

Are Vapor-Like Fluids Viable Ore Fluids for Cu-Au-Mo Porphyry Ore Formation?

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Abstract

Ore formation in porphyry Cu-Au-(Mo) systems involves the exsolution of metal-bearing fluids from magmas and the transport of the metals in magmatic-hydrothermal plumes that are subject to pressure fluctuations. Deposition of ore minerals occurs as a result of cooling and decompression of the hydrothermal fluids in partly overlapping ore shells. In this study, we address the role of vapor-like fluids in porphyry ore formation through numerical simulations of metal transport using the Gibbs energy minimization software, GEM-Selektor. The thermodynamic properties of the hydrated gaseous metallic species necessary for modeling metal solubility in fluids of moderate density (100–300 kg/m³) were derived from the results of experiments that investigated the solubility of metals in aqueous HCl- and H₂S-bearing vapors. Metal transport and precipitation were simulated numerically as a function of temperature, pressure, and fluid composition (S, Cl, and redox). The simulated metal concentrations and ratios are compared to those observed in vapor-like and intermediate-density fluid inclusions from porphyry ore deposits, as well as gas condensates from active volcanoes. The thermodynamically predicted solubility of Cu, Au, Ag, and Mo decreases during isothermal decompression. At elevated pressure, the simulated metal solubility is similar to the metal content measured in vapor-like and intermediate-density fluid inclusions from porphyry deposits (at ~200–1,800 bar). At ambient pressure, the metal solubility approaches the metal content measured in gas condensates from active volcanoes (at ~1 bar), which is several orders of magnitude lower than that in the high-pressure environment. During isochoric cooling, the simulated solubility of Cu, Ag, and Mo decreases, whereas that of Au reaches a maximum between 35 ppb and 2.6 ppm depending on fluid density and composition. Similar observations are made from a compilation of vapor-like and intermediate-density fluid inclusion data showing that Cu, Ag, and Mo contents decrease with decreasing pressure and temperature. Increasing the Cl concentration of the simulated fluid promotes the solubility of Cu, Ag, and Au chloride species. Molybdenum solubility is highest under oxidizing conditions and low S content, and gold solubility is elevated at intermediate redox conditions and elevated S content. The S content of the vapor-like fluid strongly affects metal ratios. Thus, there is a decrease in the Cu/Au ratio as the S content increases from 0.1 to 1 wt %, whereas the opposite is the case for the Mo/Ag ratio; at S contents of >1 wt %, the Mo/Ag ratio also decreases. In summary, thermodynamic calculations based on experiments involving gaseous metallic species predict that vapor-like fluids may transport and efficiently precipitate metals in concentrations sufficient to form porphyry ore deposits. Finally, the fluid composition and pressure-temperature evolution paths of vapor-like and intermediate-density fluids have a strong effect on metal solubility in porphyry systems and potentially exert an important control on their metal ratios and zoning.

Introduction

Porphyry Cu-Au-Mo deposits represent the largest source of Cu and Mo ore worldwide and contain significant resources of Au, W, Re, and Ag (Singer et al., 2005; Sinclair, 2007). They are associated with porphyritic intrusive complexes and form in the root zones of andesitic volcanoes in subduction-related, continental, and island-arc settings (Sillitoe, 1973, 2010; Cooke et al., 2005; Sinclair, 2007; Richards, 2014). Although economic porphyry deposits form mainly at shallow crustal levels, i.e., 2- to 5-km depth (Vila and Sillitoe, 1991; Proffett, 2009; Murakami et al., 2010; Schöpa et al., 2017), some, notably the Butte deposit, occur at greater depth (>6 km; Rusk et al., 2008; Mercer and Reed, 2013), and others such as those of the Maricunga belt, Chile (Muntean and Einaudi, 2000, 2001), and the Jarovie belt, Slovakia (Koděra et al., 2014), are emplaced at very shallow depth (<2 km). The economic mineralization is hosted mainly in quartz vein stockworks that provide evidence of a complex history of multiple episodes of veining, alteration, and ore mineral deposition (Sillitoe, 1973,

2010; Gustafson and Hunt, 1975; Hedenquist et al., 1998; Rusk and Reed, 2002; Redmond et al., 2004; Landtwing et al., 2005, 2010; Rusk et al., 2008; Redmond and Einaudi, 2010; Monecke et al., 2018).

Ore formation in porphyry systems (Fig. 1a, b) involves the exsolution of hydrothermal fluids in the cupolas of large-scale crustal batholiths and the transport of the metals upward and outward from the magmatic centers where they precipitate in overlapping ore shells upon cooling and decompression (Lowell and Guilbert, 1970; Gustafson and Hunt, 1975; Henley and McNabb, 1978; Dilles, 1987; Williams-Jones and Heinrich, 2005; Rusk et al., 2008; Richards, 2013). Commonly, a saline intermediate-density supercritical fluid exsolves from the magma and upon cooling and decompression separates into a low-density vapor and a high-density hypersaline liquid (Eastoe, 1978; Henley and McNabb, 1978; Bodnar and Beane, 1980; Hezarkhani and Williams-Jones, 1998; Redmond et al., 2004; Heinrich, 2005; Landtwing et al., 2005; Driesner and Heinrich, 2007; Lecumberri-Sanchez et al., 2015; Audétat, 2019; Mernagh et al., 2020). Upon separation of a moderately saline (2–8 wt % NaCl) fluid the vapor dominates volumetrically over the hypersaline brine

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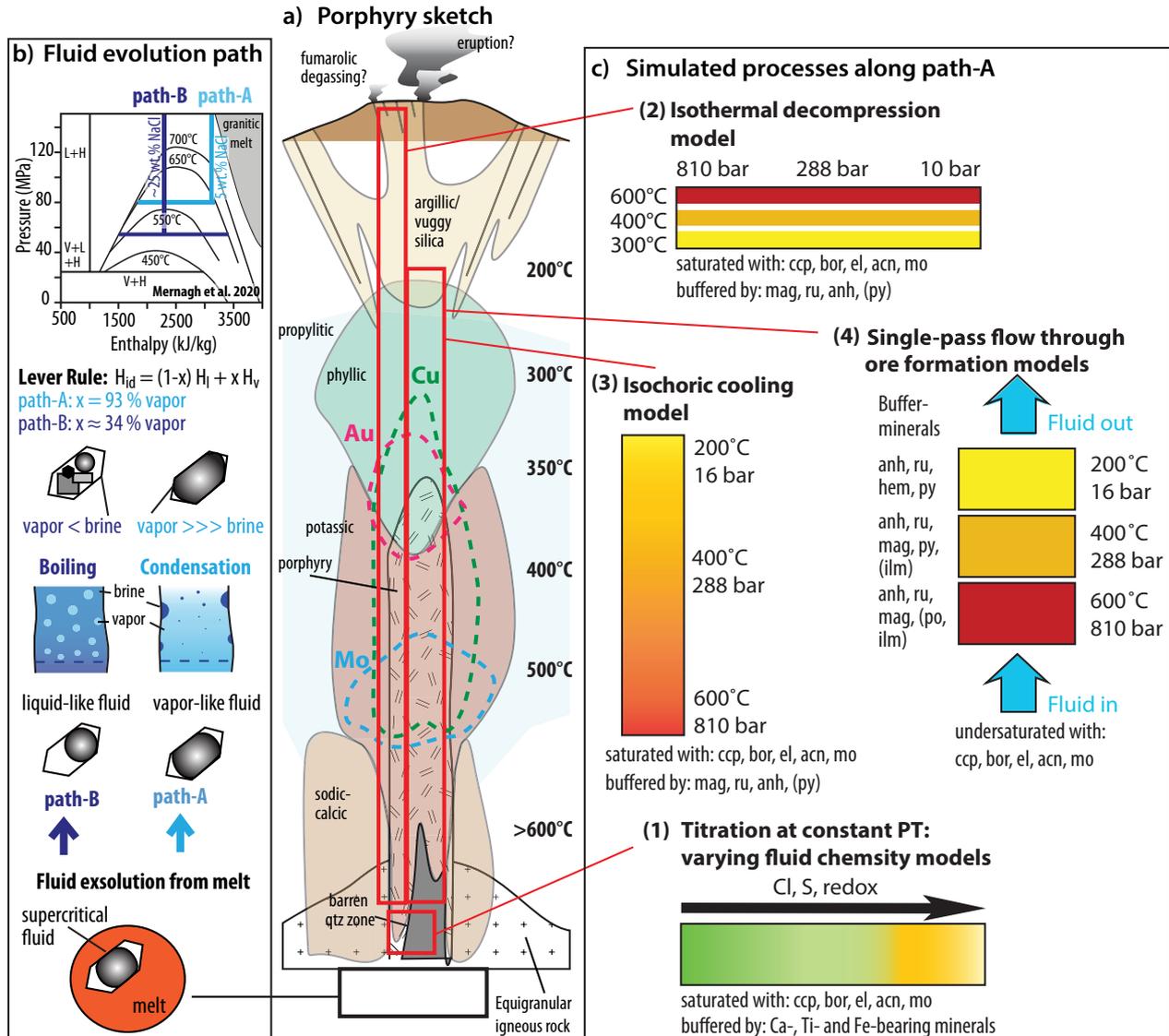


Fig. 1. (a) Schematic sketch of a porphyry ore deposit modified after Sillitoe (2010), showing the overlapping alteration and ore zones. (b) Illustration of the fluid evolution along path A for an intermediate-density vapor-dominated pathway and along path B for a liquid-dominated pathway. Phase proportions were calculated using the lever rule and the enthalpy-P- X_{NaCl} diagram from Mernagh et al. (2020). (c) Schematic sketches of simulated processes: (1) titration models of metal solubility with varying fluid chemistry (S, Cl, and redox) at 600°C and 810 bar, (2) isothermal decompression and (3) isochoric cooling models for the metal solubility of a fluid with variable composition, and (4) single-pass flow-through ore-formation models. The fluid is buffered by minerals and saturated with respect to ore-forming minerals such as chalcopyrite (ccp), bornite (bor), acanthite (acn), electrum (el), and molybdenite (mo) in models 1 through 3. Buffer minerals: anh = anhydrite, hem = hematite, ilm = ilmenite, mag = magnetite, py = pyrite, po = pyrrhotite, qtz = quartz, ru = rutile.

