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**VAPOR TRANSPORT OF METALS AND THE FORMATION
OF MAGMATIC-HYDROTHERMAL ORE DEPOSITS**

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ABSTRACT

Although most published hydrothermal ore deposit models assume that the main agent of metal transport is an aqueous liquid, there is increasing evidence from volcanic gases, geothermal systems (continental and submarine), vapor-rich fluid inclusions and experimental studies that the vapor phase may be an important and even dominant ore fluid in some hydrothermal systems. This paper reviews the evidence for the transport of metals by vapor (which we define as an aqueous fluid of any composition with a density lower than its critical density), clarifies some of the thermodynamic controls that may make such transport possible, and suggests a model for the formation of porphyry and epithermal deposits that involves precipitation of the ores from vapor or a vapor-derived fluid.

Analyses of high temperature (500 to > 900°C) gases (largely water vapor) released from volcanic fumaroles at or near atmospheric pressure typically yield concentrations of ore metals in the ppb to ppm range. These gases also commonly deposit substantial quantities of ore minerals as sublimates. Much higher metal concentrations (from ppm to wt.%) are observed in vapor inclusions trapped at pressures of 200-1000 bar in deeper-seated veins at lower temperature (400-650°C). Moreover, concentrations of some metals, notably Cu and Au, are commonly higher in vapor inclusions than they are in the coexisting brine inclusions. Experiments measuring the concentration of Cu, Sn, Ag and Au in HCl-bearing water vapor at variable although relatively low pressures (up to 180 bars) partly explain this difference. These experiments show that metal solubility is orders of magnitude higher than predicted by volatility data for water-free systems, and furthermore that it increases sharply with increasing water fugacity and correlates positively with the fugacity of HCl. Thermodynamic analysis shows that metal solubility is greatly enhanced by reaction of the metal with HCl and by hydration, which

results in the formation of species such as $\text{MeCl}_m \cdot n\text{H}_2\text{O}$. Nonetheless, the concentrations measured by these experiments are considerably lower than those measured in experiments involving aqueous liquids or determined for vapor fluid inclusions. A possible explanation for this and for the apparent preference of metals like Cu and Au for the vapor over the coexisting brine in some natural settings is suggested by limited experimental studies of metal partitioning between vapor and brine. These studies show that, whereas Cu, Fe and Zn all partition strongly into the liquid in chloride-bearing sulfur-free systems, Cu partitions preferentially into the vapor in the presence of significant concentrations of sulfur. We therefore infer that high concentrations of Cu and Au in vapor inclusions reflect the strong preference of sulfur for the vapor phase and the formation of sulfur-bearing metallic gas species.

Phase stability relations in the system $\text{NaCl-H}_2\text{O}$ indicate how vapor transport of metals may occur in nature, by showing a range of possible vapor evolution paths for the conditions of porphyry-epithermal systems. At the world class Bingham porphyry-Cu-Au deposit, evidence from fluid inclusions supports a model in which a single-phase fluid of intermediate to vapor-like density ascends from a magma chamber. On cooling and decompression, this fluid condenses a small fraction of brine by intersecting the two-phase surface on the vapor side of the critical curve, without significantly changing the composition of the expanding vapor. Vapor and brine reach Cu-Fe-sulfide saturation as both fluids cool below 425°C . Vapor, which is the dominant fluid in terms of the total mass of H_2O , Cu and probably even Cl, is the main agent in the formation of the Bingham orebody. The evolution of fluids leading to high-grade epithermal gold mineralization is initiated by a H_2S -, SO_2 -, Cu-, As- and Au-rich vapor, which separates from a FeCl_2 -rich brine in a high level subadjacent porphyry environment. In the early stages of the hydrothermal system, vapor expands rapidly and on reaching the epithermal environment,

condenses, producing acid-sulfate alteration and vuggy quartz and, in some cases, coeval high-sulfidation precious metal mineralization (e.g., Pascua). More commonly, the introduction of precious metals occurs somewhat later, after the site of magmatic fluid exsolution has receded to greater depth. Because of the higher pressure, the vapor separating from brine at this stage cools along a P-T path above the critical curve of the system, causing it to contract to a liquid capable of transporting several ppm Au to temperatures as low as 150°C. High-grade epithermal gold ore precipitates as a result of renewed boiling, fluid mixing, reduction or wall-rock reaction.

INTRODUCTION

For over 100 years, our interpretations of the genesis of hydrothermal ore deposits, other than those of mercury, have been dominated by the assumption that the agent of metal transport is an aqueous liquid. Moreover, this assumption has prevailed despite evidence that the dominant aqueous phase in several major types of ore-forming hydrothermal systems is commonly vapor. In a benchmark paper, Henley and McNab (1978) proposed a model for porphyry-type ore deposits in which the metals are transported to the site of deposition by a plume of vapor. However, with a small number of exceptions (e.g., Eastoe, 1982; Sillitoe, 1983), few researchers appear to have given much credence to this model until Heinrich et al. (1992) reported that vapor-rich fluid inclusions in the Mole granite, Australia, contain greater concentrations of Cu (up to 3 wt.% using PIXE analyses) than associated brine inclusions. In the past five years, several other studies of fluid inclusions from porphyry-style and other deposits have documented high concentrations of Cu in the vapor phase (e.g., Damman et al., 1996, Heinrich et al., 1999; Ulrich et al. 1999; Baker et al., 2004), and Ulrich et al. (1999) have shown that Au may also partition preferentially into the vapor.

Part of the reason that metal transport by vapor had not been given much consideration is that thermodynamic studies by Krauskopf (1957 and 1964) concluded that the solubility of most metals in aqueous vapor is negligible (Hg, As and Sb are exceptions), even at temperatures as high as 800 °C. However, Krauskopf based his estimates on data for the vapor pressure of metallic species over the corresponding solids, i.e., their dry sublimation or volatility, and ignored the possibility that interactions with the solvent might enhance solubility in aqueous vapor. At the time of his studies, there were few experimental data on metal solvation by aqueous vapor at hydrothermal conditions (e.g., Millner and Neugenbauer, 1949) and, until recently, such data have been largely restricted to sodium chloride (cf. Martynova, 1964; Pitzer and Pabalan, 1986; Armelini and Tester, 1993). During the past five years, however, a number of experimental studies have investigated the stability of metallic species in aqueous vapors, and in each case have demonstrated that the solubility is orders of magnitude higher than that predicted from volatility data (cf. Williams-Jones et al., 2002). Even at the low temperatures (≤ 360 °C) of these experiments, the measured metal concentrations in the vapor phase would permit formation of economic ore deposits, and experiments at magmatic conditions (e.g., Simon et al. 2004a and b) have yielded metal concentrations similar to those reported in vapor-rich fluid inclusions from natural systems (cf., Heinrich et al., 1999).

The discovery that the vapor phase is a potentially important medium of metal transport in hydrothermal systems has far-reaching consequences for our interpretation of the formation of a number of ore deposit types, and by extension for mineral exploration. Until now, the significance attributed to the vapor phase is that boiling causes sharp gradients in physicochemical parameters like temperature, pH, $a_{\text{H}_2\text{S}}$ and f_{O_2} , leading to ore deposition from aqueous liquids (Drummond and Ohmoto, 1985). Indeed, boiling models have been useful

guides in gold exploration. If, however, the vapor phase also transports metals to the site of ore deposition, it becomes important to know how that phase originates, how it dissolves metals, how effectively it sequesters metals relative to the liquid phase, how it evolves as a function of pressure and temperature, and under what conditions it might deposit metallic minerals.

In this paper, we evaluate the role of aqueous vapor as an agent of metal transport during the formation of metallic mineral deposits, by examining data currently available from natural systems and experiments. We then use these data to discuss the evolution of an upper-crustal magmatic hydrothermal system, and speculate on how a range of vapor evolution paths might explain the formation of porphyry-style and epithermal ore deposits.

PHASE STABILITY RELATIONS AND TERMINOLOGY

In pure H₂O fluids, the vapor becomes increasingly dense with increasing temperature and pressure along the two-phase equilibrium curve (boiling curve), whereas the coexisting aqueous liquid expands. At the critical point (374 °C, 225 bars), the two phases become indistinguishable, and water exists as a single supercritical fluid. With the addition of salt, the upper limit of two-phase behavior expands to much higher temperatures and pressures, allowing a lower-salinity vapor to coexist with a dense high-salinity liquid (a brine) up to at least 2000 bars and 800 °C (Fig. 1A; Sourirajan and Kennedy, 1962; Bodnar et al., 1985, Pitzer and Pabalan, 1986; Bischoff, 1991; Driesner and Heinrich, 2003). These conditions overlap with those of the water-saturated solidus of granitic melts (Burnham, 1979), so that two separate fluid phases may coexist with a hydrous silicate melt in upper-crustal magma chambers (Bodnar et al., 1985), as recorded by coexisting fluid and melt inclusions (Fig. 1B; Audétat and Pettke, 2003).

Based on a review of all available experimental data in the NaCl-H₂O system, Driesner and Heinrich (2003) have developed an equation of state linking the properties of low-salinity

vapor and high-salinity brine across the critical region. This integrated formulation covers the entire compositional range of stable fluids between pure water and pure NaCl, but describes bulk fluid properties without reference to molecular speciation. A P-T-X diagram from that paper (Fig. 2) shows that the critical curve for the NaCl-H₂O system (i.e., the crest of the limiting two-phase surface, and the highest pressure or lowest temperature at which a separate vapor phase coexists with a liquid) is strongly dependent on salinity. Vapor is defined as a fluid with a density similar to or lower than the critical density for the composition of interest (Table 1). At pressures below ~400 bars, a halite- or liquid-saturated vapor will be essentially salt-free. However, at ~1200 bars and ~700°C, for example, the vapor may contain as much as ~20 wt.% salt and reach a density of ~0.5 g/cm³, and still coexist with an even denser and more saline liquid. No physically defined boundary separates such a vapor from the state commonly referred to as ‘supercritical’ fluid, which is a term we avoid in favor of the more general but better defined term single-phase fluid. Given the general phase relations in saline fluid systems, the behavior of minor components, including ore metals, is expected to be sensitive to the highly variable density and chlorinity of vapor-like fluids. At low density and chlorinity, their concentrations are likely to be determined by the dry volatility of metallic solids, whereas at higher density and chlorinity, hydration and the formation of soluble complexes may be the controlling factors on metal behavior.

COMPOSITIONS OF VOLCANIC GASES AND GAS SUBLIMATES

Volcanic gases and their sublimates provided the first geological evidence of the capacity of aqueous vapor to dissolve significant amounts of metals. Analyses of these gases have also furnished important chemical information on how the metals might be transported, suggesting that acidic gases could act as ligands in metallic gas species. After H₂O, which typically

comprises >90 mol. % of volcanic gases, the next most important components are CO₂ (up to 10 mol. %), SO₂ (up to 6 mol. %) and HCl (up to 6 mol. %). Other gases, of which H₂, HF, and H₂S are the most important, comprise <1 mol. % of the bulk volcanic gas (Table 2). In principle, any of these gases, with the possible exception of H₂, could be involved in the formation of stable metallic gas species.

The concentrations of metals in the condensates of volcanic gases are highly variable, but commonly are on the order of ppb and in some cases ppm (Table 3). The composition of the magma and temperature are the main factors controlling metal concentrations. For example, volcanic gases derived from basaltic magmas tend to produce condensates with higher concentrations of copper than condensates of gases from dacitic or rhyolitic magmas: the highest concentration of copper ever reported for a volcanic gas condensate was 8.4 ppm from Momotombo, a basaltic volcano in Nicaragua (Gemmell, 1987). Significantly, this sample was taken from a fumarole discharging gases at a temperature of 770 °C; the other fumaroles at this volcano had substantially lower temperatures, and yielded condensates with Cu concentrations ranging between 0.4 and 0.2 ppm. Other metals reported as having high concentrations in the condensates of gases emanating from basaltic magmas include Zn, Pb, Sb, As, Ag, and Au. Gases from andesitic volcanoes yield condensates with concentrations of Cu, Zn, Pb and As comparable to those of basaltic volcanoes, but substantially higher concentrations of Mo and Hg, up to 3 ppm (Merapi, Indonesia; Symonds et al., 1987) and 340 ppb (Kudryavy, Russia; Taran et al., 1995), respectively. The only metals reported to occur in high concentrations in the condensates of gases released by rhyolitic and dacitic volcanoes are Sn (e.g., 7 ppm, at Usu, Japan; Giggenbach and Matsuo, 1991), Mo and Au (e.g., 1 ppm and 32 ppb, respectively, at Satsuma Iwojima, Japan; Hedenquist et al., 1994).

Further insights into the role of the vapor phase in transporting metals can be gleaned from the sublimates (solids precipitated from gases) forming around volcanic fumaroles (Fig. 3). As early as 1929, Zeiss described high temperature sublimates in the Valley of Ten Thousand Smokes, USA, containing ilsemanite ($\text{Mo}_3\text{O}_8 \cdot n\text{H}_2\text{O}$), sphalerite, chalcocite, covellite and galena, and low temperature sublimates containing an unidentified orange arsenic sulfide. The most comprehensive modern studies of volcanic sublimates are those by Naboko (1964) and Stoiber and Rose (1974), who, in addition to these minerals, reported the occurrence of cassiterite, barite, pyrite, pyrrhotite, orpiment, realgar, galena, and bismuthinite.

