid heating.

INTRODUCTION

One of the biggest problems facing geochemists who desire to sample fluids derived from a magmatic body is obtaining an uncontaminated sample whose composition has not changed subsequent to separation from the magma. Change of fluid composition arises primarily from the processes of boiling, wall-rock interaction and ground-water contamination. The difficulty therefore becomes one of being able to recognize an original magmatic fluid.
from those that are modified. Volatile species preferentially partition into liquid magma during the crystallization of a magma body. As crystallization progresses, the liquid volatile content is increased until one of two conditions are satisfied. Firstly, the total pressure of the volatile species could exceed the confining pressure and the volatiles form a separate phase. Alternatively, a decrease in confining pressure as the magma is emplaced may release volatiles. Magmatic volatile species include \( \text{H}_2\text{O}, \text{CO}_2, \text{CH}_4, \text{H}_2\text{S}, \text{SO}_2, \text{N}_2, \text{Ar}, \text{He}, \text{and H}_2 \). Under high temperature and pressures, these species form a single phase that we will call a magmatically-derived hydrothermal fluid. At this point, the hydrothermal fluid can separate from the magmatic body and equilibrate with crystallized magma in response to pressure and fluid temperature decrease. Two P-T cooling paths are possible for the fluid, one whereby the fluid separates into a liquid and vapor phase and the other whereby no separation occurs (Roedder, 1984). The “boiling” path is well documented in porphyry systems and results in two fluid inclusion populations; hyper-saline aqueous-dominated and a low salinity and vapor-dominated inclusions (Roedder, 1971). Fluids that do not separate are expected to have a salinity that has a maximum about 8 eq. wt. % NaCl (Burnham, 1997).

Fluids that exit an intrusive come into contact with rocks that are commonly different in composition. This contrast in rock composition can favor wall-rock interactions with hydrothermal fluids that are in equilibrium with the previous rock. Elements or molecules can be introduced or removed by wall-rock interaction resulting in hydrothermal alteration and metasomatism, along with the formation of new minerals at the expense of original mineralogy.

Magmatic fluids are expected to mix with ground water as they flux to the earth’s surface. When pressure changes from lithostatic to hydrostatic, groundwater mixing must be considered because the presence of lithostatic pressure implies fracture and open space that are accessible to surface water. Ground-water mixing is difficult to evaluate. However, it has the effect of diluting magmatically-derived fluid, in addition to changing the oxidation state, pH, dissolved gas ratios and temperature.

**GEOLOGIC BACKGROUND**

Ten quartz-calcite vein samples were collected from the Pipeline gold deposit in Nevada. The veins occur below the deposit whereas silicification (ore quartz) occurs within the deposit. Host rock is the Roberts Mountains formation carbonate, however most of the carbonate was removed during mineralization. A mineral paragenesis occurs within the veins showing euhedral quartz growth on the sidewall, followed by infilling of calcite.

**METHODOLOGY**

A Linkham TH600 heating-freezing stage and temperature controller was used for microthermometry. Doubly polished, 100-300 µm thick, rock sections for analysis were prepared. The instrument calibration is checked daily by use of a \( \text{H}_2\text{O} \) standard, and each week the calibration is checked using at least three standards. The analytical error in melting point determinations near 0°C is 0.1°C, whereas error in Th measurements in the temperature range of 200°C is 0.5°C.