(Fig. 1b). For example, Lerchbaumer and Audétat (2012) showed that the vapor to brine mass ratio at Alumbrera was 4 to 9, which translates to a volume proportion of 96 to 98% vapor. A similar conclusion was reached by Mernagh et al. (2020) based on enthalpy constraints (i.e., 90–98% vapor). The vapor to liquid phase proportions vary as a function of salinity, temperature (T), and pressure (P) and consequently may change considerably over the lifetime of an active hydrothermal plume (Landtwing et al., 2010). In shallow systems, the fluid exsolving from the melt may be vapor-like and coexist with halite, salt melts, or brine (Muntean and Einaudi, 2000, 2001; Heinrich et al., 2004; Williams-Jones

and Heinrich, 2005; Koděra et al., 2014). The path of fluid evolution varies depending on the depth at which the fluid exsolves from the melt, the composition and volume of the fluid(s) (e.g., salinity, CO_2 content), and the permeability of the host rocks (Heinrich et al., 2004; Redmond et al., 2004; Heinrich, 2005; Williams-Jones and Heinrich, 2005; Klemm et al., 2007; Driesner and Heinrich, 2007; Rusk et al., 2008; Redmond and Einaudi, 2010).

Elevated concentrations of ore metals (10–4,300 ppm Cu, 0.05–10 ppm Au, 2–190 ppm Ag, and 1–290 ppm Mo) have been detected in vapor-like and intermediate-density fluid inclusions (Heinrich et al., 1999; Ulrich et al., 1999, 2002; Au-

détat et al., 2000a, b; Rusk et al., 2004; Klemm et al., 2007, 2008; Zajacz et al., 2008; Audétat, 2010; Seo et al., 2011, 2012; Lerchbaumer and Audétat, 2013; Seo and Heinrich, 2013). The data referred to here are based on laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) measurements of the vapor in composite brine-vapor inclusion assemblages and vapor-like and intermediate-density fluid inclusions that homogenize to the vapor or by critical behavior, respectively (App. 1: all data including references). Here we loosely refer to these fluids as vapor-like fluids, with the emphasis placed on predicting metal transport in compressible fluids of low to intermediate density (i.e., 0.1–322 kg/m³ in the pure H₂O system). Elevated metal concentrations have also been documented in high-temperature (melt-)vapor-brine partitioning experiments (Frank et al., 2002, 2003; Pokrovski et al., 2005; Simon et al., 2005, 2006, 2007, 2008; Zajacz et al., 2008, 2010, 2011, 2012, 2017). They have likewise been documented in lower-temperature vapor experiments (Migdisov and Williams-Jones, 2013; Hurtig and Williams-Jones, 2014a, b; Migdisov et al., 2014). These studies establish a baseline for metal contents in vapor-like fluids, providing the fundamental evidence that vapor-like fluids can transport sufficient metals to be considered ore fluids.

Numerical simulations of the physical aspects of porphyry copper ore formation have demonstrated the transient nature of the fluid phase states and fluid miscibility within magmatic-hydrothermal fluid plumes (Gruen et al., 2012; Weis et al., 2012, 2014; Afanasyev et al., 2018). Key observations from these simulations in the NaCl-H₂O system are the occurrence of pressure fluctuations, the presence of compressible intermediate-density supercritical fluids, occasional formation of immobile brine lenses, and a correspondingly high proportion of vapor after phase separation. Processes such as fluid-rock interaction and mineral precipitation have not been considered in these physical models. Advanced coupled chemical and physical reactive transport simulations only have been performed for major elements (i.e., O, H, S, C, Ca, Na, Cl, K, Al, Mg, and Si) and have not evaluated metal transport and precipitation (Yapparova et al., 2019). To date, the only ore metal for which solubility has been coupled to physical transport models is copper (Weis et al., 2012; Weis, 2015). Weis (2015) simulated the flow of multiphase variably miscible H₂O-NaCl fluids and predicted the formation of self-organizing plumes with a stable temperature front where Cu deposition occurs as a result of efficient cooling of the hydrothermal plume by an overlying meteoric convection cell. Chemically more complex models simulating metal transport of porphyry ore formation (Heinrich et al., 2004; Heinrich, 2005; Reed et al., 2013) have used existing thermodynamic models for aqueous liquids (e.g., the HKF model; Helgeson et al., 1981). These chemical models predict the development of alteration sequences due to fluid-rock interaction comparable to those observed in porphyry deposits.

Lastly, some thermodynamic studies have approached the system from the vapor side using metal volatility to estimate ore precipitation from magmatic gases (Krauskopf, 1957, 1964; Eastoe, 1982) and/or vapor-liquid partitioning data from experiments and vapor-melt partitioning data from active volcanoes (Pokrovski et al., 2013). These simulations have not yielded metal concentrations (i.e., for Au, Cu, Ag, and

Mo) sufficient for ore formation by vapor-like fluids, because the solvating properties of water vapor were not considered (see “Hydration Model” section for more detail). The density model (Marshall and Franck, 1981; Anderson et al., 1991; Akinfiev and Diamond, 2004) has yielded promising results for predicting Ag solubility in low-density fluids for a wide range of temperature and fluid density (Akinfiev and Zotov, 2016). As this model has not been implemented into a thermodynamic code package such as GEM-Selektor, it is currently not possible to use the density model to simulate metal ratios and fluid-mineral reactions. In summary, existing models have failed to predict metal transport in multicomponent vapor-like aqueous fluids relevant to porphyry ore formation because of a paucity of experimental data for low- and intermediate-density fluids and the difficulty of introducing these data into thermodynamic code packages.

In Hurtig and Williams-Jones (2015), we presented a model for Au-Ag-Mo solubility designed specifically to treat the case of metal transport by vapor-like fluids based on experiments (Migdisov et al., 1999; Archibald et al., 2001; Rempel et al., 2006; Zezin et al., 2007, 2011; Migdisov and Williams-Jones, 2013; Hurtig and Williams-Jones, 2014a, b). Here, we expand on our earlier study by including experimental data for CuCl solubility in water vapor (Archibald et al., 2001; Migdisov et al., 2014). We present comprehensive thermodynamic simulations of the solubility of Cu, Au, Ag, and Mo in vapor-like fluids buffered by simplified vein gangue mineral assemblages using the GEM-Selektor code package (Kulik et al., 2013). These simulations approach the thermodynamic modeling from the gas phase; importantly, we consider metal solubility as a function of water vapor pressure and hydrated gaseous species. Vapor-liquid partitioning is not simulated, and cooling paths only follow metal transport and precipitation from vapor-like fluids. Four numerical simulation setups (Fig. 1c) were employed to understand (1) the effect of fluid chemistry on metal solubility and metal ratios at high temperature in a vapor-like fluid (i.e., through titration of Cl, S, and O), (2) the effect of isothermal decompression, (3) isochoric cooling on metal mobility and metal ratios, and (4) single-pass flow-through ore formation and metal zoning models. We compare the simulated metal concentrations and ratios to those of vapor-like fluid inclusions, volcanic gas condensates, and ores in porphyry deposits. Based on these comparisons, we evaluate the contributions of the simulated processes to metal enrichment and identify the key drivers of porphyry ore genesis within a magmatic-hydrothermal plume.

A Hydration Model for Predicting Gaseous Metallic Speciation

The role of water as a solvent is the key to understanding metal transport in aqueous fluids, which can be decompressed from a liquid-like to a vapor-like fluid density above the critical temperature and pressure of water without crossing any phase boundaries (Weingärtner and Franck, 2005). Water is an ideal solvent because it is a dipolar molecule with a high negative charge density near the oxygen atom and a high positive charge density near the hydrogen protons (Weingärtner and Franck, 2005). It exists as a fluid (liquid or gas) over a wide range of temperature and pressure, and, in its liquid state, dipole-dipole interaction between water molecules leads to

the formation of a strong network of hydrogen bonds (Franks, 1973). This network is responsible for the physicochemical properties of liquid water, the formation of water clusters and hydration shells around ions and other dipole molecules, and the dissociation of aqueous species (Dagade and Barge, 2016). These are essential characteristics of liquid water and control its capacity to dissolve solutes—notably those forming ionic (charged) species. In the most widely used model for the thermodynamic prediction of element transport by aqueous liquid, the HKF model (Helgeson et al., 1981), the capacity of water for ion association/dissociation at any given temperature, pressure, and density is described by the Born equation (Born, 1920; Bucher and Porter, 1986; Majer et al., 2008). The Born equation is used to estimate the electrostatic component of the Gibbs free energy of solvation of an ion of a given charge and radius. It is an electrostatic model that treats water as a continuous dielectric medium having a physical state that is an incompressible continuum. This equation, and by extension the HKF model, accurately predicts metal solubility in electrolyte solutions with liquid-like density at low to moderate temperature but fails to predict metal transport in nonelectrolyte solutions with vapor-like density.

In the gas state, the dielectric constant decreases exponentially with decreasing water vapor density and increasing temperature (Fernández et al., 1997). Consequently, in vapor-like fluids the dielectric constant is low and ion association is strong, thereby stabilizing neutral compounds at the expense of ionic species. Like liquid water, water vapor is composed of polar molecules and can therefore dissolve solids (Weingärtner and Franck, 2005). Thus, the solubility of oxides (e.g., SiO_2 , MoO_3 , and WO_3) in water vapor is orders of magnitude higher than their volatility in dry gas, i.e., the vapor pressure over the corresponding solid (Hannay et al., 1880; Morey and Hesselgesser, 1951; Morey, 1957; Wendlandt and Glemser, 1964). The importance of hydrated gaseous species was first recognized by Pitzer and Pabalan (1986) for the $\text{NaCl-H}_2\text{O}$ system. The solubility of NaCl in water vapor and liquid was subsequently modeled for a wide range of temperature and pressure and shown to increase continuously from vapor to liquid in supercritical fluids (Bischoff et al., 1986; Pitzer et al., 1987; Tanger and Pitzer, 1989; Sterner et al., 1992; Anderko and Pitzer, 1993). A solubility continuum in supercritical fluids also has been demonstrated for copper. This was done using synchrotron X-ray absorption spectroscopic (XAS) techniques in S-free and S-bearing solutions (Liu et al., 2008; Etschmann et al., 2010; Louvel et al., 2017). The same continuum for Mo had been demonstrated using the solubility method (Wendlandt and Glemser, 1964; Hurtig and Williams-Jones, 2014a). The increase in metal solubility with water density is related to the formation of metal-water and water-water molecule clusters (Fig. 2) and has been simulated using ab initio molecular dynamics and density functional theory (Godinho et al., 2005; Mei et al., 2014, 2018). Thus, metal solubility in vapor-like fluids may be viewed as a series of hydration steps with increasing hydration number for which the free energy can be calculated from experimental data or predicted by theory. For hydration numbers below 2, metal solubility (Au, Ag, Mo, and Cu) is dominated by solute-solvent interaction and consequently is heavily influenced by the electronic structure of the corresponding volatile metallic species (Fig. 2b). The latter, in