A number of investigators have induced sublimate formation by inserting meter-long silica tubes into volcanic fumaroles (e.g., Le Guern and Bernard, 1982; Quisefit et al., 1989; Kavalieris, 1994; Wahrenberger et al., 2002). This ensures almost complete precipitation of the metals dissolved in the gas, as the temperature at the exit approaches 100 °C. Moreover, the temperature at which a particular metallic mineral precipitates can be estimated from its location inside the tube. These experiments have shown that magnetite, molybdenite and wolframite generally deposit close to the entry into the tube, i.e., at temperatures >500 °C; chalcopyrite, sphalerite, and pyrite, commonly precipitate at somewhat lower temperature, and galena, Pb-sulfosalts, and native arsenic, generally at temperatures <450 °C (Fig. 4). Native gold is rarely observed in silica tube experiments, but Taran et al., (2000), reported its formation at 450 – 550 °C in a silica tube experiment at Colima, Mexico.

An interesting feature of many volcanoes and particularly well exemplified by Kudriavy volcano in the Kurile Arc, is that there may be several active and relatively closely spaced (separated by < 100 metres) fumarolic fields depositing distinctly different assemblages of ore minerals (Chaplygin et al., 2005). The Main Field at Kudriavy (700 - 870 °C) deposits

sublimates of ilsemanite ($\text{Mo}_3\text{O}_8 \cdot n\text{H}_2\text{O}$)-molybdite-molybdenite-magnetite; the Dome Field (400 - 730 °C) forms cosalite ($\text{Pb}_2\text{Bi}_2\text{S}_5$)-lillianite ($\text{Pb}_3\text{Bi}_2\text{S}_6$)-wurtzite-cadmoindite (CdIn_2S_4); the Molybdenum Field (400 - 650 °C) mainly ilsemanite-molybdite-molybdenite-hematite-magnetite-W-powellite; and the Rhenium Field (300 - 560 °C) has greenockite-rhenite (ReS_2)-magnetite as principal ore mineral assemblages. Partly, this reflects differences in the saturation temperatures of the different metallic minerals, as indicated by generally lower metal concentrations in gas condensates of the lower temperature fields. However, contents of Pb, Bi and Cd are highest in gas condensates of the Dome field, despite the fact that temperatures are lower than in the Main field, where minerals of these metals do not deposit (Chaplygin et al., 2005). This suggests that the paths traveled by fluids coming ostensibly from the same magmatic source must have influenced their bulk composition and in turn, metal concentrations.

In summary, data available on the compositions of volcanic gases and their sublimates, provide clear indication that a variety of common ore metals can be transported in appreciable concentrations in H_2O -dominated gases. Moreover, the sublimate data suggest that some metallic minerals, e.g., wolframite and molybdenite, saturate at relative high temperatures, whereas others like galena and the sulfosalts have appreciable solubility to quite low temperature. Finally, volcanic gas compositions suggest that components like HCl and H_2S could be important in enhancing metal solubility through complexation.

LIQUID-VAPOR SEPARATION IN ACTIVE GEOTHERMAL SYSTEMS

Active geothermal systems have been an important source of information for understanding metal transport in the context of hydrothermal ore formation (White et al., 1971; Ellis, 1979; Giggenbach, 1992). The main supplier of energy in such systems is aqueous liquid, but

commonly this liquid coexists with vapor, and in some cases vapor even dominates in the reservoir. This is confirmed by the presence of vapor- and liquid-rich fluid inclusions in core samples from the deep reservoir of some systems (e.g., Larderello, Italy, Cathelineau et al., 1994; Mori, Japan, Muramatsu and Komatsu, 1999). Sampling the two fluids separately is technically difficult, but there is semiquantitative evidence from partially separated fluids and the composition of pipe scalings that the vapor phase can contribute significantly, and perhaps even dominantly, to the mobilization of rare earth elements (Möller et al., 2003), or gold, arsenic and base metals (Raymond et al., 2005).

Submarine geothermal systems are dominated by heated seawater, and show very different phase behavior to those on land, because they are located under several kilometers of water. As a result of the higher fluid pressure, black smokers at mid-ocean ridges generally expel a single-phase fluid. Nevertheless, significant compositional deviations of seawater salinity and even highly transient salinity fluctuations do occur in some systems (von Damm et al., 1997, 2003). These can only be explained by liquid – vapor separation in the subsurface, which is consistent with the coexistence of liquid and vapor fluid inclusions in samples recovered from the seafloor or from ophiolites (e.g., Kelley et al., 1992; Vanko et al., 2004). Phase separation recorded by black smoker effluents occurs close to the critical point of seawater (407 °C / 298 bar), leading to two fluids that differ only modestly in their total salinity (Fig. 2), with chloride contents ranging from about one-tenth (vapor) to twice seawater salinity (residual liquid; von Damm et al., 1997). End-member vapor and liquid phases, differing in chlorinity by a factor of 1.9, were sampled separately from the Brandon Vent on the East Pacific Rise (von Damm et al., 2003). The vapor phase is typically enriched in volatiles including CO₂, H₂S, and B(OH)₃ (von Damm et al., 1997; Seyfried et al., 2003), but metal concentration ratios in

coexisting liquid and vapor phases are not measurably different (von Damm et al., 2003), consistent with the relatively small difference in salinity due to near-critical phase separation. The data from black smokers nevertheless show that ore metals have appreciable solubility in the dense vapor phase of boiling, submarine hydrothermal systems, reaching ~100 ppm for base metals like Cu and Zn that may become enriched in volcanogenic massive sulfide deposits (von Damm et al., 2003).

METAL-RICH VAPOR INCLUSIONS IN ORE DEPOSITS AND INTRUSIONS

High-temperature volcanic gases, low-density vapor in continental geothermal systems and dense vapor derived from near-critical boiling of seawater in submarine smoker systems all indicate a significant capacity of water-rich vapor to transport metals. Ore metal concentrations greatly exceed those expected from the volatility of dry metal salts. One may therefore expect that dense water vapor at elevated pressures and temperatures will be able to dissolve even higher concentrations of metals, approaching those found in supercritical fluids deeper in the earth's crust. Fluid inclusions trapped in magmatic-hydrothermal ore deposits and associated upper-crustal intrusions confirm this expectation. Moreover, they show that the separation of a lower-salinity vapor phase from a dense hypersaline liquid (Fig. 1) may lead to significant fractionation of metals and selective enrichment of ore-forming components.

Natural vapor-brine inclusion assemblages

The first evidence that magmatic vapors can have very high concentrations of copper, at weight percent levels rather than in the parts-per-million range reported for volcanic gases, came from estimates of the size of chalcopyrite daughter crystals in vapor inclusions of porphyry-copper deposits (Fig. 5; Roedder, 1971; Eastoe 1978) and from Cu-rich vesicles in silicic lavas

(Lowenstern et al., 1991). Etminan (1977) and Sawkins and Scherkenbach (1981) used the size of daughter crystals to show that copper concentrations in vapor inclusions can be higher than those in associated brine inclusions. Such observations inspired the magmatic vapor plume model of Henley and McNabb (1978) and prompted the thermodynamic analysis of vapor transport of metals by Eastoe (1978; 1982). However, the role of vapor as a medium of metal transport in ore-forming hydrothermal systems remained largely ignored until the advent of micro-analytical techniques employing PIXE, Synchrotron-XRF and LA-ICPMS for quantitative fluid inclusion analysis.

Analyses using the new techniques showed that even low-density and virtually salt-free vapor inclusions trapped below the critical point of water can have ore-metal concentrations in the 1-10 ppm range (e.g., pre-ore fluids in the Madan Pb-Zn veins, Bulgaria; Heinrich et al., 1999; Kostova et al., 2004), and that very much higher metal contents, in the weight-percent range, are possible in vapor inclusions coexisting with brine at higher temperatures and pressures (Table 4). Element-specific behavior in brine and vapor inclusions was first quantified in quartz–cassiterite veins from the Mole Granite, Australia (Heinrich et al. 1992), but unusually high Cu contents were also observed in vapor inclusions from the porphyry-copper deposits of Bingham (Bodnar, 1995) and Rosia Poeni (Romania; Damman et al., 1996), in a Pb-Zn-rich skarn deposit in Mexico (Baker et al., 2004) and in carbonic vapor inclusions coexisting with brines in Cu-Au-PGE-rich veins in the footwall of the Sudbury igneous complex (Hanley and Mungall, 2005). Laser-ablation ICPMS instruments with good petrographic control allowed quantitative microanalysis of single brine and vapor inclusions trapped simultaneously along ‘boiling trails’. Results showed that significant and element-specific fractionation between saline liquids and vapor is widespread in magmatic-hydrothermal settings and across a range of

pressures (200-800 bars) and temperatures (350-700°C; Heinrich et al., 1999; Ulrich et al., 2001; Kehayov et al., 2003; Audétat et al., 1998, 2000; Audétat and Pettke 2003; Landtwing et al. 2005).

Figure 6 shows a summary of published data on the apparent equilibrium distribution of selected elements, Me, between texturally coexisting brine and vapor inclusions in natural quartz samples. The data are expressed in terms of element distribution coefficients between the two fluid phases, by normalizing each element to Na in order to approximate a thermodynamic exchange equilibrium constant and to reduce the effects of total salinity upon brine/vapor fractionation:

$$K_d = \frac{C_{Me}^V}{C_{Na}^V} \frac{C_{Na}^L}{C_{Me}^L} \quad (1)$$

where C refers to the concentration (in weight units) of the subscripted metal (Me, Na) in either of the phases, vapor (V) or hypersaline liquid (L). This empirical fractionation constant is analogous to that used by Candela (1989a) to describe experimental fluid/melt equilibrium partitioning, and provides a measure of the preference of an element for the vapor relative to the dominant cation, Na⁺. The data show that elements like K, Mn and Fe, and possibly Rb and Cs prefer the brine slightly over the vapor, and other elements including Zn, Tl, Pb have no systematic preference. By contrast, B, Cu, As, Sb, and Au, and possibly Li partition in favor of the vapor phase, relative to Na. The magnitude of this fractionation into the vapor varies significantly from sample to sample, particularly for Cu. Based on the available data, the value of K_d shows no simple correlation with total brine salinity or with the physical conditions (P, T) of entrapment, even though it is clear that the fractionation constant must become unity where P-T conditions approach the crest of the two-phase surface, such that liquid and vapor become physically indistinguishable (Fig. 2). The lack of a correlation of K_d with pressure and

temperature is an indication that chemical factors (i.e., hydration and complex formation) rather than purely physical parameters (e.g., fluid density) exert the first-order influence on the unusual brine – vapor partitioning of some elements, including Cu.

Single-phase magmatic fluids

Single-phase fluids separating from hydrous magmas have commonly been referred to as the ‘magmatic vapor phase’ (e.g. Candela, 1989b), in recognition of the fact that they typically have moderately low salinity and density, comparable to those of many fluids that coexist as a distinct vapor phase with a more saline liquid. Rusk et al. (2004) showed that early porphyry-copper-molybdenum stockwork mineralization and spatially related sericite alteration at Butte (Montana) were caused by a single-phase fluid of relatively low salinity (~ 4 wt.% NaCl eq.) and intermediate density (~ 0.7 g cm⁻³). Prior to chalcopyrite and pyrite saturation, these fluids contained very high copper concentrations, on the order of 1 wt.%. Even though this ore fluid would be a liquid in our definition (Tab. 1), it has a composition similar to that of lower-density vapor inclusions at Grasberg, rather than coexisting inclusions of hypersaline liquid (Ulrich et al., 1999; see Table 3 in Heinrich, 2005).

In a recent study of the Bingham deposit, Redmond et al. (2004) and Landtwing et al. (2005) found a vertical transition from single-phase fluid inclusions with a density near to but less than the critical density in the deep feeder intrusion, to a two-phase fluid association of brine and vapor inclusions in the high-grade porphyry-Cu-Au-Mo orebody. This internally zoned orebody has a conspicuously sharp base in terms of copper and gold grades, which lies well above the transition from the deep single-phase to the overlying two-phase fluid regime, as recorded by the distribution of inclusion assemblages (Fig. 7). The salinity of the deep (intermediate-density) and the shallower vapor inclusions cannot be determined unambiguously

from microthermometry, because of the presence of significant CO₂ in these fluids. However, their microthermometric behavior, and element ratios as determined by LA-ICPMS analyses, are almost indistinguishable, and both were very Cu-rich prior to saturation with Cu-Fe-sulfides ($0.2 < \text{Cu/Na} < \sim 1$ (Landtwing et al., 2005).