The analysis of volatile species is done in vacuum by using the CFS (crush-fast scan) method (Norman and Sawkins, 1987). Samples are cleaned with potassium hydroxide, distilled water, and then oven dried at about 60°C (at 100°C He is rapidly lost). Samples are then placed in crushers and evacuated while heating to about 60°C until a pressure <10\(^{-7}\) Torr (10\(^{-8}\) mPascals) is attained. The analysis is performed by means of a Balzers QME125 quadrupole mass spectrometer operating in a fast-scan, peak-hopping mode. The CFS method involves opening inclusions by a swift crush in the vacuum chamber housing the mass spectrometer. Volatiles released are quickly removed by the vacuum pumping system within two sec. Meanwhile, the pulse of inclusion volatiles is recorded by operating the quadrupole in a fast scan mode with measurements every 150 to 200 msec. The mass peak areas are used to determine the concentration of each species using predetermined sensitivity factors and a peak-stripping algorithm designed by Norman. Opening a 10-20 µm inclusion or group of smaller inclusions of equivalent volume, provides the ideal amount of volatiles for CFS analysis. Five to twenty sequential crushes are made on a ∼200 mg sample. Species routinely recorded are \( \text{H}_2, \text{He, CH}_4, \text{H}_2\text{O, N}_2, \text{O}_2, \text{H}_2\text{S, Ar, C}_3\text{H}_8, \text{CO}_2, \text{and SO}_2 \).

The instrument is calibrated with commercial gas mixtures, artificial inclusions filled with gas mixtures, and an in-house fluid inclusion standard. The gas water ratio of the standard inclusions (HF1) is known to about 0.1% by Penfield-tube analysis,
thus allowing water calibration with an error less than 0.2%. Measurement precision is <5% for major gaseous species and ~10% for the minor species.

RESULTS

Microthermometry

Three fluid inclusion types are present. Type 1 are aqueous-dominated inclusions, some exhibiting clathrate melting behavior. Type 1b inclusions are also aqueous-dominated, however, these inclusions comprise liquid CO$_2$ in the vapor bubble and clathrate melting behavior is observed. In contrast, Type 2 inclusions comprise 50% or greater carbonic phase by volume.

Quartz is host to primary Type 1a, 1b, and sparse 2 to 20 mm Type 2 inclusions. Type 1 inclusion Th measurements range from 179° to 265°C and Tm measurements range from -26.0° to +10.1°C. A general observation is that Th values of Type 1b are higher than Type 1a inclusions. Calculated inclusion salinities cluster in a large group with 5 to 10 eq. wt. % NaCl with some extraneous values as high as 25 eq. wt. % NaCl. Samples that have salinities near 25 eq. wt. % NaCl exhibit eutectic melting of salt-hydrate to brine at temperatures of -21.1° to -26.0°C. Assuming that the potassium contribution can be added to the Na budget, then the Ca/Na ratio of the inclusion is determined by the transition temperature of hydrohalite to ice (see Shepherd et al., 1985, p. 103). The range of calculated Ca/Na ratios for these very saline inclusions is 0.8:1 to 1.4:1. Some Type 1a inclusions exhibit clathrate melting behavior. The calculated salinities from Tm$_{ice}$ measurements are about 7 eq. wt. % NaCl.

In Type 1b inclusions liquid-CO$_2$ and vapor homogenize to liquid in the temperature range +13° to +23°C. A general increase in Th values is observed for Type 1b inclusions in comparison to Type 1a. The highest Type1 inclusion Th of 265°C was measured on a Type 1b inclusion.

Type 2 inclusions are sparsely distributed, secondary and vary from 3 to 20 µm in size. The aqueous phase of Type 2 inclusions exhibits clathrate melting. Type 2 inclusion Th values vary from 295° to 323°C. However, measurements are few because Type 2 inclusions readily decrepitate at temperatures >250°C. The inner non-aqueous liquid in Type 2 inclusions melts at about -59° to -58°C and corresponds to 9-12 mol. % CH$_4$ in the carbonic phase (Shepherd et al., 1985). The inner liquid and vapor homogenize to liquid at +13° to +23°C, which, correspond to a CO$_2$ density of 0.76 to 0.85. Calculated brine salinity ranges from 5 to 6 eq. wt. % NaCl and the calculated salinity of the inclusion fluid as a whole is about 0.5 eq.wt. % NaCl.