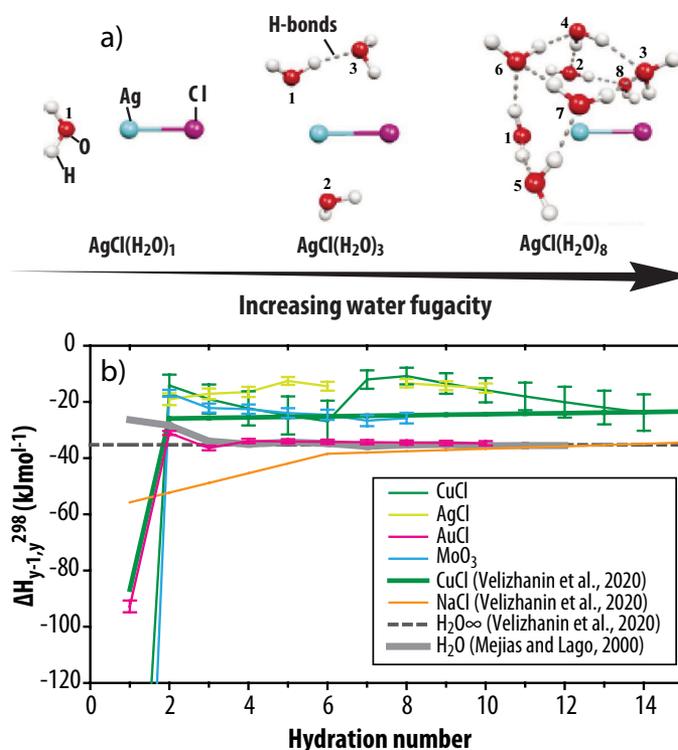


Fig. 2. (a) Hydration clusters around a gaseous AgCl molecule as a function of increasing water fugacity (AgCl clusters from Godinho et al., 2005). (b) Compilation of calculated hydration enthalpy values of various gaseous metal species, NaCl , and pure water clusters; see Table 1 for numerical values. Gaseous metallic species show a different correlation of enthalpy values with increasing hydration number compared to NaCl .

turn, is reflected by differences in the enthalpy and entropy of hydration for these species. For hydration numbers above 2, the contribution of solute-solvent interaction decreases sharply with increasing hydration number and solvent-solvent interaction dominates (Fig. 2b). Thus, above a hydration number between 3 and 6, which depends on the metal of interest (Au, Ag, Cu, and Mo), the energy of hydration (per water molecule added) approaches a constant similar to that calculated using theoretical models for water molecule cluster formation (Mejías and Lago, 2000; Velizhanin et al., 2020). Below, we use the observations described above to simulate metal transport in the continuum between vapor-like fluids and those of intermediate density.

Methods

The thermodynamic framework

The sources of the thermodynamic data for the minerals and gases used in the numerical simulations are summarized in Tables A1 to A3 (App. 2) and were managed with the GEM-Selektor code package (Karpov et al., 2001, 2002; Kulik et al., 2013). Data for the minerals were compiled from Johnson et al. (1992), Robie and Hemingway (1995), Chase (1998), Evans et al. (2010), and Holland and Powell (1998, 2011), and temperature-dependent phase transitions for the sulfides at the conditions of interest were implemented (entropy, enthalpy, volume, and c_p -function). Data for the heat capacity and

Table 1. Hydration Enthalpy and Entropy for Different Gaseous Metal Species Estimated from Experimental Data Compared to Calculated Density Functional Theory Energies of Water Clusters

Species	Hydration numbers	$H_{y-1,y}^{298}$ (kJmol ⁻¹)	$S_{y-1,y}^{298}$ (Jmol ⁻¹ K ⁻¹)
AuCl ¹	>2	-34.6 ± 0.8	-90.4 ± 1.3
AgCl ²	>2	-14.8 ± 1.6	-60.8 ± 1.8
CuCl ²	>2	-19.1 ± 5.2	-66.9 ± 9.2
CuCl ³	>2	-23.6 ± 1.6	-80.8
NaCl ⁴	1–15	-53.13 to -32.42	-91.5
NaCl ³	1–15	-55.78 to -34.05	-90.2
MoO ₃ ⁵	>2	-24.3 ± 1.8	-76.6 ± 3.6
H ₂ O ⁶	2–12	-26.4 to -35.5	-69.2 to -12.4
H ₂ O ³	2 to ∞	-16.6 to -35.3	-79.0 to -11.6

¹Hurtig and Williams-Jones (2014b)

²Calculated, this study

³Velizhanin et al. (2020)

⁴Pitzer and Pabalan (1986)

⁵Hurtig and Williams-Jones (2014a)

⁶Mejias and Lago (2000)

enthalpy of the phase transition for acanthite were taken from Grønvd and Westrum (1986) and for bornite, chalcopyrite, and chalcocite from Robie et al. (1994). Thermodynamic data for the major gases—H₂O(g), H₂(g), CO₂(g), CH₄(g), CO(g), Cl₂(g), O₂(g), HCl(g), H₂S(g), and SO₂(g)—were compiled from Frenkel (1994), Robie and Hemingway (1995), and Chase (1998), and parameters for the Peng-Robinson-Stryjek-Vera (PRSV) equation of state were taken from Proust and Vera (1989) and Stryjek and Vera (1986).

The gaseous metallic species considered in this study were limited to Au, Ag, Mo, and Cu, the only metals for which the required experimental data are available. The experimental data for the metallic gaseous species were fitted using the linear relationship of log K_s to the inverse of temperature, and the species were added as reaction-dependent components in GEM-Selektor. The fitted parameters for the hydrated gold chloride species, AuCl(H₂O)_y, were taken from Hurtig and Williams-Jones (2014b) and for hydrated molybdenum trioxide, MoO₃(H₂O)_y, from Hurtig and Williams-Jones (2014a). Experimental data for the hydrated silver chloride species, AgCl(H₂O)_y, (Migdisov et al., 1999; Migdisov and Williams-Jones, 2013) and for solvated gold sulfide species, AuS(H₂S)_{x-1}(H₂O)_y, (Zezin et al., 2007, 2011) were fitted in Hurtig and Williams-Jones (2015). Experimental data for solvated copper chloride species, CuCl(H₂O)_y and CuCl(HCl)(H₂O)_y, (Archibald et al., 2002; Migdisov et al., 2014) were fitted in this study (Table A2). The experimental data for AgCl, CuCl, and AuS species were refitted for consistent implementation into GEMS. Details of the fitting these experimental data and the validity range of all gaseous hydrated metallic species used in this study can be found in Appendix 2.

The activity models and equations of state are summarized in the TSolMod library class (Wagner et al., 2012). The reference state is 25°C and 1 bar. The standard state for all solids was that of a pure phase and for the gases was that of an ideal gas at 1 bar. A subregular solid-solution model for Au-Ag alloys (White et al., 1957) was introduced as a set of user-defined temperature-dependent equations (see App. 2 for details). In the gas-mineral equilibrium simulations, all gases were treated as ideal and ideal mixtures (see “Limitations of the numerical simulations” section). This is currently

a limitation of the GEM-Selektor code package, which cannot treat nonideal gas mixtures with reaction-dependent components, our only method for implementing the experimentally derived gaseous metallic species. The experimental data for the metallic gaseous species were fitted to water fugacity and thus were modeled at water fugacity instead of total pressure (see App. 2 for pressure tables using IAPW-95). This adaptation was necessary to preserve the observed exponential increase in solubility of the metallic gaseous species (Fig. 3) with water vapor density and to ensure that the correct P-T behavior of these species was modeled. The simulated metal solubility was tested against the experimental data and was reproducible within the experimental uncertainty (see App. 2, Table A3).

Numerical simulations

The geochemical simulations of the behavior of Ag-Au-Cu-Mo-bearing vapors were carried out using GEM-Selektor v.3.7 (<http://gems.web.psi.ch/GEMS3/>), which employs a Gibbs energy minimization approach (Karpov et al., 2001, 2002; Kulik et al., 2013). We present four numerical simulations (Fig. 1c), namely (1) titration at constant (high) temperature and pressure with variable fluid chemistry, (2) isothermal decompression, (3) isochoric cooling, and (4) single-pass flow-through reaction. The titration models at constant temperature and pressure evaluate the effects of S, Cl, and the redox condition on the solubility of the ore-forming minerals. The isothermal decompression models show the solubility as a function of fluid density, providing a connection between the conditions of volcanic gases (~1 bar) and those of porphyry systems (100–1,800 bar). The isochoric cooling models evaluate the mobility of ore metals along a constant-density fluid evolution path. The simulated P-T paths only consider the vapor path after phase separation, i.e., the aqueous liquid was not activated in these simulations. Thus, by not considering the liquid, the conditions minimized metal solubility and maximized mineral precipitation from vapor-like fluids. The single-pass flow-through reaction simulations represent the progressive reaction of a batch of vapor-like fluid with buf-

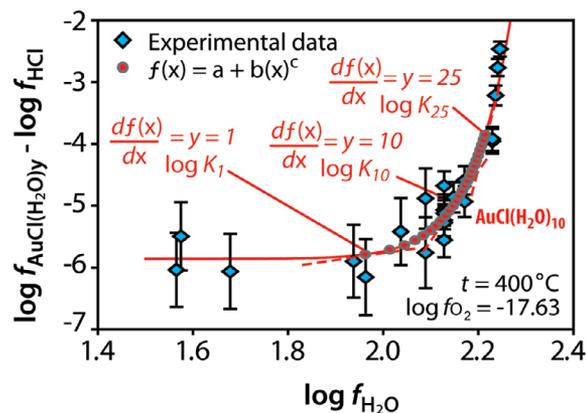


Fig. 3. An experimentally determined solubility isotherm (400°C) in which measured gold fugacity normalized to HCl fugacity is shown as a function of water fugacity buffered by the assemblage of molybdenum dioxide-molybdenite (blue diamonds). The experimental data were fitted to a power function $f(x)$ (red line) for the purpose of extracting integer hydration numbers (y) equivalent to the tangents (dashed red lines) and logarithmic equilibrium constants (K_y).

fer minerals while simultaneously cooling and decompressing. This model was used to investigate metal zoning. The modeling conditions are summarized in Table 2.