BRINE AND VAPOR METAL PARTITIONING EXPERIMENTS

Further insights into the capacity of the gas phase to transport ore metals have been provided by a small number of experiments designed to measure the partitioning of elements among silicate melt, brine and vapor (e.g., Williams et al., 1995; Schatz et al., 2004; Simon et al., 2004a and b) or simply between the two aqueous phases (e.g., Shmulovich et al., 2002; Pokrovski 2004; Nagaseki and Hayashi, 2004; Pokrovski et al., 2005) (for an introduction to the thermodynamic theory of vapor-liquid partitioning see Palmer et al., 2004). In the first such experiments involving ore metals, Williams et al. (1995) investigated the partitioning of copper among high-silica rhyolite melt (Bishops Tuff glass), brine and vapor in rapid-quench, cold-seal vessels at temperatures of 800 and 850 °C and pressures of 1000 and 500 bars, respectively; oxygen fugacity was controlled to be two log units above NNO. Although the experimental method did not allow for direct measurement of the concentration of copper in the two aqueous phases, it was possible to evaluate the partitioning of copper between these phases by plotting the apparent equilibrium constants for copper-sodium exchange between melt, brine and vapor given by the expression

$$K_{\text{Cu,Na}}^{\text{aqm/mlt}} = \frac{C_{\text{Cu}}^{\text{aqm}}}{C_{\text{Cu}}^{\text{mlt}}} \frac{C_{\text{Na}}^{\text{mlt}}}{C_{\text{Na}}^{\text{aqm}}} \quad (2)$$

(where C refers to concentration, aqm is the aqueous mixture at room temperature and mlt is silicate melt; Candela, 1989a) against ΣCl . In the two fluid phase region, the composition of brine and vapor are fixed, and thus a change in ΣCl simply indicates a change in the proportions of the two phases. Thus if the two components (Cu and Na) have the same brine-vapor partition coefficients, the value of the equilibrium constant will not change with ΣCl .

The results of the above experiments showed that $K_{\text{Cu,Na}}^{\text{aqm/mlt}}$ does not vary systematically over a range of chloride concentrations between approximately 0.1 and 3.7 molal, indicating that the partitioning of Cu between the two phases is similar to that of Na, i.e., that, in this chemical system, Cu partitions strongly into the brine. Actual distributions for Cu between brine and vapor ($D_{\text{Cu}}^{\text{brine/vap}}$) were determined by assuming that $C_{\text{Cu}}^{\text{vap}}$ was given by $C_{\text{Cu}}^{\text{aqm}}$ for experiments conducted at conditions just outside the low salinity limb of the solvus (~20 ppm at 850 °C and 500 bars and ~120 ppm at 800 °C and 1000 bars), and then evaluating $C_{\text{Cu}}^{\text{brine}}$ from the total chlorinity and $C_{\text{Cu}}^{\text{aqm}}$ for experiments conducted in the two phase region. Based on this modeling, Williams et al (1995) reported values for $D_{\text{Cu}}^{\text{brine/vap}}$ ($C_{\text{Cu}}^{\text{brine}} / C_{\text{Cu}}^{\text{vap}}$) of 200 at 850 °C and 500 bars and 120 at 800 °C and 1000 bars, suggesting that the partition coefficient increases with increasing temperature and/or decreasing pressure or vapor density. The results of these experiments, however, do not explain the findings of fluid inclusion studies, which indicate that copper partitions preferentially into the vapor phase. .

More recently, Simon et al. (2004a and b) used LA-ICPMS analyses to measure the solubility of iron and gold in synthetic vapor and brine fluid inclusions trapped from an assemblage of vapor + brine + haplogranite + magnetite + gold metal. The experiments were conducted in cold-seal pressure vessels at 800 °C and pressures varying from 1100 to 1450 bars;

oxygen fugacity was controlled by the NNO buffer. The results of the study show that vapor containing from 2.3 to 19 wt.% NaCl eq. coexisted with brine ranging in composition from 57 to 35 wt. % NaCl eq., respectively. The concentrations of Fe in vapor and brine decreased from 2.0 to 0.19 wt.% and 7.3 to 0.39 wt. %, respectively as pressure decreased from 1450 to 1100 bars (Table 5). The corresponding partition coefficients, $D_{Fe}^{vap/brine}$ ranged from 0.56 to 0.04, respectively. The data indicate that iron is an important component of both brine and vapor but that the brine is preferred. Gold concentrations in the vapor decreased from 36 to 5, and in the brine from 50 to 28 ppm, as pressure decreased from 1450 to 1100 bars, i.e., partitioning of gold between vapor and brine was subequal at the higher pressure (close to the critical pressure; (Fig. 8)) but brine was strongly favored at the lower pressure (Table 5).

Pokrovski et al. (2004, 2005) determined liquid-vapor partition coefficients for Ag, As, Au, Cu, Fe, Sb and Zn in the system $H_2O-NaCl\pm HCl$ at temperatures between 350 and 450 °C using rigid Ti-alloy and flexible-cell reactors, both of which allow sampling of the vapor and liquid during the experiment. The results of these experiments showed that in all cases the metals partitioned into the liquid, but that the preference for liquid was strongest for Fe, Cu, Zn and Ag, i.e., metals that are known to form strong complexes with chloride ions in the liquid phase (Fig. 9). In the case of Cu (and Fe), the results also confirmed the finding of Williams et al. (1995) that the partition coefficients for this metal are similar to those for Na. Vapor/liquid partition coefficients were significantly higher for Au, Sb, and as might be expected from its very high volatility, were highest for As. Significantly, the partition coefficients for As and Sb predict the degree of preference of these elements for the vapor phase, as determined by analyses of natural brine + vapor inclusion pairs, reasonably well (Fig. 6). By contrast, all experiments in the Cu-Cl-O-H system have failed to explain the preference of Cu for the vapor in these natural

systems, which seems to be at variance with the suggestion of Mavrogenes et al. (2002) that Cu is volatilized as a simple hydroxy complex, and probably implies that ligands other than Cl serve to enhance the solubility of Cu in natural vapors..

Nagaseki and Hayashi (2004) conducted a preliminary experimental study of the partitioning of Cu and Zn between vapor and liquid at temperatures between 400 and 600 °C and pressures between 200 and 500 bars in a NaCl-H₂O system containing variable amounts of sulfur. The experimental method involved trapping the fluids as inclusions in quartz and analyzing them using synchrotron X-ray fluorescence. The starting solutions contained HCl, 10 to 30 wt.% NaCl and had total concentrations of Cu and Zn ranging from 1,000 to 12,000 ppm. Sulfur was added in elemental form as a powder. Analyses showed that vapor inclusions from the sulfur-free experiments contained negligible Cu and Zn. By contrast, vapor inclusions from the experiments in which sulfur powder was added to the solutions (1.4 – 1.7 mol/kg) contained about 3000 ppm Cu and 100 ppm Zn, whereas the coexisting brine inclusions contained 100 ppm Cu and 3000 to 4000 ppm Zn. The results of these experiments support the suggestion of Heinrich et al. (1992, 1999), that high concentrations of sulfur are responsible for preferential stabilization of Cu in the vapor phase.

EXPERIMENTAL STUDIES OF METAL SOLUBILITY IN WATER VAPOR

Lessons from the system NaCl-H₂O

In order to be able to successfully model the solubility of metals in water vapor at hydrothermal temperatures, we need experimental data on appropriate H₂O vapor solutions involving metals and ligands analogous to those accumulated for aqueous liquid solutions (cf. Seward and Barnes, 1997). As discussed above, such data are extremely limited, and until the late 1990's were

restricted to alkali metal chlorides. The system that has been studied most extensively by experimentalists is NaCl-H₂O (Martynova, 1964; Styrikovich, 1969; Galobardes et al., 1981; Bischoff et al., 1986; Armellini and Tester, 1993), which provides a valuable template for studies of reactions involving other very weakly volatile minerals and H₂O-bearing gas mixtures.

The sublimation of crystalline NaCl (halite) can be described by the following reaction:

The thermodynamic properties of both phases are well known (e.g., Pankratz, 1982, 1984), and thus the equilibrium constant of this reaction and the partial pressure of NaCl^{gas} can be calculated for any temperature that might be of interest in modeling metal transport in ore-forming hydrothermal systems. If NaCl^{gas} were to behave ideally, its solubility in water vapor could be calculated from its partial pressure and the total gas pressure in the H₂O-NaCl system

($C_{\text{NaCl}^{\text{gas}}} = \frac{P_{\text{NaCl}^{\text{gas}}}}{P_{\text{total}}}$). However, the experimental studies mentioned above have clearly

demonstrated that dissolution of NaCl in water vapor is highly non-ideal under hydrothermal conditions, and that the difference between the experimentally measured solubilities and those calculated using the Ideal Gas Law can be many orders of magnitude.

One way of dealing with this non-ideality is to distinguish between a simple reactant gas species and a mixed product gas species. Thus, experimentalists have shown that the equilibrium between NaCl^{gas} and the mixed gas species can be described by a solvation reaction of the type:

This approach offers an important advantage over other approaches, e.g., using equations of state, in that the fugacity of the mixed gas (NaCl-H₂O) can be predicted to a first approximation by the Lewis-Randall rule for ideal mixtures of non-ideal gases (e.g., Galobardes et al., 1981;

Armellini and Tester, 1993b), and therefore can be applied to complex systems such as those found in nature.

Experimental Approach

As has already been mentioned, the volatility of most ore metals is extremely low, and thus like NaCl, which also has very low volatility, their behavior in water vapor will be highly ideal at elevated temperatures. However, as for NaCl their solubility in water vapor can be modeled using the Lewis-Randall rule for ideal mixtures of non-ideal gases. This rule states that the fugacity of the mixed gas is the sum of the products of the partial pressures and fugacity coefficients of the individual gases in the mixture. Consequently, if the fugacities of metallic gas species in pure gases or simple binary gas systems can be determined (e.g., H₂O-HCl-MeX or H₂O-H₂S-MeX, where Me refers to the metal and X the ligand), their corresponding fugacities in more complex gas systems can be predicted by adding the products of their partial pressures and fugacity coefficients in the simple systems. Using this philosophy, Williams-Jones and coworkers have begun conducting experiments aimed at measuring the solubility of selected metals and metallic compounds in pure gases, e.g., H₂S and H₂O or simple binary gas systems such as HCl-H₂O, in the hope of eventually using these data to predict their behavior in more complex systems (e.g., Migdisov et al., 1999; Archibald et al., 2001, 2002; Zakaznova-Iakovleva et al., 2001; Migdisov and Williams-Jones, 2005; Rempel et al., 2005). An important finding discussed below, is that the species identified to date in these experiments have the form MeX·(H₂O)_n or MeX·(H₂S)_n. They therefore represent solute molecules or inner sphere complexes surrounded by solvation shells (hydration shells in the case of H₂O), where the

subscript “n” is simply a statistical value indicating the average number of solvent molecules surrounding the solute molecule (Fig. 10).

The experiments were carried out in autoclaves constructed from titanium alloy, and loaded with a known mass of liquid and pre-weighed quartz holders containing ampoules with the solid of interest; the ampoules are open at the top but are isolated from the liquid at ambient temperature. At the conditions of the experiment, the liquid is converted entirely to gas, which fills the autoclave and reacts with the solid in the holder. After an experiment, the autoclave is air-cooled to room temperature, and the condensates collected for analysis.

Metal Speciation

In order to test for solvation and the formation of inner-sphere Me-Cl complexes, experiments were conducted for a range of $P_{\text{H}_2\text{O}}$ at fixed P_{HCl} and vice versa. Results of these experiments show that, in all cases, the solubility of the metal or metallic compound, and thus its mole fraction in the gas phase, increased significantly with increasing $P_{\text{H}_2\text{O}}$, providing clear evidence that solvation (hydration) enhanced solubility (Fig. 11a). If hydration had not played a role in dissolving the metal or metallic compound, the vapor pressure of the metallic species would have remained constant, and its mole fraction in the gas phase would have decreased with increasing $P_{\text{H}_2\text{O}}$. Solubility also increased with increasing P_{HCl} except for experiments investigating the solubility of silver and copper, which were conducted with AgCl and CuCl. In these latter cases, the solubility was independent of P_{HCl} (Fig. 11b). These results show that solubility was enhanced by the formation of inner sphere Me-Cl complexes and that, in the case of Ag and Cu, the species has a 1:1 Me:Cl ratio. This does not necessarily mean a stoichiometry of MeCl, although this was interpreted to be the case for silver, as the dominant species in the H_2O -free

gas system has been shown to be AgCl (Tagirov et al., 1993; Hildenbrand and Lau, 1996). The dominant gaseous species in the system Cu-Cl are Cu_3Cl_3 and Cu_4Cl_4 (Peterson, 1973; Krabbes and Opperman, 1977). Based on this and a relatively high hydration number (see below), it was concluded that the inner sphere complex in the copper experiments most likely had the stoichiometry Cu_3Cl_3 (Archibald, 2002).