Calcite exhibits primary fluid inclusions that commonly occur in zones. Calcite-hosted fluid inclusions are generally submicron; secondary inclusions are not observed. Calcite Tm$_{ice}$ measurements range from -1.8° to -2.0°C and Th values range from 219° to 235°C. Calculated salinities are 3.0 to 3.3 eq. wt. % NaCl. Fluid inclusion data is summarized in Table 1.

<table>
<thead>
<tr>
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<th>Quartz Type 1</th>
<th>Quartz Type 2</th>
<th>Calcite Type 1</th>
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<tr>
<td>Tm$_{ice}$ (°C)</td>
<td>+10.1 to -26</td>
<td>+7 to +7.9</td>
<td>-1.8 to -2.0</td>
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<tr>
<td>Th (°C)</td>
<td>179 to 265</td>
<td>295 to 323</td>
<td>219 to 235</td>
</tr>
<tr>
<td>Salinity (eq.wt.% NaCl)</td>
<td>5 to 25</td>
<td>5 to 6</td>
<td>3.0 to 3.3</td>
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<tr>
<td>Th$_{CO2}$</td>
<td>+13 to +23</td>
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<tr>
<td>Density$_{CO2}$</td>
<td>0.76 to 0.85</td>
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</tr>
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</table>

Table 1. Summary of fluid inclusion data for quartz and calcite.

Gas Analysis

Quartz inclusion analyses show gaseous species ranging from 0.54 to 13.21 mol. %. The H$_2$S content is highly variable ranging from 0.00001 to 0.03 mol. % and CO$_2$ ranges from 0.22 to 11.3 mol. %. Plotting the quartz data on a CO$_2$/CH$_4$ vs. N$_2$/Ar diagram shows a broad spread of CO$_2$/CH$_4$ ratios (Fig. 1). Most N$_2$/Ar ratios are well above 500, indicating a significant magmatic component.

![Figure 1. CO$_2$/CH$_4$ vs. N$_2$/Ar discrimination diagram (template from Norman et al., 1998).](image-url)
A linear relationship exists between CO$_2$/CH$_4$ and H$_2$S (Fig. 2). Analyses made on quartz samples bearing inclusions with 5 to 10 eq. wt. % NaCl salinities have higher H$_2$S levels than analyses of quartz that contain inclusions with 15 to 25 eq. wt. % NaCl. A CO$_2$ versus total gas content shows a highly linear relationship between CO$_2$ and gas content of fluid inclusions, as well as CO$_2$ and CH$_4$ concentrations are not coupled (Fig. 3). There is also no discernible relationship between N$_2$/Ar and total gas content.

Calcite inclusions generally have lower concentration of gaseous species and a different gas chemistry than inclusions hosted in quartz. Calcite gaseous species mostly range from 0.24 to 1.5 mol. %, although a few analyses indicate up to 5 mol. %. Calcite CO$_2$/CH$_4$ ratios are similar to those measured in quartz, but the N$_2$/Ar ratios are much lower. There is appreciably less H$_2$S in calcite-hosted inclusions; analyses range from 0.001 to 0.00001 mol. % H$_2$S. Calcite analyses show a mixing relationship between a shallow meteoric and a composite magmatic-sedimentary sources. A linear trend between two end member compositions is shown for calcite analyses (Fig. 4).

DISCUSSION

The gas analyses indicate fluids trapped in quartz have a significant magmatic component. Mixing with meteoric fluid is further indicated (Fig. 1). The P-T conditions during quartz growth are constrained to 295-323°C and 2 kbar by the carbonic inclusions and isochoke calculations (Blamey and Norman, 2000). A pressure of 2 kbar in the unmetamorphosed host sediments is only possible if the geothermal system was at hydrostatic pressure. The Pipeline deposit is hosted in sediments, hence the source magma must be deep beneath the deposit. Fluid inclusion observations contrast from those reported in porphyry copper and molybdenum systems that are considered to be mineralized by magmatic fluids (Roedder, 1971). Hence, the data suggest that quartz mineralizing fluids had a significant magmatic component and were little affected by phase separation as a consequence of deep emplacement of a magma. Pressure conditions were lithostatic.