The titration models at 600°C and 810 bar (density of 300 kg/m³) involved ore mineral saturation and were conducted at varying redox conditions for variable S and Cl contents (Fig. 1c). In order to select realistic concentration ranges for major components in the simulations, we turned to the compositional data available for volcanic gases and vapor-like and intermediate-density fluid inclusions from porphyry deposits (Table 3; see App. 1 for individual data sets and references). The S (SO₂ and H₂S), Cl (HCl), and C (CO₂) contents of volcanic gases range widely, from 0.002 to 26, 0.002 to 16, and 0.02 to 55 wt %, respectively (Gemmell, 1987; Symonds et al., 1987, 1990, 1992, 1994, 1996; Giggenbach and Matsuo, 1991; Hedenquist et al., 1994; Taran et al., 1995, 2000, 2001; Giggenbach, 1996; Scher et al., 2013; Zelenski et al., 2014; Taran and Zelenski, 2015, and references therein; Nadeau et al., 2016). The ranges in the concentrations of these components reported for vapor-like and intermediate-density fluid inclusions from porphyry deposits are similar, namely 0.1 to 1.3 wt % S, 1.0 to 8.9 wt % Cl, and 1.1 to 13 wt % C (Ulrich et al., 1999, 2002; Audéat et al., 2000a, b; Tarkian et al., 2003; Redmond et al., 2004; Rusk et al., 2004, 2008; Klemm et al., 2007, 2008; Zajacz et al., 2008; Seo et al., 2009, 2012; Audéat, 2010, 2019; Landtwing et al., 2010; Lerchbaumer and Audéat, 2013; Seo and Heinrich, 2013; Zaheri-Abdehvand et al., 2020). The contents of S and Cl considered in the simulations range from 0.0002 to 10 wt % and 0.01 to 1 wt %, respectively; the C content was held constant at 2 wt %, which is the median value for high-T vapor-like and intermediate-density porphyry fluids (see Table 3; see App. 1).

Measuring the sulfur content of fluid inclusions is challenging, and consequently only a small data set is available. From our simulations (see the section “Effect of fluid composition on ore metal solubility and metal ratios”) it is apparent that the amount of S in the fluid exercises an important control on metal ratios. Therefore, we decided to expand the range of S contents to be consistent with that for volcanic gases. The Cl range chosen for our simulations is narrower than that re-

ported by Audéat (2019) for single-phase ore fluids (5–15 wt % NaCl). Our compilation of fluid inclusion data returned a range of 1 to 9 wt % NaCl, averaging 4.4 wt % NaCl (i.e., 2.9 wt % Cl), because we excluded single-phase fluids with a liquid-like density. In the simulations, we further reduced this amount of Cl by not considering Cl that would have complexed with Na, K, and Fe and thus would not have been available for complexation with Au, Ag, and Cu.

The redox condition was described as the redox potential, $R_H = \log (f_{H_2}/f_{H_2O})$, which represents the most meaningful probe into the redox states of volcanic gases (Giggenbach, 1987, 1996). In Appendix 1, we also report the sulfidation potential (Einaudi et al., 2003) as $R_S = \log (f_{H_2}/f_{H_2S})$. The use of the Gibbs energy minimization method in GEM-Selektor allowed for evaluation of the redox potential for each local equilibrium step by varying the amount of H_{2(g)} and O_{2(g)} in the vapor-like fluid. All simulations were performed in the vapor-solid system by employing vapor-mineral equilibria in which the mineral assemblage changed from the reducing assemblage, calcite-ilmenite-magnetite(± pyrrhotite) to the oxidizing assemblage, hematite-anhydrite-rutile(± pyrite). Owing to the lack of direct measurements of redox sensitive species in fluid inclusions, the redox potential of porphyry-ore forming fluids can only be estimated (see “Mineral-Gas Reactions in Numerical Simulations” section).

We present two types of cooling and decompression simulations (Fig. 1c)—namely isothermal decompression and isochoric cooling (red and orange pathways in Fig. 4h)—at ore mineral saturation. Isothermal decompression was simulated for three temperatures (600°, 400°, and 300°C), constant Cl concentration (500 ppm), and two S contents (0.1 and 5.5 wt %). Isochoric cooling (600°–180°C) was modeled for a constant Cl content (500 ppm), S contents of 0.2 and 5.5 wt %, and a density of 300 and 100 kg/m³. The isochoric cooling pathways modeled in this study represent projections of a plausible P-T fluid pathway recorded in fluid inclusion data projected from the NaCl-H₂O system to that of pure water (red and orange paths in Fig. 4h; App. 2). Below the critical point of water, the vapor density corresponds to that of water vapor at the water vapor saturation pressure. The pressure in

Table 2. Numerical Modeling Setup and P-T-x Simulation Conditions

Model	T (°C)	P _{total} (bar)	f _{H₂O} (bar)	Density (kg/m ³)	R _H	Cl (ppm)	S (wt %)	C (wt %)	Ore minerals
Equilibrium models at constant P-T									
Cl titration	600	810	564	300	-3.8 to -3.9	0–10,000	0.2, 5.5	2.0	Saturated
S titration	600	810	564	300	-2.7 to -4.3	500, 3,000	0–10	2.0	Saturated
Redox titration	600	810	564	300	-1.5 to -4.5	500	0.2, 5.5	2.0	Saturated
Cooling and/or decompression models									
Isothermal decompression	600	10–810	8–564	5–300	-3.2 to -3.9	500	0.2, 5.5	2.0	Saturated
	400	10–288	8–174	5–300	-4.5 to -5.1	500	0.02, 4.8	2.0	
	300	10–86	8–68	5–46	-5.6 to -5.9	500	0.002, 3.8	2.0	
Isochoric cooling	180–600		F _{H₂O} (T) ₃₀₀	300	-3.8 to -8.2	500	0.2, 5.5	2.0	Saturated
			F _{H₂O} (T) ₁₀₀	100	-3.8 to -8.4	500	0.2, 5.5		
Single-pass flow-through reactor scheme									
Metal precipitation	180–600		F _{H₂O} (T) ₃₀₀	300	-3.1 to -8.1	500–100,000	3.0, 1.0, 0.1	2.0	Under-saturated at 600°C

For detailed fluid compositions see Appendix 1; F_{H₂O}(T) = water fugacity as a function of temperature (T) at constant density above the water vapor saturation pressure and then on the saturation pressure water vapor curve; ore minerals: electrum, acanthite, bornite, chalcopyrite, molybdenite (see App. 2 for details)

Table 3. Composition of Natural Volcanic Gases and Low- and Intermediate-Density Fluid Inclusions of Porphyry Deposits

Data	T (°C)	P (bar)	NaCl (wt %)	S (wt %)	Cl (wt %)	C (wt %)	Mo (ppm)	Cu (ppm)	Au (ppm)	Ag (ppm)
Volcanic gases and condensates (references 1–16)										
Minimum	82	~1		0.002	0.002	0.02	0.0006	0.003	7.0×10^{-6}	0.0030
Maximum	1,131	~1		25.6	16.3	55.0	2.80	59.4	0.0050	0.0140
Median	642			1.46	0.49	1.59	0.18	0.30	0.0010	0.0060
Average	646			3.23	1.48	4.01	0.42	3.38	0.0011	0.0084
Standard deviation	150			5.07	2.95	8.51	0.58	10.4	0.0014	0.0048
Number of data points	150			136	146	103	62	64	23	18
Vapor and intermediate density fluid inclusions (references 16–31)										
Minimum	323	2,500	1.0	0.10	0.61	1.07	1.00	10.0	0.05	2.00
Maximum	720	88	8.9	1.25	9.30	13.3	290	4,300 ¹	10.2	190
Median	431	494	4.4	0.50	2.73	2.00	50.5	850	0.87	23.0
Average	473	649	4.4	0.57	2.85	3.28	71.9	1,116	1.84	42.5
Standard deviation	110	551	2.0	1.47	1.47	2.68	69.3	977	2.50	53.7
Number of data points	68	42	69	24	69	(7 ²)	40	46	16	17

References: 1 = Symonds et al. (1987), 2 = Gemmill (1987), 3 = Symonds et al. (1990), 4 = Symonds et al. (1992), 5 = Giggenbach and Matsuo (1991), 6 = Hedenquist et al. (1994), 7 = Symonds et al. (1994), 8 = Taran et al. (1995), 9 = Symonds et al. (1996), 10 = Giggenbach (1996), 11 = Taran et al. (2000, 2001), 12 = Scher et al. (2013), 13 = Zelenski et al. (2014), 14 = Taran and Zelenski (2015, and references therein), 15 = Nadeau et al. (2016), 16 = Ulrich et al. (1999), 17 = Audétat et al. (2000a, b), 18 = Ulrich et al. (2002), 19 = Tarkian et al. (2003), 20 = Rusk et al. (2004), 21 = Redmond et al. (2004), 22 = Klemm et al. (2007, 2008), 23 = Seo et al. (2009), 24 = Zajacz et al. (2008), 25 = Rusk et al. (2008), 26 = Audétat, 2010, 27 = Landtwing et al. (2010), 28 = Seo et al. (2012), 29 = Lerchbaumer and Audétat (2013), 30 = Seo and Heinrich (2013), 31 = Audétat (2019); see Appendix 1 for full tables

¹Cu data were reduced by removing data points that do not follow systematic P-T trends (Fig. 4c, d; App. 1)

²Compiled from seven deposits with documented CO₂-bearing inclusions

these simulations was expressed as a temperature-dependent user-defined polynomial function (see App. 2).