Where the solid dissolved was not a chloride, the nature and stoichiometry of the inner sphere complexes were interpreted by postulating reactions for their formation and corresponding expressions for their equilibrium constants. Thus, in the case of gold, which was introduced as the native metal, the proposed reaction is:

and the expression for the equilibrium constant:

$$\log K_f = \log f_{\text{AuCl}_m \cdot (\text{H}_2\text{O})_n} + \frac{m}{2} \cdot \log f_{\text{H}_2} - n \cdot \log f_{\text{H}_2\text{O}} - m \cdot \log f_{\text{HCl}} - \log f_{\text{Au}} \quad (6)$$

If $\log K_f$ is differentiated with respect to $\log f_{\text{HCl}}$, while holding temperature, f_{O_2} and $f_{\text{H}_2\text{O}}$ constant, and if the equilibrium constant of a homogeneous gaseous reaction is independent of total pressure, equation (6) becomes:

$$\left(\frac{\partial \log K_f}{\partial \log f_{\text{HCl}}} \right)_{T, f_{\text{H}_2\text{O}}, f_{\text{O}_2}} = 0 = \left(\frac{\partial \log f_{\text{AuCl}_m \cdot (\text{H}_2\text{O})_n}}{\partial \log f_{\text{HCl}}} \right)_{T...} + \frac{m}{2} \cdot \left(\frac{\partial \log f_{\text{H}_2}}{\partial \log f_{\text{HCl}}} \right)_{T...} - m \cdot \left(\frac{\partial \log f_{\text{HCl}}}{\partial \log f_{\text{HCl}}} \right)_{T...} + \left(\frac{\partial \log f_{\text{Au}}}{\partial \log f_{\text{HCl}}} \right)_{T...} \quad (7)$$

If it is further assumed that f_{H_2} is constant, at constant $f_{\text{H}_2\text{O}}$ and f_{O_2} , and that the dependence of f_{Au} on f_{HCl} is negligible, Equation (7) simplifies to:

$$\left(\frac{\partial \log f_{\text{AuCl}_m \cdot (\text{H}_2\text{O})_n}}{\partial \log f_{\text{HCl}}} \right)_{T, f_{\text{O}_2}, f_{\text{H}_2\text{O}}} = m \quad (8)$$

where m , the ligation number, is the slope of a trend describing the experimental data by the orthogonal co-ordinates, $\log f_{\text{AuClm}(\text{H}_2\text{O})_n}$ and $\log f_{\text{HCl}}$. In Figure 12a, the data for gold are shown in these co-ordinates at 300 °C, and as can be seen from this diagram, the slope is ~ 1 , indicating that Au and Cl are present in the gas species in a 1:1 ratio (as fugacity coefficients for HCl and the gold species are not known, it was assumed that $P_{\text{gas}} = f_{\text{gas}}$). The same slope was obtained for 340 and 360 °C. As discussed for Ag and Cu, this 1:1 ratio does not necessarily indicate the stoichiometry of the inner sphere complex, but as there are no comparable data for the H₂O-free system Au(I)-Cl, it was tentatively assumed that the species in the experiments had the stoichiometry AuCl (Archibald et al, 2001).

The hydration number of the different metal species in the vapor was calculated by differentiating the logarithm of the expression for the equilibrium constant of the speciation reaction with respect to $\log f_{\text{H}_2\text{O}}$ holding f_{O_2} and f_{HCl} constant. Using the example of the gold speciation reaction (equation 5) to illustrate this process, it can be seen that differentiation of equation 6 with respect to $\log f_{\text{H}_2\text{O}}$ yields:

$$\left(\frac{\partial \log K_r}{\partial \log f_{\text{H}_2\text{O}}} \right)_{T, f_{\text{HCl}}, f_{\text{O}_2}} = 0 = \left(\frac{\partial \log f_{\text{AuClm}(\text{H}_2\text{O})_n}}{\partial \log f_{\text{H}_2\text{O}}} \right)_{T, \dots} + \frac{m}{2} \left(\frac{\partial \log f_{\text{H}_2}}{\partial \log f_{\text{H}_2\text{O}}} \right)_{T, \dots} - \left(\frac{\partial \log f_{\text{Au}}}{\partial \log f_{\text{H}_2\text{O}}} \right)_{T, \dots} - n \left(\frac{\partial \log f_{\text{H}_2\text{O}}}{\partial \log f_{\text{H}_2\text{O}}} \right)_{T, \dots} \quad (9)$$

Thus

$$\left(\frac{\partial \log f_{\text{AuClm}(\text{H}_2\text{O})_n}}{\partial \log f_{\text{H}_2\text{O}}} \right)_{T, f_{\text{O}_2}, f_{\text{HCl}}} = n - \frac{m}{2} - \left(\frac{\partial \log f_{\text{Au}^{\text{gas}}}}{\partial \log f_{\text{H}_2\text{O}}} \right)_{T, \dots} \quad (10)$$

(the derivative of the log fugacity of H₂ with respect to the log fugacity of H₂O equals unity at constant fugacity of O₂). As the system investigated was not homogeneous (i.e., it contained both solid and vapor), a Gibbs-Pointing correction was applied to make it effectively homogeneous for the purpose of thermodynamic description. This involved correcting the

change in the partial pressure of Au^{gas} over the crystalline phase from that for a total pressure of $P_1 = 1$ bar (standard state) to that for P_2 , the pressure of the run:

$$\ln \frac{f_2^\circ}{f_1^\circ} = \frac{V^\circ \cdot (P_2 - P_1)}{R \cdot T} \quad (11)$$

(where V° is the molar volume and f_1° and f_2° , are the fugacities of this component in states 1 and 2).

Substitution of equation 11 into equation 10 results in the following expression:

$$\left(\frac{\partial \log f_{\text{AuClm}(\text{H}_2\text{O})_n}}{\partial \log f_{\text{H}_2\text{O}}} \right)_{T, f_{\text{O}_2}, f_{\text{HCl}}} = n - \frac{m}{2} - \left(\frac{V^\circ \cdot (P_2 - P_1)}{R \cdot T} \right) \quad (12)$$

The slope of a trend describing the experimental data by the orthogonal co-ordinates, $\log f_{\text{AuClm}(\text{H}_2\text{O})_n}$ and $\log f_{\text{HCl}}$ (Fig. 12b) yields the right hand side of equation 12, and as the values of all other parameters on this side of the equation except n , the hydration number, are known, the equation can be solved for n .

This analysis yielded hydration numbers (n), which varied according to the system investigated, and in some cases varied significantly with temperature in the same system. Thus, whereas the hydration number was three for the silver gas species ($\text{AgCl} \cdot 3\text{H}_2\text{O}^{\text{gas}}$) over the range of temperatures investigated, for gold it decreased from five at 300 °C to three at 360 °C (Table 6). A similar finding was obtained for copper, consistent with the observation that these two metals undergo retrograde solubility (Archibald et al., 2001, 2002). Overall, these hydration numbers are similar to those found in aqueous liquids. In the case of Ag, they predict that the metal is coordinated by three molecules of water and one of chlorine, i.e., that it is in tetrahedral coordination. Significantly, Monte Carlo and molecular dynamic simulations of the hydration of Ag^+ in the vapor phase predict the same co-ordination (Abraham and Matteoli, 1983, Shevkunov,

1996; Martinez et al., 1997). Moreover, the coordination of the first hydration shell around Ag^+ in aqueous solutions has been shown to be tetrahedral using electron spin echo modulation (Kevan et al., 1977), ultraviolet spectroscopy (Texter et al., 1983) and X-ray absorption spectroscopic studies (EXAFS; Seward et al., 1996).

Thermodynamic data

In order to be able to apply the results of the experiments to natural systems, the solubility data were used to calculate equilibrium constants for the different speciation reactions postulated. Unfortunately, except for the silver species, there was no justification in extracting thermodynamic data, such as the Gibbs free energy, entropy and heat capacity, as the hydration number, and thus the nature of the gaseous metallic species changed with temperature. To illustrate how the formation constants for the gaseous metallic species were calculated, we continue with the example of gold. As discussed above, the speciation reaction for gold is given by equation 5, and the expression for the corresponding equilibrium constant by equation 6. However, as gold in its standard state is a solid, equation 6 must be modified by replacing Au^{gas} with Au^{solid} as follows:

and

$$\log K_f = \log f_{\text{AuCl}_m \cdot (\text{H}_2\text{O})_n} + \frac{m}{2} \cdot \log f_{\text{H}_2} - n \cdot \log f_{\text{H}_2\text{O}} - m \cdot \log f_{\text{HCl}} \quad (14)$$

The value of $\log K_f$ can thus be calculated knowing $f_{\text{AuCl}_m \cdot (\text{H}_2\text{O})_n}$, f_{H_2} , f_{HCl} , and $f_{\text{H}_2\text{O}}$, and as the last three parameters were evaluated as part of the experimental methodology (see above)

only $f_{AuCl_m \cdot (H_2O)_n}$ remains to be evaluated. This was done from the concentration of gold in the quenched condensate, assuming that the mole fraction of gold is given by the equation:

$$X_{AuCl_m \cdot (H_2O)_n} \cong \left(\frac{M_{AuCl_m \cdot (H_2O)_n}}{M_{H_2O}} \right) \quad (15)$$

where M is the number of moles of the corresponding compound (the effect of M_{HCl} on the total mass of fluid in the autoclave was assumed to be negligible). Assuming that the gases form an ideal mixture, it therefore follows that:

$$X_{AuCl_m \cdot (H_2O)_n} \cong \left(\frac{f_{AuCl_m \cdot (H_2O)_n}}{f_{H_2O}} \right) \quad (16)$$

or

$$f_{AuCl_m \cdot (H_2O)_n} = X_{AuCl_m \cdot (H_2O)_n} f_{H_2O} \quad (17)$$

Values of $\log K_f$ calculated in this manner for the different metallic species investigated in the experiments described above are listed in Table 6

Implications for natural systems

The most important conclusions that can be drawn from the experiments summarized above are that (a) in all cases there is a positive logarithmic correlation of metal solubility with partial pressure of water vapor, that (b) the metallic gas species is hydrated and that (c) the partial pressure or solubility of this species is many orders of magnitude greater than the values predicted for ideal systems based on the dry volatility of metallic solids. It thus follows that, because of its power of solvation (hydration), water vapor is a much more effective agent of metal transport than previously suspected.

It is important to note that calculations employing the equilibrium constants listed in Table 6 are valid only for the conditions of the experiments, and that the latter were designed for systems with properties approaching those of pure water, i.e., in which vapor is only stable at pressures below ~220 bars. However, many natural ore-forming hydrothermal systems, notably those associated with subduction-related magmatism, are characterized by high salinity, and in such systems, two-phase behavior extends to much higher pressure than for pure water. Therefore, as the solubility of metals in water vapor increases strongly with increasing water fugacity, the already significant solubilities of metals in pure water vapor will increase to even higher values in the denser vapor phase existing at higher pressures in saline fluid systems. In addition to the solubility-enhancing effect of increasing hydration with higher water pressure, the presence of chloride and probably hydrogen sulfide as complexing ligands will further enhance the metal transporting capacity of the denser vapor in natural systems. The recent experiments, even though of still quite limited applicability, are thus in accord with the observation of orders-of-magnitude greater concentration of ore metals in natural vapor inclusions compared with low-pressure volcanic gases.

MAGMATIC VAPOR IN PORPHYRY – EPITHERMAL SYSTEMS: SOURCE, ASCENT AND MINERAL DEPOSITION

Recent fluid-inclusion studies of ore-forming magmatic-hydrothermal systems, including those generating porphyry copper and epithermal gold deposits, indicate a far more important role for magmatic vapor as a metal-transporting ore fluid than is generally acknowledged. Reviving some of the pioneering ideas of Henley and McNabb (1978) and Eastoe (1982), we propose a fresh interpretation of fluid processes linking hydrous magmas to porphyry-type and epithermal ore deposits. A key consideration in interpreting the range of compositions and pressure-

temperature-density conditions experienced by magmatic-hydrothermal fluids is that low- to moderate-salinity fluids have a continuous stability range, extending from a low-density vapor at high temperature and low pressure, to an intermediate-density fluid at elevated pressure and intermediate temperature, to a dense aqueous liquid at lower temperature and any pressure above the boiling surface (Fig. 2). Such continuity in fluid stability implies that a single-phase magmatic vapor ($\rho < \rho_{\text{crit}}$) can cool and contract to an aqueous liquid at lower temperature without breaching the two-phase surface and changing its composition. Thus, even liquid-like epithermal ore fluids of low salinity may be entirely magmatic in origin, and may have acquired their metal load from a precursor vapor that exsolved directly from a silicate melt (Hedenquist et al., 1998) or separated from a hypersaline aqueous liquid (Fig. 13).

Figures 13 and 14 schematically depict three fluid regimes, in which vapor-driven mass transfer plays a dominant role: a) in fumarole-related alteration and volatile metal deposition; b) in porphyry-Cu(-Mo-Au) mineralization; and c) in the transport of gold into high-sulfidation epithermal ore forming environments. These regimes may develop separately, or they may spatially overlie and temporally overprint each other, as the magmatic-hydrothermal system gradually cools and isotherms retract to greater depth above the fluid-generating magma chamber (Fig. 14). In the following sections, we discuss the three fluid regimes, using specific geological examples.

Fumarole-related ore deposits

Magmatic vapors emanating from active volcanoes or shallow subvolcanic intrusions at near-atmospheric pressure are salt-poor, but usually rich in SO_2 , H_2S and HCl , leaving behind some hypersaline liquid or solid salt, as shown by arrow 'a' in Figure 13 and in the schematic cross-

section of Figure 14a. The vapor can condense on cooling (Fig. 13; tip of arrow 'a') to form an extremely acid liquid rich in HCl and H₂SO₄. Such fluids are responsible for the acid-sulfate alteration (kaolinite, pyrophyllite, alunite) and intense rock leaching (e.g., 'vuggy quartz') observed in fumaroles and in most high-sulfidation epithermal Au ± Cu ± As deposits (Brimhall and Ghiorso, 1983; Stoffregen, 1987; Delmelle and Bernard, 1994). In some cases, the magmatic vapors causing this alteration may also transport the ore metals, and form economic deposits by precipitation directly from the vapor phase or after condensation and mixing with meteoric water.