Since analyses indicate a range in fluid salinities and gas chemistry, the question is “what is the nature of the most primary fluid?” One end-member composition has about 7-8 eq. wt. % NaCl with about 5.5 mol. % CO$_2$ and 0.013 mol. % H$_2$S and
Na>Ca; the other has about 20-25 eq. wt. % NaCl, <1 mol. % CO₂, 0.00003 mol. % H₂S and has Ca:Na ratios as high as 1.4 (Blamey, 2000). The explanation that best fits the data is that the high CO₂ fluids are the most primitive, and that the changes in fluid composition recorded in the fluid inclusions were the result of wall rock reactions.

Other gaseous species do not vary between the end-member compositions. The decrease in CO₂ and H₂S, coupled with an increase in Ca and salinity in eq. wt. %, are consistent with changing composition of a fluid by wall-rock interaction by the following reactions:

\[
\begin{align*}
H_2O + CO_2 &= H_2CO_3 \\
H_2CO_3 + (Ca_{0.98} Fe_{0.02})CO_3 &= .98Ca^{++} + .02Fe^{++} + 2HCO_3^- \\
Fe^{++} + 2H_2S &= FeS_2 + 4H^+
\end{align*}
\]

These reactions explain the increase in fluid salinity and Ca/Na ratio that is coupled with a decrease in CO₂ and H₂S concentrations. Gold solubility calculations support the hypothesis: the CO₂-rich end member may have gold concentrations as high as ppm range, whereas the low CO₂ fluid will only transport ppb concentrations of gold. Wall-rock reactions as we postulate will result in gold deposition as well.

The most primitive or most magmatic fluid therefore has 7-8 eq. wt.% NaCl, 5-6 mol. % CO₂, 0.5-1 mol. % CH₄, 0.01-0.02 mol. % H₂S and N₂/Ar >400. The amount of H₂S is well above equilibrium with iron oxide and iron silicate minerals (Fig. 4). Fluid salinity at 7 to 8 eq. wt. % is about that estimated for non separated magmatic fluids (Burnham, 1997). The variable N₂/Ar ratio can be explained by mixing small amounts of meteoric water into fluids being evolved from the magma as envisioned by Henley and McNabb (1978).

Calcite deposition is an example of the introduction of meteoric water into a geothermal system. The N₂/Ar ratios indicate mostly meteoric water source. Fluid salinity, the trapping pressure, and Th values are lower. Deposition of calcite is consistent with open fractures to shallow fluids and deposition of calcite because of its reverse solubility as the cooler meteoric-dominated solutions entered the geothermal fracture system.

CONCLUSIONS

1) Quartz samples collected support that a magmatic fluid was present at Pipeline. Because it was marginally boiling and is gas charged, it must have transported from a magma as a supercritical vapor that condensed without significant phase separation.

2) Trapping conditions of about 300°C at ±2 kbar pressure have inhibited boiling although sporadic phase separation of a carbonic vapor is documented. A typical gas analysis has 5.5 mol. % CO₂, 0.7 mol. % CH₄, 0.013 mol. % H₂S, and N₂/Ar ratios >500. Fluid salinity was 7 to 8 eq. wt. % NaCl. The fluid and gas chemistry are one example of a magmatic fluid that was trapped outside of a magma, under lower temperatures than existed within the intrusive body.

3) Wall-rock interaction between the source fluid and carbonate rocks occurred causing depletion of CO₂ and H₂S whereas other gaseous species are unaffected. An increase in Ca⁺⁺ occurs as well as salinity reported in eq. wt. % NaCl.

4) Influx of meteoric water enriched in dissolved carbonate has resulted in precipitation of calcite. In addition, fluid salinity and gas content is diluted, whereas a change of N₂/Ar ratio occurs from >500 to <100.

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