Ore mineral precipitation during cooling and decompression was modeled using a single-pass flow-through reaction simulation (Fig. 1c). The metal ratios of the simulated fluids were taken from the compositional models at 600°C, 810 bar, and a density of 300 kg/m³. These fluids were slightly undersaturated with respect to the ore minerals, molybdenite, electrum, chalcocite, bornite, chalcocite, and acanthite (see Table 4 for starting fluid compositions). Because we used the metal ratios determined in the titration models and employed a similar degree of undersaturation, the ore precipitation models clearly illustrate the effects of the initial S, Cl, and R_H fluid composition on the P-T evolution paths. The fluids become saturated during cooling and decompression and precipitate ore minerals during each step while equilibrating with a constant buffer mineral assemblage needed to constrain the redox potential of the evolving fluid (see “Mineral-Gas Reactions in Numerical Simulations” section). The simulated fluid varied compositionally from 0.05 to 10 wt % Cl, 0.1 to 3 wt % S, and -3.2 to 4.0 R_H at 2 wt % C. In simulations at 1 and 10 wt % Cl, the HCl/ΣCl ratio provides a measure of the excess Cl and illustrates the control on metal zonation with various degrees of ore mineral undersaturation in the starting fluid. User-defined

GEM-Selektor scripts and additional information on the modeling setup can be found in Appendices 1 and 2.

Mineral-Gas Reactions in Numerical Simulations

Mineral-gas buffering is a widely used concept involving the interaction of a gas with minerals and has been employed frequently to describe active geothermal and volcanic gas systems (Giggenbach, 1981; Stefánsson and Arnórsson, 2002; Henley and Seward, 2018). The concept is based on the exchange of elements between minerals and gases as these phases adjust their compositions during the attainment of a steady state (“equilibrium”). In a multicomponent system, the redox potential and S content of the gas are controlled by several competing mineral-gas reactions and thus can only be described in terms of boundary conditions (i.e., minimum and maximum values) and not a single value (e.g., those of the hematite-magnetite or nickel-nickel oxide buffers; Fig. 5).

The application of mineral-gas buffers in our numerical simulations was essential in providing a basis for relating the simulated fluids to natural ore-forming systems, because they allowed us to realistically evaluate the redox condition and S contents for different parts of the porphyry ore-forming environment. The vapor-like fluid (H-O-S-Cl-C-Au-Ag-Mo-Cu) is equilibrated with solid phases that also include Ca, Fe, and Ti

Table 4. Summary of Starting Fluid Compositions for the Mineral Precipitation Models

Model	S (wt %)	Cl (wt %)	HCl/ΣCl	R _H	R _S	Cu (ppm)	Mo (ppm)	Au (ppm)	Ag (ppm)	Cu/Au	Cu/Mo
11a	0.53	0.05	0.19	-4.0	-3.2	406	65.7	0.09	3.27	4,295	6.2
11b	1.03	0.05	0.23	-4.0	-2.8	380	12.7	0.14	2.62	2,763	30
11c	3.17	0.05	0.86	-3.9	-2.1	65.5	0.21	0.74	3.98	89	318
11d	2.92	0.05	0.69	-3.2	-1.8	144	0.02	0.47	2.18	309	8,169
11e	0.13	0.29	0.08	-3.8	-3.4	2,620	81.3	0.16	8.72	16,624	32
11f	0.50	0.29	0.76	-3.9	-3.0	655	6.27	0.18	7.09	3,694	104
11g	0.50	1.07	0.93	-3.9	-3.0	655	6.37	0.18	7.09	3,694	103
11h	0.50	10.65	0.99	-3.8	-2.8	655	0.09	0.18	7.09	3,694	7,426

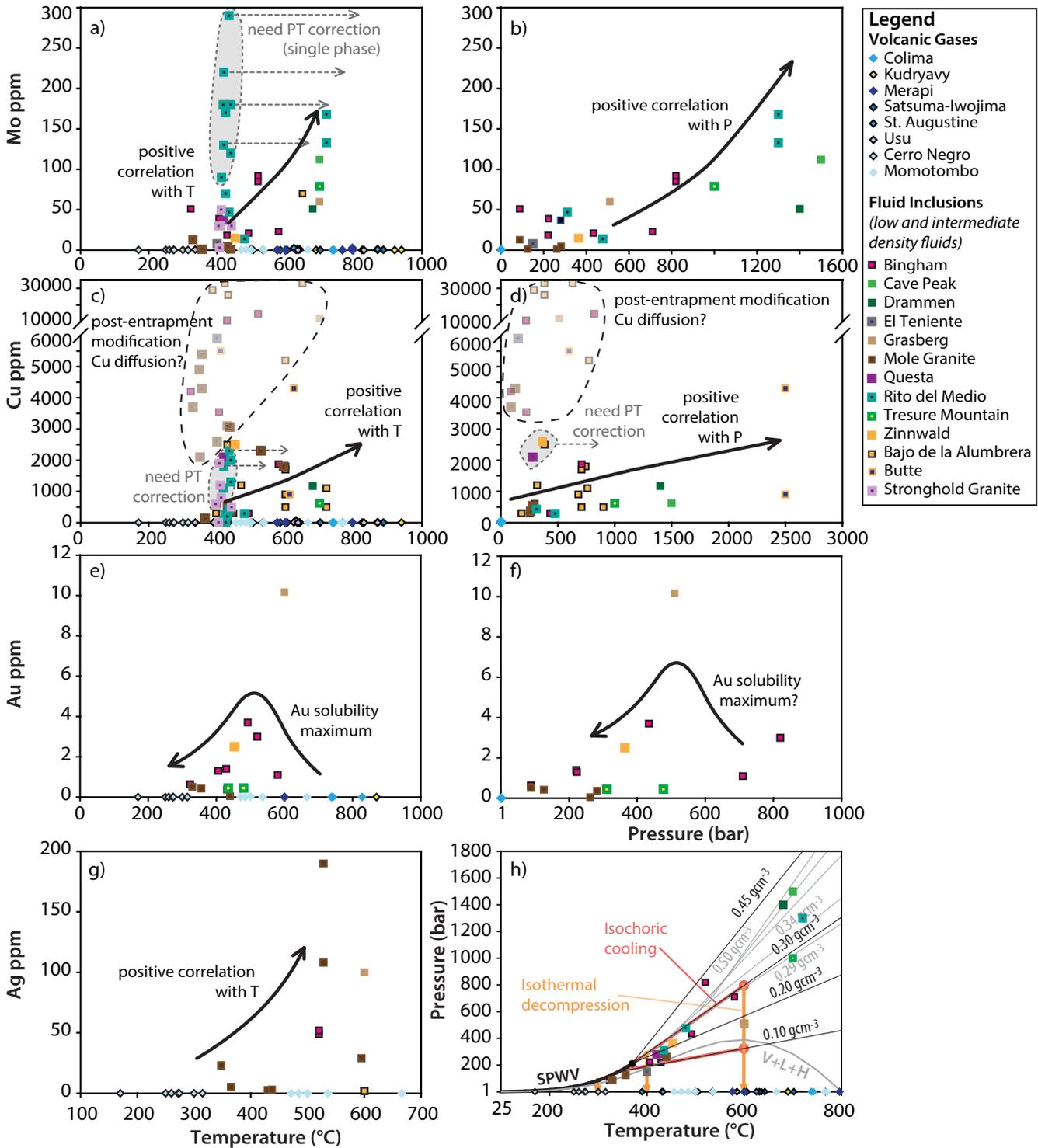


Fig. 4. Compilation of pressure-temperature (P-T) conditions and metal contents in natural low- and intermediate-density fluids from porphyry deposits and in volcanic gas condensates (Table 3). (a) Molybdenum concentrations as a function of temperature and (b) as a function of pressure. (c) Copper concentrations showing a clear correlation with temperature and (d) pressure for Cu below ~4,000 ppm. The systematics for Cu could be disturbed due to postentrapment modification in fluid inclusions. Copper values from single-phase vapor-like and intermediate-density fluid inclusions were accepted if a moderate P-T correction reasonable for the respective ore deposit could move the data to intersect the general P-T trends. (e) Gold solubility maximum ~500°C expressed in the Bingham fluid inclusion data and (f) possible solubility maximum for Au with pressure. (g) Silver concentrations show a positive correlation with temperature mainly expressed by the Mole granite fluid inclusion data. (h) A temperature-pressure diagram showing the saturation pressure water vapor curve (SPWV; thick black line) with isochores for density lines of pure water (thin black lines) overlying the vapor-liquid-halite (V + L + H; thick gray line) surface and isochores of the NaCl-H₂O system (thin gray lines) projected onto the P-T surface.

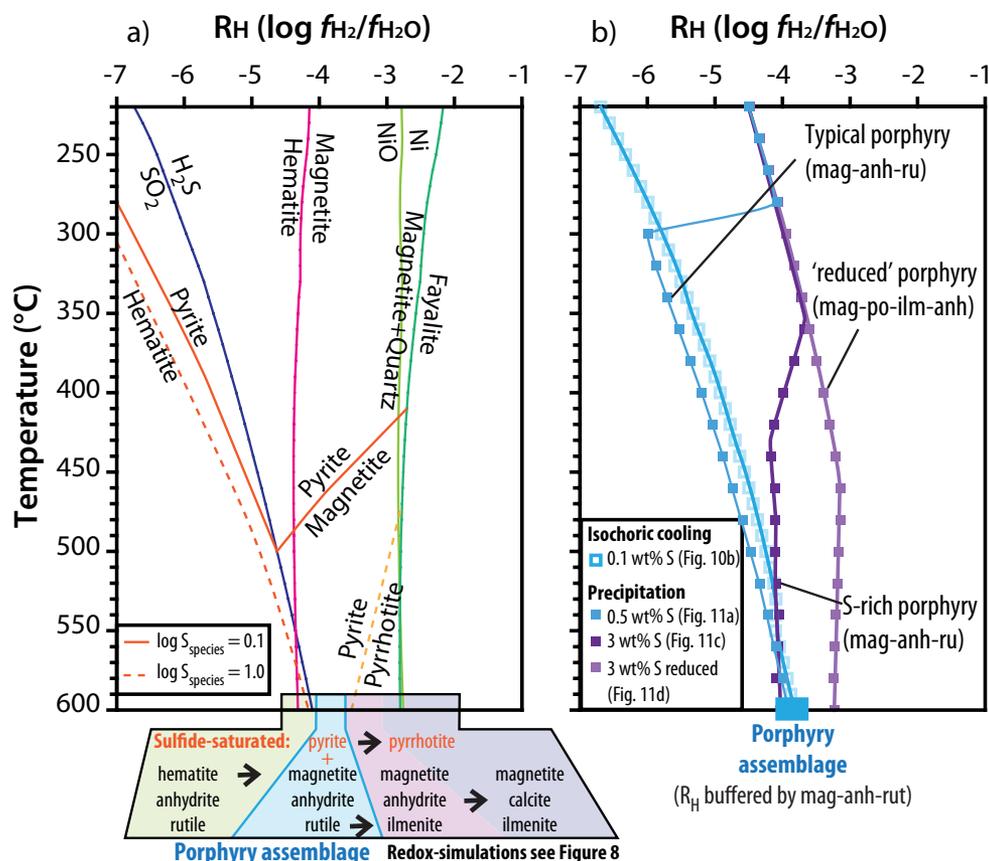
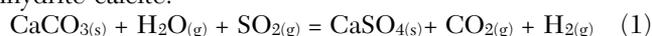


Fig. 5. Redox potential (R_H) of various commonly used mineral and gas buffers in comparison to R_H simulation traces as a function of isochoric cooling of a fluid with a density of 300 kg/m³. (a) Redox conditions considered in this study cover a wide range of commonly used mineral buffers such as the nickel-nickel oxide, the quartz-magnetite-fayalite, and the magnetite-hematite buffer. The mineral assemblage of magnetite-anhydrite-rutile typically found as gangue minerals in high-temperature porphyry systems defines a narrow range of R_H to define the redox potential of porphyry ore-forming fluids. (b) The R_H traces of isochoric cooling models of different starting compositions show that a typical porphyry fluid largely evolves along the H_2S - SO_2 gas buffer, whereas an S-rich fluid may follow the hematite-magnetite and/or pyrite-magnetite buffers. Abbreviations: anh = anhydrite, ilm = ilmenite, mag = magnetite, po = pyrrhotite, ru = rutile.