Mercury deposits include some clear-cut examples of metal transport by the vapor phase (Varekamp and Busek, 1984), generally forming in fumarole environments hosted by highly reducing rocks (organic-rich sediments or serpentinites). The Ngawa geothermal field in New Zealand is an active vapor-dominated geothermal system, in which mercury precipitates as cinnabar and liquid metal in swamp sediments rich in organic material, and locally condenses as liquid metal on open metal surfaces such as roof guttering (Davey and van Moort, 1987; Barnes and Seward, 1997b). Mercury transport by a gas phase is envisaged for the formation of the Culver-Baer deposit (Peabody and Einaudi, 1992) and other deposits in California (White et al., 1971). The metal sources of the world's largest mercury deposits, Almadén (Spain; Saupé and Arnold, 1992) and Idrija (Slovenia; Palinkas et al., 2004), are inferred to be in black shales that also host the deposits. Fluid inclusions in cinnabar and associated gangue minerals indicate that Hg was mobilized by a variably saline aqueous liquid rather than a low-density vapor. However, both deposits show evidence of coeval mantle-derived magmatism (rift basalts and alkali basaltic diatremes), so that an input of Hg-rich magmatic vapor at depth cannot be excluded.

Mexican-type tin deposits, including microcrystalline cassiterite known as ‘wood tin’, show clear evidence for ore metal deposition by fumarolic vapor, which may have exsolved directly from F-rich rhyolite flows at near-atmospheric pressure (Duffield et al., 1990). More recent melt-inclusion studies led Webster et al. (1996) to conclude that the Sn-F-rhyolite magmas were already volatile saturated prior to extrusion, which is consistent with the conclusion from experimental studies (above) that a somewhat denser magmatic vapor phase is more likely to transport economic metal concentrations than a fumarolic gas at atmospheric pressure.

Advanced argillic alteration in high sulfidation epithermal deposits usually predates $\text{Au} \pm \text{Ag} \pm \text{Cu} \pm \text{As}$ introduction by later aqueous fluids of low to intermediate salinity and liquid-like density (Stoffregen, 1987; Arribas, 1995; Heinrich 2005). However, in some high sulfidation deposits, including the Pascua deposit in Chile, mineralization appears to have been contemporaneous with acid leaching and alteration (Chouinard et al., 2005a), indicating that gold and associated copper may have been deposited directly from a low-density magmatic vapor or its condensate. This scenario is consistent with experimental data presented above, which indicate that the concentration of gold in a low-density vapor phase at the conditions typical of epithermal environments (e.g., at 300°C, 80 bars $P_{\text{H}_2\text{O}}$, 0.3 m Cl, pH ~ 1 and $\log f_{\text{O}_2} \sim -28$) would be ~ 1 ppb Au, an amount that theoretically is sufficient to produce an economic gold deposit within the typical lifespan of hydrothermal systems (Archibald et al., 2001; see also Hedenquist et al., 1993). Interestingly, over 50% of the gold at Pascua is incorporated in the structure of pyrite and enargite, which Chouinard et al. (2005b) have attributed to gold adsorption onto sulfide surfaces, a potentially effective mechanism for scavenging gold from a relatively Au-poor vapor that may have been undersaturated with respect to native gold. Metal transport by a low density vapor may also have formed the banded quartz veinlets characterizing

the porphyry gold deposits of the Maricunga Belt of northern Chile. These veinlets are unusual in containing dark botryoidal, inclusion-rich quartz and a fluid inclusion population comprising over 99% vapor inclusions without recognizable liquid. Muntean and Einaudi (2000) interpreted these features to reflect the unusually shallow level of intrusion (< 1 km), which led to exsolution of a brine – vapor mixture that ‘flashed’ in response to abrupt decompression from a < 250 bars lithostatic pressure to a hydrostatic pressure of < 100 bars. They concluded that the gold was transported in the brine, and that the ‘flashing’ led to its supersaturation and deposition from this phase. However, it is equally reasonable to infer that the exsolved fluid was dominantly vapor, that vapor rather than brine transported the gold, and that the latter deposited in response to a sharp density reduction, accompanying expansion of the vapor into open veins. This interpretation is consistent with experimental evidence that gold solubility decreases sharply with decreasing P_{H_2O} (Fig. 12B).

Although low-density fumarolic vapors may deposit economic amounts of gold and copper, metal concentrations in such vapors are predicted to be generally marginal for ore formation. This is despite the fact that major quantities of Cu and probably other ore metals are transferred to the vapor phase by low-pressure devolatilization of hydrous lavas, as shown by Cu-enriched vesicles (Lowenstern et al., 1991) and by the low bulk Cu content of lavas compared to that of melt inclusions contained in phenocrysts (Halter et al., 2005). Instead of transporting these metals to efficient ore traps, the low density vapor phase will, in most cases, simply disperse them at low concentrations in the atmosphere and in near-surface waters. Much greater transport efficiency is predicted for denser vapor at higher pressure and temperature, as discussed below, and such a fluid is also more likely to follow a cooling path leading to trapping of the metals in high-grade orebodies.

Porphyry Cu-Au-Mo ore formation by expanding vapor

The salinity, density and phase state of magmatic fluids involved in porphyry copper ($\pm$ Au $\pm$ Mo) mineralization are variable, as indicated by fluid inclusion assemblages in and below the deposits. Exsolution of magmatic volatiles from a crystallizing hydrous magma can occur in the single-phase fluid stability region at high pressure (> 1000 bar), or brine and vapor may separate simultaneously from the magma if its solidus intersects the two-phase surface of the salt – water fluid system. Direct two-phase fluid exsolution may occur if the pressure is relatively low (< 1000 bar; Bodnar et al., 1985; Audétat and Pettke, 2003), or if the Cl/OH ratio in the melt is relatively high (Burnham, 1979; Cline and Bodnar, 1991; Webster et al., 1999).

In the majority of porphyry copper deposits, potassic alteration and Cu-Fe-sulfide deposition occur in the stability field of two coexisting fluids, as recorded by intimately associated brine and vapor inclusions. Boiling trails typically indicate pressures between 300 and 1200 bars, which correspond to a lithostatic load of 1 to 4 km overburden (e.g., Alumbraera; Ulrich et al., 2001; Bingham: Redmond et al., 2004). Some porphyry deposits, including Butte (Montana), formed at pressures in excess of 2000 bars from a single-phase magmatic fluid of relatively low salinity (~ 4 wt.% NaCl eq.) and liquid-like to near-critical density ($\sim 0.6 - 0.4$ g cm^{-3} ; Rusk et al., 2004). Others, like the Far South East porphyry Cu-Au deposit in the Philippines, which were emplaced at the cool and shallow end of the porphyry spectrum, at a depth of 1-2 km based on geological evidence, also formed from a relatively low-salinity magmatic liquid. The latter occurred during sericitization, which overprinted barren potassic alteration associated with a hotter two-phase fluid (brine + vapor; Hedenquist et al., 1998).

Although great emphasis has been placed on the study of the spectacular and relatively easy-to-measure brine inclusions present in many deposits, fluids of low to moderate salinity (2-

10 wt.% NaCl eq.) but highly variable density are in fact the most widespread inclusion type. Unlike brine inclusions, low-salinity fluid inclusions are common in *all* porphyry copper deposits, and frequently also represent the most abundant inclusion type during the ore-forming stage (e.g., Bingham, Fig. 7c; Bell, Wilson et al., 1971). LA-ICPMS and PIXE microanalyses of low-salinity fluid inclusions from porphyry-Cu and skarn deposits (Table 4) show elevated to very high Cu/Na ratios (up to 1 in many cases), commonly exceeding the Cu/Na ratio expected from partitioning experiments involving intermediate to acid silicate melts and chloride fluids in the single-phase (Candela and Holland, 1986; Candela, 1989a; Candela and Piccoli, 1995) or in the two-phase fluid stability field (Williams et al., 1995). Sulfur is difficult to analyse in fluid inclusions, and experiments at high sulfide activity are sparse and preliminary (Nagaseki and Hayashi, 2004), but we see no plausible explanation for the variably high Cu and Au contents in porphyry-related low-salinity fluids, other than selective complexation with sulfur, in Cu-S-species of still unknown stoichiometry.

The distribution of fluid inclusions in the deeply explored Bingham porphyry-Cu-Au system (Fig. 7) indicates that low-salinity vapor was the dominant agent of metal transport for that deposit. Fluids trapped as a single-phase fluid ~ 1 km below the Bingham orebody have near-critical density and similar salinities to vapor inclusions in the overlying orebody (both <11 wt.% NaCl eq.), and both fluids are at least four times less saline than the brine inclusions coexisting with vapor within the orebody (Redmond et al., 2004; Landtwing et al., 2005). If the three fluids are indeed related by phase separation, as a result of decompression near the lithostatic to hydrostatic transition (Redmond et al., 2004), then mass-balance imposed by the salinity relationships indicates that only a small proportion of brine (<25% by mass) can have condensed from the ascending fluid, which was dominated by vapor (>75% by mass). Indeed,

the highest Cu/Na ratios in the intermediate-density fluid are similar to those in the vapor (prior to Cu-Fe-sulfide deposition), and both low-salinity fluids have higher Cu/Na ratios than the brine.

These data indicate that Bingham formed according to a process shown schematically in Figure 14b. A single-phase fluid ascending from a hidden magma chamber beneath the Quartz Monzonite Porphyry (Fig. 7) started to condense out a relatively small fraction of brine after intersecting the two-phase surface on the vapor side of the critical curve (Fig. 13; branching point of arrow 'b'), but without significantly changing its composition. The expanding vapor ascended further in the presence of minor brine, reaching Cu-Fe-sulfide saturation as the coexisting fluids cooled below 425°C near the sharply defined base of the orebody (Fig. 7). The vapor phase was the dominant fluid in terms of the total mass of H₂O, of Cu and probably even of Cl. This is required to explain silica dissolution attending bornite and chalcopyrite precipitation between 425 and 350°C (shown by inclusion analyses mapped by cathodoluminescence imaging; Landtwing et al., 2005), and is consistent with experimental evidence for retrograde silica solubility in low-salinity fluids in the same temperature interval (Fournier, 1999). The vapor therefore represents the main ore fluid, whereas the coexisting brine (although providing a better-quantifiable fluid inclusion record during Cu-Fe-sulfide precipitation) never carried more than a small fraction of the total metal that is now contained in the giant Bingham orebody. The 'spent' ore fluid may have expanded to a low-density vapor contributing to argillic alteration above the present mine level, as sketched in Figure 14b for a system in which fluid pressure above the ore zone approaches vaporstatic conditions. Other fluid aliquots may have contracted to aqueous liquid along hydrologically more constrained pathways, in which fluid pressure was between hydrostatic and lithostatic, aided by vein sealing due to the

re-precipitation of late quartz (Fournier 1999; Redmond et al, 2003; Landtwing et al., 2005, and further discussed for Fig. 14c, below).

Co-transportation of S, Cu and Au by magmatic vapor implies that the supply of sulfur by the igneous fluid source may be the limiting factor in the generation of economic porphyry copper deposits (cf., Gustafson and Hunt, 1975). A sulfide deficit in the magma could explain the exceptionally low Cu concentrations in vapor inclusions from the barren Rito del Medio pluton, which otherwise has normal Cu contents in the coexisting brine (Table 4; Audétat and Pettke, 2003). Conversely, exceptionally high sulfur availability with only modestly elevated copper contents characterize the magmas of the Farallón Negro Volcanic Complex that formed the Bajo de la Alumbrera porphyry-Cu-Au deposit, as indicated by Cu, Au and S mass balance constraints from the composition of silicate and sulfide melt inclusions (Halter et al., 2005).

Contracting vapor to aqueous liquid: the link to epithermal gold

Paragenetic vein relations and fluid inclusion data indicate that economic gold ($\pm$ Ag, As, Cu) deposition in high sulfidation ore deposits is generally not effected by the acid vapor, but by an aqueous liquid of somewhat lower acidity and low to intermediate salinity, which enters the deposits through veins that postdate acid leaching of the wall rocks (e.g., Stoffregen, 1987; Arribas, 1995; review in Heinrich, 2005). This fluid is similar to the low- or moderate-salinity aqueous fluid trapped in quartz-sericite-pyrite $\pm$ chalcopyrite veins underlying some high-sulfidation gold deposits (e.g., Rodalquilar; Arribas et al., 1995) and cutting through the upper parts of many porphyry-copper deposits (Gustafson and Hunt, 1975; Hedenquist et al., 1998).

The paragenetically late timing of gold mineralization by aqueous liquids of relatively low salinity had originally been interpreted to indicate mixing of minor magmatic brine into

dominantly meteoric water (e.g., Berger and Henley, 1989; Hedenquist et al., 1994), but stable isotope data indicate that the mineralizing fluid is dominantly magmatic (Vennemann et al., 1993; Rye, 1993; Hedenquist et al., 1998). Low-salinity magmatic fluid can originate by cooling from the single-phase stability region without ever intersecting the two-phase surface (Hedenquist et al., 1998; Muntean and Einaudi, 2001). Alternatively a low-salinity aqueous liquid can form by separation of vapor from brine at near-magmatic temperatures and pressures, and subsequent cooling and contraction of the vapor to an aqueous liquid (Heinrich et al., 2004; Heinrich, 2005). This process is indicated by arrow 'c' in Figure 13, and schematically depicted by stage (C) in Figure 14. Vapor can be cooled in the single-phase stability field along any P-T path that passes above the critical curve to lower temperature, and will thereby contract from a vapor-like state to an aqueous liquid without crossing any phase boundary. The resulting liquid, although originally derived from a vapor of the same composition, may eventually boil by separation of low-density vapor bubbles (Fig. 14C).