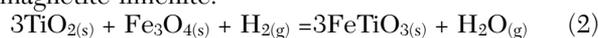
(Table A1 in App. 2). We currently cannot simulate the mobility of Ca, Fe, and Ti in vapor-like fluids, because of a lack of thermodynamic data for species involving these elements. Thus, the model assumes that Ca, Fe, and Ti are only present in the minerals that buffer the vapor-like fluid and are present at all conditions, whereas ore-forming metals (Au, Ag, Mo, and Cu) are mobile. In porphyry ore deposits, Ca occurs as anhydrite, plagioclase, and apatite, Ti as rutile/anatase, titanite, or as a trace component in biotite and quartz, and Fe occurs as magnetite, hematite, biotite, and various Fe and Fe-Cu sulfides. These minerals are abundant in porphyry deposits as documented by numerous petrographic studies (Lowell and Guilbert, 1970; Sillitoe, 1973, 2010; Gustafson and Hunt, 1975; Hedenquist et al., 1998; Rusk and Reed, 2002; Redmond et al., 2004; Landtwing et al., 2005, 2010; Rusk et al., 2008; Redmond and Einaudi, 2010; Richards, 2014; Zaheri-Abdehvand et al., 2020).

The following list of simplified mineral-gas and gas-gas reactions buffer the boundary conditions for the simulated vapor-like fluids:

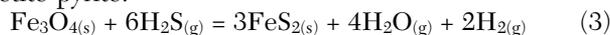
Anhydrite-calcite:



Rutile-magnetite-ilmenite:



Magnetite-pyrite:



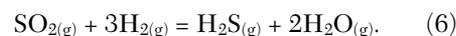
Hematite-magnetite:



Pyrite-pyrrhotite:



S gas buffer:



The range of redox conditions covered by these mineral and gas buffers represent R_H values between the nickel-nickel oxide, the quartz-magnetite-fayalite and the hematite-magnetite buffers (Fig. 5a). Based on petrographic analysis of the deep barren stockwork zone of porphyry deposits, we can associate the assemblage magnetite-anhydrite-rutile with porphyry ore formation (Macdonald and Arnold, 1994; Audétat et al., 2004; Reed et al., 2013). This mineral assemblage is stable at R_H values ranging between -3.6 and -4.1 at S contents below pyrite saturation (<4.8 wt % S), thus providing a relatively well constrained field of R_H values for a typical porphyry ore fluid

in equilibrium with magnetite, anhydrite, and rutile. The R_H porphyry field is constrained by equation (4) (hematite-magnetite) toward more oxidizing conditions and by equation (2) (rutile-magnetite-ilmenite) toward more reducing conditions. The reducing boundary condition is expanded in pyrite saturated simulations to R_H values of -3.0 bounded by equation (5). The R_H conditions identified here overlap with predicted f_{O_2} - T ranges in Richards (2014), which indicate that porphyry Cu-Au ore formation is favored by the H_2S - SO_2 gas buffer over more reducing mineral buffers.

The dominant Fe-bearing mineral assemblage affects the stability field of Fe^{2+} -bearing minerals and constrains R_H values relevant for porphyry ore-forming fluids. The only other Fe-bearing mineral phase occurring in high-temperature porphyry alteration zones is biotite, which contains Fe^{2+} and/or Fe^{3+} and, for simplification, was not simulated in this study. Simulations designed to investigate the redox potential in silicate-bearing systems (App. 1) predict mineral assemblages typical of the high-temperature stage of porphyry deposit evolution (biotite, K-feldspar, plagioclase, quartz, andalusite, magnetite, rutile, anhydrite). The R_H values of these simulations are -3.3 and -4.2 , which are within the range represented by the simplified assemblages that exclude silicate phases.

The S content of the fluid is reflected in the mineral buffering assemblage through saturation of different S-bearing minerals. At low S content (~ 0.09 wt %), anhydrite becomes stable over calcite in a fluid with 2 wt % C (~ 7 wt % CO_2), and in the Si-bearing calculations anhydrite is stable at parts per trillion levels of S in vapor-like fluids (App. 1). At a high S content (> 4.8 wt %), pyrite and pyrrhotite are stabilized over magnetite. This reaction is also observed in simulations involving silicates, for which the S content is > 4.6 wt % (see App. 1). These reactions constrain the S content of vapor-like fluids with R_H values ranging between -3.0 and -4.1 . As explained above, a typical high-temperature porphyry mineral assemblage includes magnetite, anhydrite, and rutile, whereas pyrite and pyrrhotite are generally not present. Nonetheless, inclusions of intermediate and monosulfide solid solutions (iss and mss) have been observed in magmatic minerals from several porphyry ore deposits and active volcanic analogues (Halter et al., 2002, 2005; Nadeau et al., 2010, 2016; Wilkinson, 2013; Richards, 2014; Rottier et al., 2019). The presence of these high-temperature sulfide phases is attributed to sulfide saturation in silicate melts. In the context of the simulations presented here, the occurrence of pyrite and pyrrhotite in the buffering mineral assemblage may be viewed as representative of magmatic sulfide saturation during the exsolution of aqueous fluids.

Numerical Simulation Results

Effect of fluid composition on ore metal solubility and metal ratios

The titration models were designed to determine the controls of Cl, S, and redox conditions on metal solubility and metal ratios in vapor-like porphyry ore fluids. The titration models were performed at $600^\circ C$ and 810 bar (i.e., a density of 300 kg/m^3) to represent the conditions of a high-temperature vapor-like fluid after it had exsolved from a magma (Fig. 1). The fluid was saturated with ore minerals and buffered by various Ca, Ti, and Fe minerals. The results of these simulations are summarized in Table 5, Figures 6 through 8, and Appendix 1.

The effect of Cl was modeled by progressively increasing the Cl content in the gas from 0.01 to 1.0 wt % at a constant S concentration of 0.2 and 5.5 wt %, respectively (Fig. 6). The simulated Cl contents (0.01–1.0 wt %) overlap with the range of Cl concentrations measured in volcanic gases (0.002–16.3 wt % Cl) and in NaCl-bearing vapor-like and intermediate-density inclusions from porphyry ore deposits (0.6–9.3 wt % Cl; Table 3). Although at the lower end of the Cl concentration range for fluid inclusions, the simulated contents are considered to be realistic, as only a small proportion of the Cl in the porphyry fluids is available for complexation with Cu, Au, and Ag. Thus, the Cl content used in this model can be considered equivalent to the excess Cl in the form of HCl (i.e., the Cl not complexed with Na, K, and Fe) in porphyry ore fluids. For example, for a total chlorinity of 5 wt % NaCl equiv at 0.01 HCl/ Σ Cl, the HCl content is 0.05 wt %, and for 0.1 HCl/ Σ Cl, the HCl content is 0.5 wt %. Numerical simulations conducted at higher Cl contents result in orders of magnitude higher simulated metal solubility, greatly exceeding reliably measured metal contents in vapor-like and intermediate-density fluid inclusions (Table 3). The buffering mineral assemblage was magnetite-anhydrite-rutile for the low-S model (Fig. 6a) and pyrite-anhydrite-rutile for the sulfide-saturated model (Fig. 6d). Gaseous metal chloride species of Cu, Ag, and Au increase in concentration with increasing Cl content, whereas concentrations of Mo and the AuS species remain constant (Fig. 6b, e). The Cu/Mo and Cu/Au ratios increase with increasing Cl content (Fig. 6c, f).

To investigate the effect of S on metal solubility, the S content of the fluid was increased progressively from 0 to 10 wt % at constant Cl concentrations of 500 ppm and 0.3 wt % (Fig. 7). The gas phase was initially buffered by the assemblage magnetite-anhydrite-rutile at low S contents. The redox con-

Table 5. Summary of Metal Concentrations and Ratios from the Equilibrium Models at $600^\circ C$ and 810 bar with Varying Fluid Chemistry

Model	S (wt %)	Cl (wt %)	Cu (ppm)	Au (ppm)	Mo (ppm)	Ag (ppm)	Cu/Au	Cu/Mo
Cl titration ¹	0.1	0.01–1.0	0.01–8,817	0.002–0.5	130	0.0002–22	7–17,143	6.0–560,444
Cl titration ²	5.5	0.01–1.0	27–7,533	1.8–4.7	0.2	0.9–18	15–1,598	135–40,761
S titration ^{1,2}	0–10	0.05	219–794	0.0001–7.6	0.03–322	0.1–4.2	29–601,871	1.5–8,324
S titration ^{1,2}	0–10	0.3	1,937–4,727	0.008–8.2	0.03–344	0.7–11.7	238–611,715	7.9–66,782
Redox titration ¹	0.1	0.05	483–507	0.07–0.12	85–221	4.2–4.3	4,046–6,960	2.3–5.7
Redox titration ¹	0.1	0.3	2,731–2,785	0.2–0.4	80–230	11.6–12.1	7,604–14,910	12–34
Redox titration ²	5.5	0.05	163–324	0.8–3.7	0.006–1.7	2.3–3.4	55–391	190–25,785

¹Buffered by the typical porphyry mineral assemblage: magnetite-anhydrite-rutile

²Buffered by the sulfide saturated mineral assemblage: pyrite-anhydrite-rutile(-magnetite)

Cl-Titration model at 600°C and 810 bar

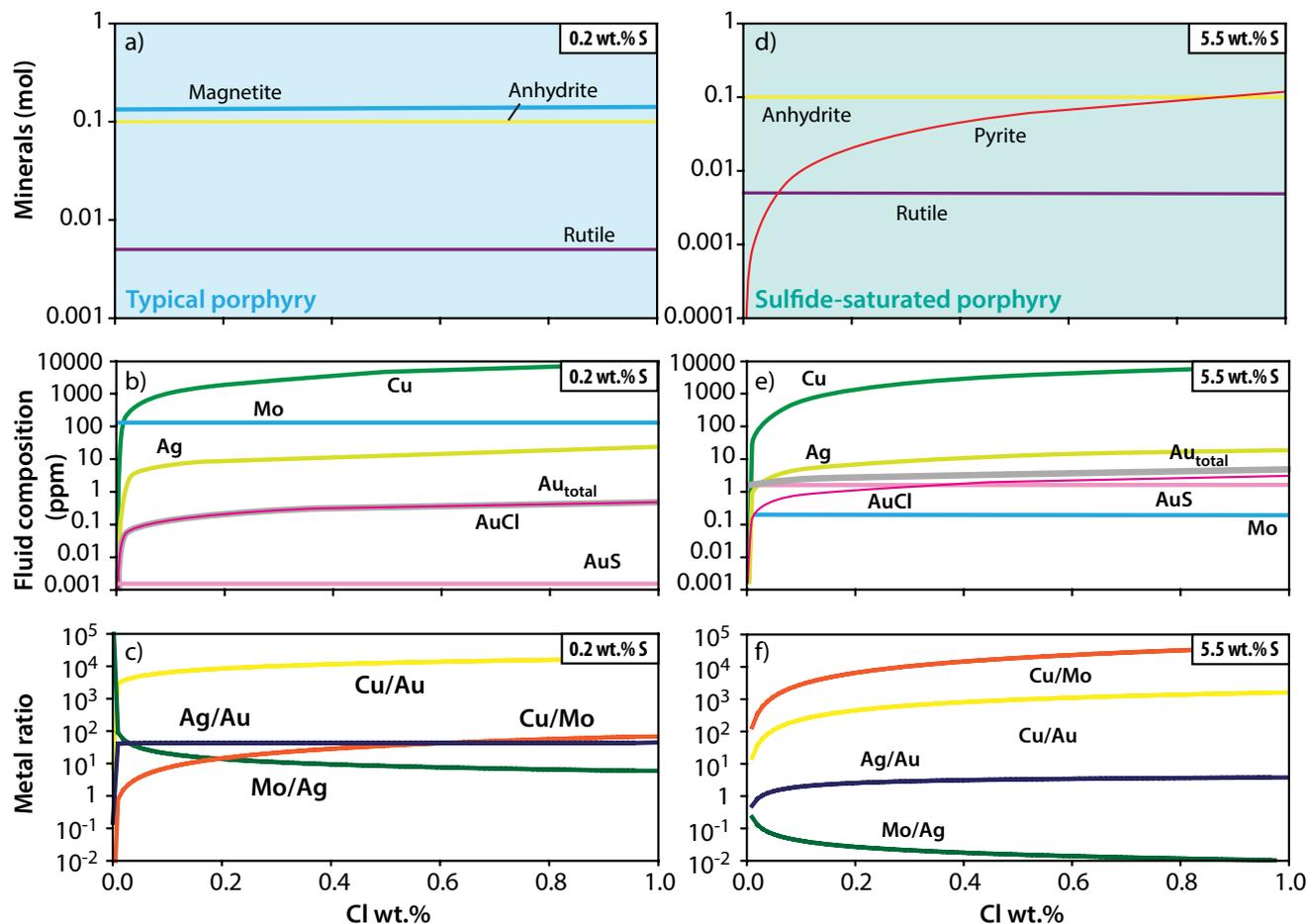


Fig. 6. Chlorine titration models at 600°C and 810 bar and ore mineral saturation showing (a, d) the buffering mineralogy, (b, e) the fluid composition, and (c, f) the metal ratios. (a) The redox condition is buffered by the mineral assemblage magnetite-anhydrite-rutile at low S concentrations (0.2 wt %) and (d) magnetite-anhydrite-rutile-pyrite at sulfide-saturated conditions (5.5 wt %). (b, e) The chlorine content correlates positively with Cu, Ag, and Au solubility. (c, f) The Ag/Au ratios are relatively constant, whereas the Cu/Au and Cu/Mo ratios increase slightly, and the Mo/Ag ratio decreases with increasing Cl content.

ditions between ~0.5 and ~1.7 wt % S were buffered mainly by hematite, whereas between ~1.7 and 4.8 wt % S magnetite was the dominant buffer. At higher S content (>4.8 wt %), pyrite stabilized at the expense of magnetite. The replacement of magnetite by pyrite as the main redox buffering mineral represents an upper limit for the S content of a porphyry ore fluid buffered by the assemblage magnetite-anhydrite-rutile (Fig. 7a, d). The lower limit for the S content of porphyry fluids is controlled by reaction (1), which converts calcite to anhydrite. Anhydrite became stable when the S content of the gas reached ~0.01 wt % S at 2.0 wt % C. This range of S contents (0.01–4.8 wt %) is within that observed in volcanic gases (0.004–25 wt % S) and overlaps with the range of S contents measured in fluid inclusions (0.17–1.3 wt % S) from porphyry ore deposits (Table 3). Copper and Ag concentrations decreased slightly with increasing S content (Fig. 7b, e). Molybdenum concentrations decrease sharply with increasing S content, whereas Au concentrations increase with S content due to the importance of AuS (short for $\text{AuS}(\text{H}_2\text{S})_{x-1}(\text{H}_2\text{O})_y$) species. Consequently, the Cu/Au ratio decreased with increasing S content and the Cu/Mo ratio increased (Fig. 7c, f).

The effect of the redox condition, $R_H = \log(f_{\text{H}_2}/f_{\text{H}_2\text{O}})$, was evaluated for three different fluid compositions (Table 2; Fig. 8). The low-S model (0.1 wt %; Fig. 8a) was simulated for two Cl contents (500 ppm and 0.3 wt %; Fig. 8b, c) and the sulfide-saturated model (5.5 wt %; Fig. 8d) was simulated for low Cl concentration (500 ppm; Fig. 8e). In the low-S model, the buffering mineral assemblage evolved with increasing $\text{O}_{2(g)}$ content of the fluid from calcite-ilmenite-magnetite, through magnetite-anhydrite-rutile to hematite-anhydrite-rutile (Fig. 8a). In the sulfide-saturated model, the evolution of the buffering mineral assemblages was from calcite-rutile-pyrrhotite through anhydrite-rutile-pyrite(-magnetite) to hematite-anhydrite-rutile (Fig. 8a). Molybdenum concentration decreased by three to seven orders of magnitude under reducing conditions, whereas Cu and Ag contents remained roughly constant (Fig. 8b, c, e). The Au solubility reached a maximum at conditions buffered by magnetite-anhydrite-rutile in the low-S model and anhydrite-rutile-pyrite(-magnetite) at sulfide-saturated conditions (Fig. 8b, c). At a constant Cl content of 500 ppm, the Cu/Au ratio was about two orders of magnitude lower in the sulfide-saturated model than in the low-S

S-Titration model at 600°C and 810 bar

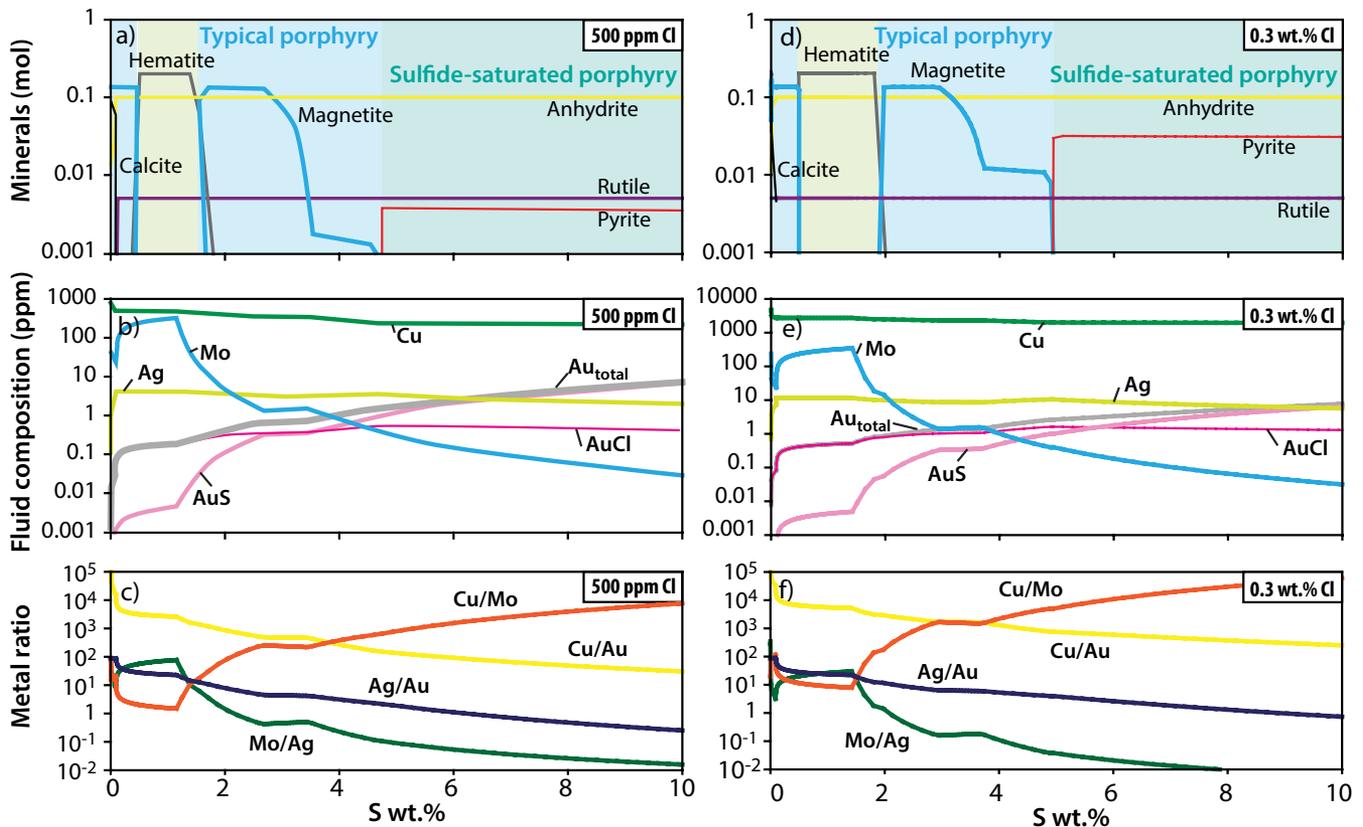


Fig. 7. Sulfur titration models at 600°C and 810 bar and ore mineral saturation showing (a, d) the buffering mineralogy, (b, e) the fluid composition, and (c, f) the metal ratios. The intermediate-density (300 kg/m³) fluid is mainly buffered by the mineral assemblage magnetite-anhydrite-rutile at lower S content and becomes saturated with pyrite at ~4.8 wt % S. The Au and Mo solubility is greatly affected by increasing S content and changes by several orders of magnitude.