Fluid inclusion analyses discussed above indicate that a deep magmatic source can generate weakly saline vapor with Cu, As and Au concentrations that are many orders of magnitude higher than those in a low-density vapor at epithermal conditions. The key question is how an intervening step of phase separation at high temperature and pressure (~450-600°C, 400-1000bars) affects the chemical composition of the vapor and its ability to transport ore metals, notably gold, to the much cooler epithermal ore environment. Segregation of Fe (selectively partitioning into the dense NaCl-rich brine) from H₂S, SO₂, Cu, As and Au (significantly fractionating into the buoyant vapor; Fig. 6) is likely to have a decisive influence on the chemical evolution of magmatic fluids at lower temperatures (Heinrich, 2005). Below 400°C, experimental data for the stability of metal complexes in aqueous fluids (Gammons and

Williams-Jones, 1995; Stefansson and Seward, 2004; Xiao et al., 1998) permit quantitative thermodynamic modeling of gold and copper solubility based on analyzed fluid inclusion compositions. If the total concentration of FeCl_2 in a high-temperature fluid exceeds that of H_2S , the precipitation of pyrite and Cu-Fe-sulfide minerals will lead to rapid exhaustion of reduced sulfur during cooling, which severely limits the ability of a low-salinity fluid to transport gold into the epithermal environment. If, on the other hand, separation of a FeCl_2 -rich brine increases the molality ratio of $\text{H}_2\text{S}/\text{Fe}$ in the high-temperature vapor above ~ 2 , then FeS_2 precipitation during cooling leads to an Fe-depleted but still sulfide-rich fluid at lower temperatures. Such a fluid can carry very high gold concentrations even at epithermal temperatures well below 300°C (Gammons and Williams-Jones, 1997), at ppm levels as analysed in porphyry-hosted vapor inclusions (Ulrich et al., 1999), rather than at ppb levels as observed in volcanic gases or in rock-buffered geothermal waters of meteoric origin.

Thus, the combination of high-temperature brine condensation with subsequent contraction of the residual vapor phase, as indicated schematically in Figure 14c, can increase the efficiency of epithermal gold mineralization by orders of magnitude, compared to any alternative process such as low-pressure vapor transport, meteoric water circulation, brine injection, or single-phase magmatic fluid cooling.

CONCLUSIONS AND OUTLOOK

The combination of experimental and geological evidence summarized in this paper shows that vapor can play a major role as a medium for ore-metal transport in the formation of magmatic-hydrothermal ore deposits. Two fundamental conclusions regarding the metal-transporting

capacity of vapor emerge from studies of active volcanoes, microanalyses of natural fluid-inclusions, laboratory experiments and thermodynamic analysis.

First, the metal transporting capacity of aqueous vapor increases dramatically with increasing water fugacity, due to the hydration of inner sphere metal-ligand complexes to form species of the type $\text{MeL}_m \cdot n\text{H}_2\text{O}$. As a result, metal solubility in water-rich vapor depends not only on the available ligands (e.g., Cl, H_2S as in aqueous liquids) but also on the density of the water-dominated vapor, which increases with increasing pressure. Hydration explains measured metal concentrations in low-pressure volcanic gases, which are orders of magnitude higher than those calculated from the dry volatility of metal salts, but generally too low to be effective ore fluids, except for mercury which has long been known to be deposited from volcanic gases. As expected from the hydration experiments, base and precious metal concentrations are much higher in dense vapor inclusions, in which percent levels of Cu and ppm levels of Au have been analysed.

Second, vapor transport may contribute to the selective enrichment of certain metals in economic orebodies, if some metals are partitioned preferentially into vapor and others into liquid. According to fluid inclusion analyses, such preferential fractionation between coexisting dense vapor and hypersaline liquid is significant. However, very few experiments designed to investigate this phenomenon have been undertaken, and consequently the controls of such partitioning are still poorly understood. Nonetheless, it is clear from thermodynamic theory and demonstrated by experimental partitioning studies that selective element fractionation vanishes as P-T-conditions approach the critical point of the system, i.e., where properties of liquid and vapor approach each other, as is common in boiling black smoker systems.

It follows from these basic conclusions that vapor transport and selective ore-metal enrichment is geologically most important in those regions of pressure-temperature-composition space where two hydrothermal fluids with strongly contrasting properties coexist at elevated pressure. Such conditions prevail in hot and saline magmatic-hydrothermal systems at depths of 1 to 5 km. Based on thermochemical considerations and geological observations of specific porphyry-style and epithermal ore deposits, we conclude that vapor of highly variable density (typically 0.01–0.5 g/cm³) plays a central role in the transport and local enrichment of ore metals as well as sulfur.

The evolution of porphyry – epithermal systems can be interpreted as a continuous process driven by the cooling of a large hydrous magma chamber . The early stage begins with the release of a single-phase vapor of low density and very low salinity from the top of the intrusion. This vapor may immediately condense a small proportion of brine or precipitate solid halite. On ascent, the fumarolic vapor expands and cools, producing acid sulfate alteration and vuggy quartz, and locally also Hg, Sn or Au-Ag mineralization. As the magmatic system cools and a solid carapace develops beneath a few kilometers of overburden, fluids of higher density and salinity exsolve from the underlying magma. This favors metal hydration and complexation in a vapor that condenses a small proportion of brine during ascent and cooling. If the fracture permeability of the overlying rocks permits further expansion of the resulting vapor, most of the metal will be deposited within a porphyry ore shell, because the solubility of metals decays rapidly with decreasing vapor density. High-grade epithermal gold deposits are most efficiently formed by low-salinity aqueous liquids derived by contractive cooling of dense metal-enriched magmatic vapor. Ideal physical and chemical conditions are met where magmatic vapor first loses some Fe-enriched brine, and then contracts to a gold- and sulfur-rich liquid of low to

intermediate salinity, by cooling at elevated pressure above the critical curve of the fluid system. This occurs during the late stages in the cooling of a magmatic-hydrothermal system, when brine – vapor separation takes place at a depth of several kilometers above an even deeper-seated magmatic fluid source. In partly eroded systems, such a fluid evolution is represented by slightly earlier potassic alteration and porphyry-style mineralization, cut by quartz-sericite-pyrite veins acting as fluid channelways for low-salinity fluids en route to overlying epithermal ore deposits.

Testing the range of geological processes discussed in this paper will require much more experimentation, to determine the speciation of metals in the vapor phase and their partitioning between liquid and vapor, as well as new measurements of the P-V-T-properties of appropriate fluid systems. In conjunction with continued field-based and microanalytical observations, such experimental data will permit numerical modeling of two-phase fluid flow and fluid – rock reaction, to help understanding of the dynamic processes of ore formation. Eventually, these process models should help in predicting the location and composition of economic orebodies within large magmatic-hydrothermal systems.

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Table 1: Terminology for fluid phases in saline hydrothermal systems

Fluid	Any mobile phase dominated by volatile constituents of the H-O-C-N-S system (e.g., H ₂ O, CO ₂ , N ₂ , H ₂ S, SO ₂ ...) with variable concentrations of dissolved components such as chloride salts.
Single-phase fluid	A fluid of any composition and density at a pressure above (or a temperature below) the two-phase (liquid + vapor) surface.
Liquid	A water-rich, salt-bearing fluid with a density above the critical density of the corresponding salt-water mixture (e.g., $\rho_{\text{crit}} = 0.32 \text{ g cm}^{-3}$ for pure water; $\rho_{\text{crit}} = 0.48 \text{ g cm}^{-3}$ for 7 wt.% NaCl; $\rho_{\text{crit}} = 0.59 \text{ g cm}^{-3}$ for 20 wt.% NaCl).
Hypersaline liquid (= Brine)	A liquid with > 26 % wt. NaCl (commonly called ‘brine’; halite-saturated at room temperature)
Aqueous liquid	A dense water-rich (< 26 % wt.% NaCl) liquid at a temperature below the critical point of water (374°C / 225 bar) and a pressure at or above the boiling curve of water
Vapor	A water-rich, salt-bearing fluid ($\pm \text{CO}_2$ and other gases) with a density below the critical density of the corresponding salt-water-gas mixture.

We recommend avoidance of the term ‘supercritical fluid’, because it cannot be clearly defined with reference to P and T for binary or multicomponent fluid systems. For pure water, supercritical refers to a fluid at pressures and temperatures above its critical point

Table 2. Proportions of major species in gases released by selected volcanoes.

Volcano	Momotombo ^a	Poas ^a	Mt. Etna ^a	Merapi ^a	Kudriavy ^b	Colima ^c	Mt. St. Helens ^a	Usu ^a
Magma Type	Basalt		Andesite			Dacite		Dacite
Temp (°C)	658 - 820	960 - 1045	1075	767 - 915	605 - 940	740 - 820	663 - 802	656 - 678
H ₂ O	97.1 - 97.9	95.28 - 97.08	22.71 - 53.69	88.53 - 95.83	93.1 - 95.6	89.18 - 98.7	91.58 - 98.60	95.80 - 97.30
H ₂	0.17 - 0.7	0.39 - 0.67	0.30 - 0.57	0.71 - 1.54	0.24 - 1.3	0.06 - 0.63	0.27 - 0.85	0.27 - 0.34
CO ₂	1.44 - 1.47	0.53 - 1.00	17.08 - 33.93	3.26 - 7.56	1.81 - 2.80	0.8 - 2.62	0.89 - 6.94	1.70 - 3.02
CO	0.002 - 0.010	0.003 - 0.01	0.36 - 0.71	0.02 - 0.16	0.001 - 0.23		0.0013 - 0.06	0.003 - 0.005
SO ₂	0.3 - 0.5	1.232 - 2.004	14.69 - 47.7	0.06 - 1.15	1.07 - 2.33	0.24 - 2.79	0.067 - 0.208	0.142 - 0.258
H ₂ S	0.16 - 0.29	0.006 - 0.420	0.12 - 0.27	0.12 - 1.16	0.18 - 0.68		0.099 - 0.355	0.350 - 0.714
HCl	2.68 - 2.89	0.011 - 0.121	—	0.59	0.09 - 0.74	0.25 to 0.51	0.076 - 0.089	0.024 - 0.160
HF	0.240 - 0.259	0.011 - 0.121	—	0.4	0.013 - 0.083	0.015 - 0.051	0.03	0.012 - 0.033

a) Symonds et al., 1994; b) Taran et al., 1995; Taran et al., 2000. Dashes indicate not detected and blanks not analysed.

Table 3. Concentrations of metal species in fumarole gas condensates . All data are reported in ppm, except gold (ppb). NA: Not analyzed; -: Not detected.

Volcano	Cerro Negro ^a	Momotombo ^a	Poas ^a	Tobalchik ^b	Etna ^c	Colima ^d	Kudryavy ^e	Merapi ^f	Mt St Helens ^g	Usu ^h	Iwo Jima ⁱ
Magma type	Basalt			Alkali basalt		Andesite			Dacite		Rhyolite
Temp (°C)	300-315	456 - 770	344 - 852	1010	928	738 - 828	535 - 940	576 - 796	710	649	165 - 877
Hg	0.004 - 0.005	0.006 - 0.021	0.01 - 0.30	–	–	NA	0.02 - 0.34	–	0.02	0.0001	–
As	0.03 - 0.09	0.23 - 0.49	–	24	6.146	0.4 - 0.5	0.6 - 1.6	0.28-0.96	1.4	0.02	1.7 - 4.6
Sb	0.002 - 0.004	0.003 - 0.96	0.003 - 0.008	13	0.02	0.04 -0.13	0.02-0.510	≤ 0.16	0.008	0	0.02 - 0.03
Au	1 - 2	1 - 24	–	4	24	1.0 - 5.0	NA	NA	0.03	0.007	1.5 - 32
Ag	3 - 11	5 - 14	6 - 250	6	120	NA	NA	NA	0.01	0.5	–
Cu	0.2 - 0.8	0.2 - 8.4	0.1 - 0.6	6	–	0.4 - 0.9	0.03 - 0.91	0.01 - 1.0	0.05	0.01	0.006 - 0.064
Pb	NA	1.9 - 7	0.8 - 5.4	0.6	12	0.08 - 0.48	0.110 - 9.7	0.3 - 1.6	0.5	0.006	0.2 - 1.8
Zn	0.3 - 0.6	0.4 - 7.6	0.5 - 8.6	9.8	13	5 - 8	0.25-13.5	4 - 82	0.019	0.04	0.03 - 0.24
Sn	0.8 - 1.0	1.1 - 2.4	1.4 - 3.9	0.09		NA	0.1-0.38		–	7	0.2 - 0.8
W	–	–	–	–	–	NA	0.002 - 0.060	0.05-0.13	0.003	0.003	–
Mo	0.18 - 0.27	0.15 - 0.5	–	–	–	0.09-0.18	0.002 - 0.270	0.08 - 2.8	0.094	0.06	0.005 - 1.07

a) Gemmell, 1987; b) Menyailov and Nikitina, 1980; c) Le Guern, 1988; d) Taran et al., 2000; e) Taran et al., 1995; f) Symonds et al., 1987; g) Bernard, 1985; h) Giggenbach and Matsuo, 1991; i) Hedenquist et al., 1994.

Table 4. Chemical composition of selected fluid inclusion assemblages analyzed by LA-ICPMS and PIXE methods. Low density vapor inclusions trapped together with coeval brine inclusions are listed on adjacent lines indicated by identical sample numbers.

	Th	NaCl	Li	B	Na	K	Mn	Fe	Cu	Zn	As	Rb	Sb	Cs	Au	Tl	Pb	Bi
	°C ⁻²	eq. wt%	ppm	ppm	wt%	wt%	wt%	wt%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Mole Granite (Australia) Sn-W vein deposits, all texturally unambiguous 'boiling trails'; (Heinrich et al.,1999; Audétat et al., 2000)																		
Brine GOLD1 ¹	430	34.5	520 ± 70		6.5 ± 0.2	6.3 ± 0.1	1.20	9.3 ± 0.12	120 ± 50	2800 ± 80	200 ± 70	2400 ± 200	45 ± 4	1400 ± 10		70 ± 9	1700 ± 90	28 ± 1
Vapor GOLD1 ¹					0.80	0.3 ± 0.08	0.10		2800 ± 1100			110 ± 50		66 ± 7			75	
Brine WOLF12 trail 2 ¹	398	32.5	400 ± 100		7.2 ± 1.1	4.6 ± 0.1	1.9 ± 0.1	6.77 ± 1.8	165 ± 10	5200 ± 1100	170 ± 60	1100 ± 500	150 ± 10	2200 ± 500			3400 ± 1100	30 ± 11
Vapor WOLF12 trail 2 ¹			1800		1 ± 0.1	0.4 ± 0.1	0.10	0.5 ± 0.1	2600 ± 1400	570 ± 150	71 ± 35	95 ± 21	49 ± 28	130 ± 20			190 ± 30	1
Brine LowW9 ¹	470	35.7	1300 ± 400	2700 ± 300	5.8 ± 0.9	9.9 ± 1.1	1.6 ± 0.2	8.6 ± 1.7	220 ± 190	9400 ± 200	350 ± 120	2200 ± 600	160 ± 50	2400 ± 500		70 ± 30	2300 ± 700	20 ± 9
Vapor LowW9 ¹			150 ± 40	1600	1 ± 0.5	1.2 ± 0.9	0.3 ± 0.4	0.2 ± 0.1	1400 ± 900	440 ± 430	300 ± 300	62 ± 60	9	40 ± 6			77 ± 24	
Brine YANKEE ¹	528	28	1500 ± 100	2400 ± 200	7.2 ± 0.5	3.5 ± 0.4	1.4 ± 0.2	4 ± 1	600 ± 200	3200 ± 800	180 ± 30	1400 ± 300	100 ± 60	3100 ± 400			2600 ± 600	6 ± 2.3
Vapor YANKEE ¹			600 ± 160	3500 ± 700	1.7 ± 0.1	0.6 ± 0.1	0.20	1.2 ± 1.1	2300 ± 400	370 ± 50	190 ± 30	150 ± 60	49 ± 12	330 ± 110			320 ± 10	1.85 ± 0.5
Zinnwald (Erzgebirge,Germany) quartz - cassiterite vein (Heinrich et al.,1999)																		
Brine ZIN-2 ¹	476	42.7	500 ± 200	1400 ± 500	10.2 ± 1.6	7.1 ± 1.4	2.8 ± 0.4	2.3 ± 0.2	40 ± 80	28000 ± 11000	1300 ± 400	11000 ± 1900	61 ± 9	5600 ± 1600		290 ± 60	57000 ± 18000	21 ± 5.9
Vapor ZIN-2 ²			1200 ± 400		1.5 ± 0.3	0.4 ± 0.2	0.2 ± 0.1	0.5 ± 0.4	1100 ± 700	1500 ± 900	530 ± 190	600 ± 310	24 ± 12	310 ± 130		31 ± 9	4000 ± 1700	
Bajo de la Alumbrera (Argentina) Cu-Au porphyry (Ulrich et al.,1999, 2001; Heinrich et al.,1999)																		
Brine BLA-I (1/97A,2a) ¹	700	58	70 ± 20		10.4 ± 1.2	12.6 ± 0.6	1.8 ± 0.4	9.8 ± 1.4	10000 ± 8700	18000 ± 8300		960 ± 320		90 ± 40		57 ± 6		25 ± 11.5
Vapor BLA-I (1/97A,2a) ¹			50 ± 40		1 ± 0.1	0.4 ± 0.2	0.10	0.3 ± 0.1	510 ± 200			37 ± 1		4 ± 2		2		0.1
Brine BLA-I (1/97A,2b) ¹	700	58	40 ± 20	130 ± 50	12.4 ± 1	11.7 ± 0.7	1.3 ± 0.1	15.5 ± 1.5	4800 ± 3900	7400 ± 800		690 ± 80	10 ± 14	49 ± 4		52 ± 6	3300 ± 100	14 ± 2.5
Vapor BLA-I (1/97A,2b) ¹			30 ± 40		0.30	0.2 ± 0.1	0.03	0.6 ± 0.7	1100 ± 1700	170 ± 100		14 ± 3	2 ± 2	1		1	72 ± 24	0.6 ± 0.4
Brine BLA-A (1/97A 1,3) ¹	430	40.3			12.3 ± 1.2	7 ± 2.2	1.01 ± 0.1	10.9 ± 0.3	2200 ± 1200	4600 ± 1100		360 ± 60		25 ± 15		26 ± 5	1600 ± 300	18.2 ± 2
Vapor BLA-A (1/97A 1,3) ¹					1.1 ± 0.52	0.5 ± 0.3	0.01	0.6 ± 0.3	1200 ± 400	440 ± 180		27 ± 11		2 ± 1			140 ± 80	
Brine BLA-H (49-52,21/3 A) ¹	700	52	60 ± 60		11 ± 1.2	8.1 ± 0.9	1.9 ± 0.1	9.2 ± 1.7	2600 ± 900	5400 ± 700		490 ± 40		42 ± 2		12 ± 3	1700 ± 120	
Vapor BLA-H (49-52,21/3 A) ¹					0.3 ± 0.2	0.7 ± 0.5	0.01	0.10	260 ± 220	75 ± 7		13 ± 8		0			26 ± 11	
Brine BLA-J (1/97B,3 J) ¹	700	65.5			10 ± 0.9	13 ± 0.1	2.3 ± 0.4	22.1 ± 2.8	500 ± 600	8900 ± 800		550 ± 50		45 ± 5		36 ± 8	2800 ± 200	11.3 ± 0.9
Vapor BLA-J (1/97B,3 J) ¹					0.7 ± 0.1	0.8 ± 0.1	0.10	1.4 ± 0.7	900 ± 400	660 ± 230		31 ± 9		3 ± 1		4 ± 2	210 ± 50	1.5 ± 0.6
Brine BLA-K (45-61.3, 13/2 K) ¹	400	43			8.5 ± 3.5	9.5 ± 3.5	2.3 ± 0.8	12.6 ± 5.3	7700 ± 6200	7500 ± 4200		500 ± 90		40 ± 12		25 ± 16	2300 ± 1200	122 ± 11.9
Vapor BLA-K (45-61.3, 13/2 K) ¹					0.6 ± 0.1	0.5 ± 0.1	0.10	0.6 ± 0.3	3000 ± 2200	280 ± 20		26 ± 4		5 ± 1			99 ± 25	5.7 ± 0.3

Table 4 (continued)

	Th	NaCl	Li	B	Na	K	Mn	Fe	Cu	Zn	As	Rb	Sb	Cs	Au	Tl	Pb	Bi
	°C ²	eq. wt%	ppm	ppm	wt%	wt%	wt%	wt%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Grasberg (Irian Jaya) porphyry-Cu-Au deposit (Ulrich et al., 1999; Henrich et al., 1999)																		
Brine all assemblages ³	680	73			16.2 ± 1	15.4 ± 4.7	2.4 ± 0.8	13.5 ± 3.5	2900 ± 1300	13000 ± 4500	21 ± 13	960 ± 240		71 ± 34	0.3 ± 0.2	32 ± 9	5100 ± 2600	22 ± 22
Vapor all assemblages ³		7			3 ± 1	1.4 ± 0.2	0.2 ± 0.1	1 ± 0.5	9900 ± 9900	1400 ± 700	190 ± 220	80 ± 30		4 ± 1	11 ± 11	4 ± 1	360 ± 140	6.1 ± 1.6
Bingham, Utah (Heinrich et al., 1999; Landtwing et al., 2005)																		
Single-phase A57-5889.5 ⁴	375				1 ⁵	0.40	0.05	0.42	3500	330	130	390			1.0		210	
Brine D211-19 ⁴	375	43			11.0	7.80	0.42	5.61	6050	3080	51	450		0	2.1 ⁽¹⁾		3190	
Vapor D211-19 ⁴					1 ⁵	0.60	0.03	0.51	8100	300	83	90		0	2.2 ⁽¹⁾		880	
Brine D211-19 ¹	426	47			12.0	7.92	0.34	5.64	2.52	2900					0.6		2400	12
Vapor D211-19 ¹					1 ⁵	0.44	0.02	0.72	0.53	350					6.0		210	3.4
Brine, BING-2A late Mo vein ¹	470	40	300	600 ± 300	9.8 ± 1.9	8.7 ± 3.1	0.5 ± 0.3	3.8 ± 1.8	1700 ± 700	2900 ± 1200	40 ± 1	600 ± 300		47 ± 23		21 ± 5	2100 ± 600	10 ± 24
Vapor, BING-2A Mo vein ¹			200	1200 ± 700	2.5 ± 0.3	1 ± 0.6	0.1 ± 0.1	0.8 ± 0.4	3000 ± 3000	1200 ± 700	140 ± 80	70 ± 40	100 ± 100	24 ± 23			1000 ± 800	44 ± 64
Butte (Montana) porphyry-Cu-Mo deposit (Rusk et al., 2004; Table 2, averages of several assemblages)																		
Liquid 11172-2756 r=0.65	~625	2.7			0.7 ± 0.1	0.3 ± 0.1	0.005	0.2 ± 0.1	4300 ± 3100	180 ± 40		17 ± 5		6 ± 4			20 ± 8	
Liquid 11172-3186 r=0.65	~600	2.5			0.7 ± 0.2	0.2 ± 0.1	0.009	0.1 ± 0.1	900 ± 890	100 ± 33		13 ± 3		6 ± 4			29 ± 21	
Vapor 11552-6673 r=0.40	~400	4.1			0.8 ± 0.2	0.8 ± 0.2	0.050	0.2 ± 0.1	9800 ± 5800	540 ± 510		33 ± 9		6 ± 4			58 ± 24	
Elatsite (Bulgaria) porphyry Cu-(Au) deposit (Kehayov et al., 2003)																		
Brine early qtz-mt-bn-cpy vein ¹	550	51			13.2	8.6	1.45	7.3	6900	2700	330	580		58			1700	14
Vapor early qtz-mt-bn-cpy vein ¹					1.02	3.8	0.05	0.88	28000	150		30		3	1.2		100	53
Brine cpy-py ore stage ¹	450	47			10.2	6.1	0.66	7.4	1300	1500	250	550		52			1101	20
Vapor cpy-py ore stage ¹					1.12				11000						0.26			
Rito del Medio (New Mexico) barren pluton (Audétat and Pettke, 2003)																		
Single-phase intermed Rito5-2IGZ	425	4.5	510		1.3 ± 0.1	0.9 ± 0.2	0.2 ± 0.1	0.10	260 ± 80					6 ± 1			50 ± 1	
Brine Rito 8-D miarolitic cavity ¹	480	26.3	4200		5.2 ± 0.4	3.7 ± 0.3	6.8 ± 0.7	1.6 ± 0.2	1600 ± 270	16000 ± 7000		1300 ± 100	80	1300 ± 30			2200	248
Vapor Rito 8-D miarolitic cavity ¹		3.7	3100 ± 1700		1.1 ± 0.1	0.40	0.50		245	930 ± 70		50 ± 1	15	70 ± 20			140 ± 30	19 ± 1
Brine Rito 5-B miarolitic cavity ¹	450	29.5	1100	800	6.7 ± 0.5	3.6 ± 0.7	5.6 ± 0.7	1.9 ± 0.1	866 ± 12	7900 ± 752	80	590 ± 140	35	850 ± 200			1265 ± 191	208 ± 45
Vapor Rito 5-B miarolitic cavity ¹	?	2.1			0.8 ± 0.1	0.3 ± 0.1	0.30	0.10	187 ± 87	816 ± 61	89	35 ± 3		51 ± 15			103 ± 23	25.5 ± 3

Table 4 (continued)

	Th	NaCl	Li	B	Na	K	Mn	Fe	Cu	Zn	As	Rb	Sb	Cs	Au	Tl	Pb	Bi
	°C ²	eq. wt%	ppm	ppm	wt%	wt%	wt%	wt%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Canada Pinabete (New Mexico) barren pluton (Audétat and Pettke, 2003)																		
Single-phase intermediate Cana12	410	3.9			1.2 ± 0.2	0.4 ± 0.1	0.10	0.18	110 ± 40	440 ± 80			12	24 ± 5			60 ± 10	7 ± 1
Brine Cana 2 ¹	500	40	1100		15.8 ± 0.5	1 ± 1	0.40	5.5 ± 0.8	80 ± 40	8000 ± 1000			2.6 ± 1	80 ± 20			1200 ± 100	22 ± 8
Vapor Cana 2 ¹		4.5			1.3	0.40	0.26	0.21	2000	600				13			60	13
Bismarck Zn-(-Pb-Cu-Ag) skarn, Mexico (Baker et al., 2004)																		
Brine average	~500	~47			Cl=29%	6.10	0.81	0.61	90	3100	440						3400	
Vapor average					Cl=1.6%	1.10	0.12	0.15	400	800	440						2500	
Single-phase near-critical density	~400	~9.6			Cl=3.1%	1.10	0.03	0.06	190	450	80						730	
Madan (Bulgaria) Mogilata Pb-Zn vein and manto deposit, quartz predating ore deposition (Heinrich et al., 1999)																		
Liquid MAD-7 isolated incls.	354	0.4	16	80	0.20	0.10	0.10	0.10			33 ± 20	5 ± 5	5 ± 9	3 ± 4		0.5 ± 0.2	5 ± 7	
Vapor MAD-7 isolated incls.	~350	0.4	120		0.2 ± 0.1	0.10	0.10	0.10	110 ± 120		66 ± 87	6 ± 3		3 ± 3			90 ± 110	

1) Fluid inclusions representing a single boiling trail trapped along a plane; 2) Temperature of homogenization to liquid phase closely corresponding to entrapment pressure; 3) Fluid inclusions representing several boiling trails; 4) Average for all inclusions analyzed; 5) Averages for all coexisting brine and vapor inclusions in the sample. Vapor inclusions have a density <2 g/cm³ and were observed to homogenize. Single-phase fluid inclusions from Bingham, Rito del Medio, Canada Pinabete, and some from Butte homogenize mainly by the fading of the meniscus reflecting near critical behaviour. The homogenization temperature represents a minimum trapping temperature.

Table 5. Partition coefficients ($\pm 2\sigma$) for iron and gold between coexisting vapor and brine at 800 °C and variable pressures (Simon et al., 2004 a and b).

P (MPa)	Wt.% NaCl eq.	Wt.% NaCl eq.	Vapor	Fe $\mu\text{g/g}$ ($\pm 2\sigma$) brine	$D^{v/b}$	Vapor	Au $\mu\text{g/g}$ ($\pm 2\sigma$) Brine	$D^{v/b}$
	Vapor	Brine						
110	2.1 - 2.4	56 - 58	$3.1 \pm 0.74 \times 10^3$	$6.4 \pm 0.3 \times 10^4$	0.05 ± 0.02	5 ± 2	29 ± 4	0.17 ± 0.04
130	4.9 - 5.3	50 - 53	$1.0 \pm 0.26 \times 10^4$	$7.2 \pm 1.0 \times 10^4$	0.14 ± 0.08	4 ± 1	28 ± 4	0.14 ± 0.07
140	8.8 - 9.3	42 - 44	$2.0 \pm 0.1 \times 10^4$	$7.3 \pm 0.9 \times 10^4$	0.27 ± 0.08	28 ± 8	40 ± 1	0.70 ± 0.26
145	18.7 - 19.2	35 - 37	$4.1 \pm 0.77 \times 10^4$	$7.2 \pm 0.8 \times 10^4$	0.57 ± 0.02	36 ± 11	50 ± 7	0.72 ± 0.12

Table 6. Hydration numbers for metallic species in water vapor and equilibrium constants for reactions describing the formation of these species.

T°C	n	log K
$\text{AgCl}^{\text{cryst}} + n \text{H}_2\text{O} = \text{AgCl}(\text{H}_2\text{O})_n^{\text{a}}$		
360	3	-12.53
350	3	-12.537
340	3	-12.507
330	3	-12.707
310	3	-12.668
300	3	-12.975
$\text{Au}^{\text{metal}} + \text{HCl} + n \text{H}_2\text{O} = \text{AuCl}(\text{H}_2\text{O})_n + 0.5 \text{H}_2^{\text{b}}$		
300	5	-17.28
340	4	-18.73
360	3	-18.74
$3\text{CuCl}^{\text{cryst}} + n \text{H}_2\text{O} = \text{Cu}_3\text{Cl}_3(\text{H}_2\text{O})_n^{\text{c}}$		
280	7.6	-21.46
300	6	-19.03
320	6.1	-19.45
$\text{SnO}_2^{\text{cassiterite}} + 2 \text{HCl} + n \text{H}_2\text{O} = \text{SnOCl}_2(\text{H}_2\text{O})_{n+1}^{\text{d}}$		
300	1.9	-8.48±0.35
320	1.7	-7.29±0.33
350	1.5	-7.27±0.22

a) Migdisov et al.(1999); b) Archibald et al. (2001; Archibald et al. (2002); d) Migdisov and Williams-Jones (2005)

FIGURE CAPTIONS

Figure 1. A) Photomicrograph of a ‘boiling’ trail showing a few hypersaline liquid inclusions trapped on the same healed fracture as numerous vapor-rich inclusions. Questa Mo-porphyry deposit, New Mexico. B) Photomicrograph of two large and a few smaller low to intermediate-density fluid inclusions trapped in the single-phase fluid stability field together with a granitic silicate melt, recorded by numerous crystallized melt inclusions (quartz crystal from a miarolitic cavity in the Rito del Medio Pluton, New Mexico, as described by Audétat and Pettke, 2003).

Figure 2. Perspective representation of phase stability relations for the binary NaCl – H₂O system in temperature – pressure – salinity space, emphasizing the tunnel-shaped two-phase miscibility surface and the critical curve indicated by the red crest line. At pressures above this surface, a single-phase fluid of vapor-like to liquid-like density is stable, limited towards the right side of the diagram by the solubility of halite (near-vertical saturation surface). Below the gridded miscibility surface, a low-density liquid of low to moderate salinity (left of the critical curve) coexists with a liquid of higher salinity and density (right). At very low pressures but high temperatures, halite coexists with nearly pure water vapor (salinity too low to show on linear scale). Numbers along the two-phase surface denote fluid density in g cm⁻¹ (modified from Driesner and Heinrich, 2003; Heinrich et al., 2004)

Figure 3. A) Sublimates around a recently extinct fumarole at Merapi volcano, Indonesia, displaying the characteristic blue color of the phase, ilsemanite (Mo₃O₈.nH₂O) known

otherwise as molybdenum blue. B) A sample of the sublimate shown in A viewed with a binocular microscope. The photomicrograph shows characteristic globular coatings of amorphous ilsemanite sublimate on highly altered (kaolinized) andesite

Figure 4. Temperatures of formation of ore metal-bearing sublimate minerals deposited in silica tubes inserted into high temperature volcanic fumaroles. The data were taken from Quisefit et al., 1989 (Momotombo; green bars); Le Guern and Bernard, 1982, Bernard, 1985, and Kavalieris, 1994 (Merapi; red bars); Bernard and Le Guern, 1986 (Mount St. Helens; blue bars); Taran et al., 2000 (Colima; yellow bars) and Wahrenberger et al., 2002 (Kudriavy; brown bars).

Figure 5. A single vapor-rich inclusion with a clearly visible triangular chalcopyrite crystal in ore-stage vein quartz from the Granisle porphyry copper deposit, British Columbia.

Figure 6. A Summary of microanalytical data from natural assemblages of texturally coexisting but separately trapped vapor (V) and liquid (brine, B) inclusions in high-temperature magmatic-hydrothermal ore deposits and miarolitic cavities of barren granites. The relative preference of each element for the vapor phase in each sample is shown, normalized to the behavior of Na according to equation (1) in the text. Elements such as B, As and Cu, consistently plotting above $K_d = 1$, fractionate preferentially into the vapor phase, relative to Na, which together with most other chloride-complexed cations is enriched in the liquid phase in absolute concentration terms (data from Heinrich et al., 1999 and other sources indicated in legend; Na in vapor data by Baker

et al. (2004) was estimated from the average Na/K ratio in all other vapor analyses; Hanley and Mungall (2005) includes unpublished data for CH₄-rich vapor inclusions from Sudbury; J. Hanley and T. Pettke, pers. comm.).

Figure 7. A) A cross-section through the Bingham orebody showing the distribution of high salinity brine inclusions, vapor-rich inclusions and inclusions with near critical density. Also shown are the distribution of quartz veins, and contours representing >0.35 and >0.7 wt. % Cu grades. As is evident from this figure, the fluid evolved from a single phase with near critical density to a two-phase association of brine and vapor. The orebody has a conspicuously sharp base defined by a sharp drop in copper and gold grades, and as is also evident from the figure this base lies well above the transition from the deep single-phase to the overlying two-phase fluid regime. B) Multi-solid bearing brine inclusion. C) Vapor-rich fluid inclusion. D) Coexisting chalcopryite-bearing vapor-rich and near critical-density fluid inclusions. (Modified after Landtwing, et al., 2005).

Figure 8. A) Experimentally-determined partition coefficients from Simon et al. (2004a) for gold between coexisting vapor and brine (NaCl-H₂O) as a function of pressure at 800 °C and oxygen fugacity buffered at NNO. B) Distribution of the partition coefficients in A as a function of pressure and X_{NaCl}. Also shown is the solvus for the system NaCl-H₂O.

Figure 9. Ray diagram from Pokrovski et al. (2005) showing apparent vapor/liquid partition coefficients of a number of elements as a function of the density ratio of the two phases, based on experimental data for temperatures between 350 and 450 °C. The symbols represent experimental data for the different elements: (○) As(III) at < 400°C, (⊕) As(III) at 450°C (●) Si, (△) Sb(III), (⊕) Au(I), (+) Na, (×) Fe(II), (□) Cu(I), (⊖) Zn, (☆) Ag(I).

Figure 10. A sketch illustrating the statistical nature of a hydration shell (large open circle) forming around molecules of an inner sphere complex (MeCl) indicated by the two green solid circles. The upper molecule is surrounded by four water molecules, whereas the lower molecule only has two water molecules in close proximity. Based on this diagram, the average number of water molecules surrounding molecules of the inner sphere complex (MeCl) is 3 and thus the statistical hydration number of the species is 3.

Figure 11. A) Plot of the concentration of CuCl in the vapor phase as a function of $\log f_{\text{H}_2\text{O}}$ at constant f_{HCl} . The increase in CuCl concentration with increasing $f_{\text{H}_2\text{O}}$ indicates that copper solubility was enhanced by hydration. B) Plot of the concentration of CuCl as a function of $\log f_{\text{HCl}}$ at constant $f_{\text{H}_2\text{O}}$. The independence of CuCl concentration from $\log f_{\text{HCl}}$ indicates the formation of an inner sphere complex involving Cu and Cl in the ratio 1:1. (Modified from Archibald et al., 2002)

Figure 12. A) The log fugacity of the gaseous species $\text{AuCl}_m(\text{H}_2\text{O})_n$ as a function of $\log f_{\text{HCl}}$ at constant $f_{\text{H}_2\text{O}}$. The subscripts m and n refer to the ligation number of the inner sphere complex and the hydration number, respectively. The slope of ~ 1 of the linear regression through the experimental data indicates that the ligation number (m) is 1 and therefore that the inner sphere complex has the stoichiometry, AuCl . B) The log fugacity of the gaseous species $\text{AuCl}_m(\text{H}_2\text{O})_n$ as a function of $\log f_{\text{H}_2\text{O}}$ at constant f_{HCl} . The slope of the linear regression through the experimental data (2.53) corresponds to the right hand side of equation 13. As $m = 1$ and the Gibbs Poynting correction for these data is ~ 0.11 , the corresponding statistical hydration number (n) is 3.14. See text for further details. (Modified after Archibald et al., 2001).

Figure 13. $\text{NaCl} - \text{H}_2\text{O}$ phase diagram represented in Figure 2, showing three possible paths of fluid evolution illustrated by arrows, two of which bifurcate where a single-phase fluid intersects the two-phase surface and separates into a lower-salinity vapor and a higher-salinity liquid (brine). Fluid characteristics are indicated by varying color shade (salinity) and darkness (density) along the arrows, according to the approximate scale shown in the inset (right).

Figure 14. Schematic cross-sections showing paths of fluid evolution during progressive stages in the life of an ore-forming porphyry – epithermal system. The paths in the three sections correspond to those shown in Figure 13, as do the darkness/shade of colour used to depict density, salinity and phase state of fluids in schematically indicated

fracture channelways. Fluid processes, rock alteration and mineral precipitation are explained by text at the corresponding level to the right of of each section.

Successive overprinting of magmatic vapor processes may proceed from an early fumarole stage (A) through a porphyry stage (B) to a final epithermal stage (C), as a result of overall cooling and retraction of the fluid-generating magma front towards a subjacent magma chamber.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14