model (Fig. 8f). However, the Cu/Au ratio increased by only ~0.2 orders of magnitude in the low-S models in response to an increase in the Cl concentration from 500 ppm to 0.3 wt % (Fig. 8f). The Cu/Mo ratio decreased by four to six orders of magnitude for the oxidized mineral assemblage relative to the reduced mineral assemblage (Fig. 8g). There was also a large increase in the Cu/Mo ratio (1–4 orders of magnitude) from the low-S to the sulfide-saturated model; the corresponding increase from the low- to the high-Cl model was only one to two orders of magnitude.

Isothermal decompression

The isothermal decompression models were developed to better understand the effects of pressure fluctuation and decompression on metal solubility in magmatic-hydrothermal systems. In porphyry ore deposits, pressure fluctuations are well documented by fluid inclusion data (Heinrich et al., 1999; Ulrich et al., 1999, 2002; Audétat et al., 2000a; Klemm et al., 2007; Zajacz et al., 2008; Seo et al., 2011, 2012; Lerchbaumer and Audétat, 2013; Mercer and Reed, 2013; Seo and Heinrich, 2013), multigenerational quartz textures (Rusk and Reed, 2002; Landtwing et al., 2005; Monecke et al., 2018), and studies of vein density and geometry (Gruen et al., 2010).

The vapor-like fluid was saturated with ore minerals during decompression at 600°C from 810 to 10 bar, at 400°C from

296 to 10 bar, and at 300°C from the water vapor saturation pressure to 10 bar. The low-S model was buffered by the mineral assemblage, magnetite-anhydrite-rutile, and the sulfide-saturated model by magnetite-anhydrite-rutile-pyrite. Metal solubility decreased gradually with decreasing pressure at all temperatures for both low-S and sulfide-saturated models (Fig. 9a-f). The Cu/Au and Cu/Mo ratios decreased over the range 600° to 400°C in the low-S model, but the Cu/Au ratio at 300°C increased with decreasing pressure exceeding that at 400°C for pressures below 35 bar; the Cu/Mo ratio at 300°C exceeded that at 600°C for pressures below ~50 bar (Fig. 9g, i). At sulfide-saturated conditions, the Cu/Au ratio decreased with decreasing temperature by four to five orders of magnitude (Fig. 9h-j). In contrast, the Cu/Mo ratio increased by three to four orders of magnitude in the isothermal decompression models performed at lower temperature.

The orders of magnitude decrease in metal solubility predicted by the decompression models described above are analogous to those observed in going from the porphyry to the volcanic gas environment (Fig. 4). The metal contents measured in porphyry-hosted fluid inclusions increase with both temperature and pressure, whereas in the low-pressure volcanic gas environment they vary only slightly as a function of temperature (Fig. 4).

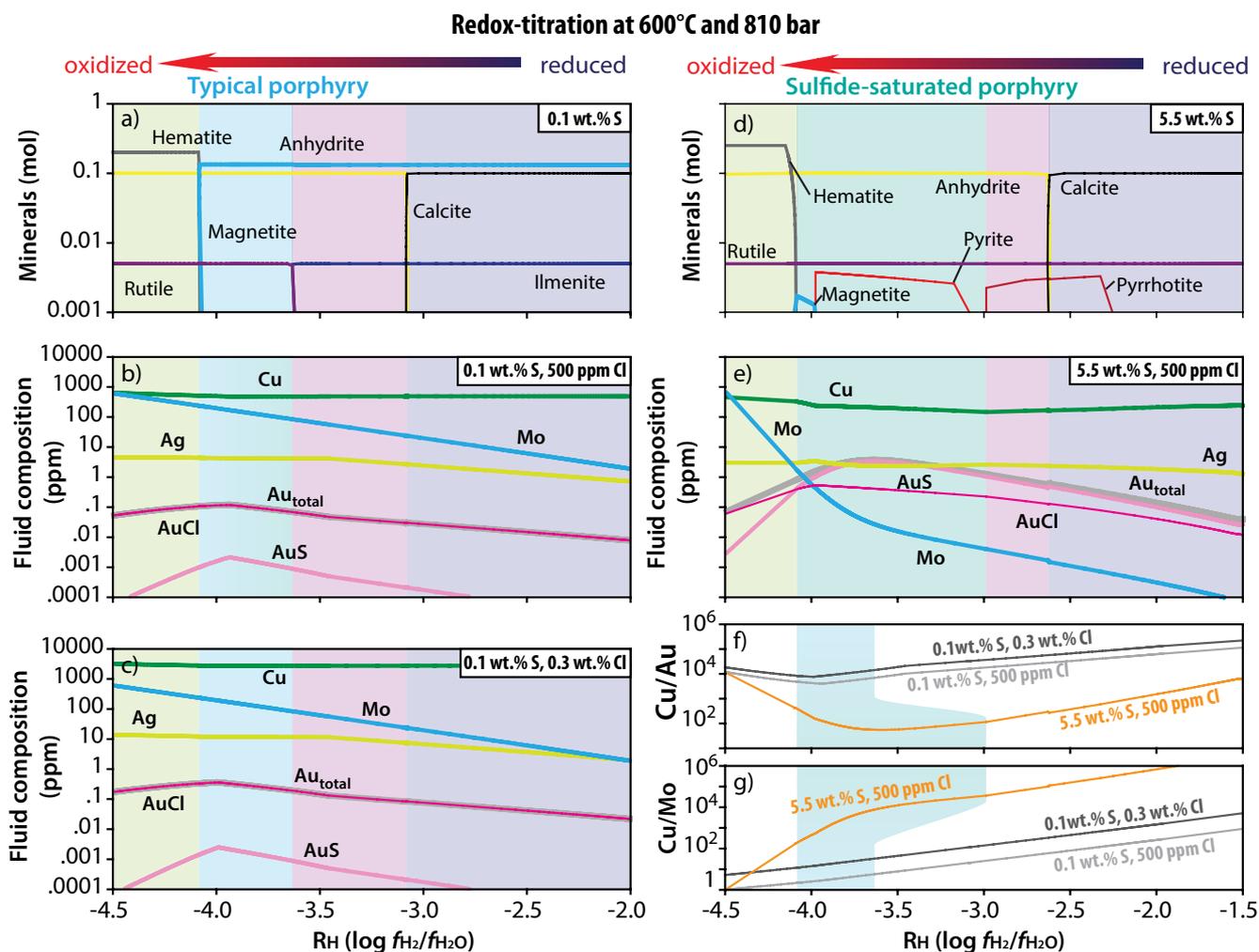


Fig. 8. Redox titration ($R_H = \log f_{H_2}/\log f_{H_2O}$) models at 600°C and 810 bar and ore mineral saturation showing (a, d) the buffering mineralogy and (b–e) the fluid composition and metal ratios. The attention of readers is drawn to the fact that the solubility of the Au chloride and particularly the Au sulfide species reaches a maximum at moderately oxidizing conditions corresponding to those buffered by minerals commonly observed in porphyry systems (i.e., magnetite-anhydrite-rutile).

Isochoric cooling

Isochoric cooling models combine cooling and decompression and were performed at constant density, and the fluid was saturated with ore minerals. Vapor-like intermediate-density fluids (300 kg/m³) and lower-density (100 kg/m³) vapors were cooled from 600° to 180°C at constant density above the critical point of water and along the liquid-vapor curve below the critical point of water (Fig. 4h; App. 2). The models only follow the vapor path below the critical point of water and vapor-liquid partitioning is not considered. The isochoric cooling models were performed for concentrations of 0.1 and 5.5 wt % S at 500 ppm Cl and 2.0 wt % C. The low-S models were buffered by magnetite-anhydrite-rutile at high temperature and below 530°C by hematite-anhydrite-rutile, whereas the sulfide-saturated models were buffered by anhydrite-rutile-pyrite between 600° and 180°C. The R_H traces follow a similar path for both S contents as shown by the representative R_H trace for isochoric cooling models in Figure 5b (App. 1).

Copper, Mo, and Ag solubility decreased with decreasing temperature, whereas Au solubility reached a maximum of

95 ppb to 2.6 ppm between 330° and 510°C depending on the density and S content of the vapor (Fig. 10a–d). The Au solubility maximum is more pronounced in the low-S models at 500 ppm Cl, for which the dominant species is hydrated AuCl. At sulfide-saturated conditions, the AuS species is dominant for a Cl concentration of 500 ppm. At higher Cl content (>0.4 wt %; see Fig. 6e), the hydrated AuCl species would be dominant even at sulfide-saturated conditions. As expected from the Au solubility profiles, the Cu/Au ratios reached a minimum at ~300°C (Fig. 10e, f). At sulfide-saturated conditions, the Cu/Au ratio decreased continuously during isochoric cooling (Fig. 10g, h), and the Cu/Mo ratio exceeded the Cu/Au ratio. The effect of fluid density (i.e., the P-T pathway) on metal ratios in the sulfide-saturated model is much less pronounced than in the low-S models buffered by magnetite-anhydrite-rutile.

Mineral precipitation models

The deposition of ore minerals (electrum, acanthite, molybdenite, chalcopyrite, and bornite) during isochoric cooling of a vapor-like intermediate-density (300 kg/m³) fluid was evalu-

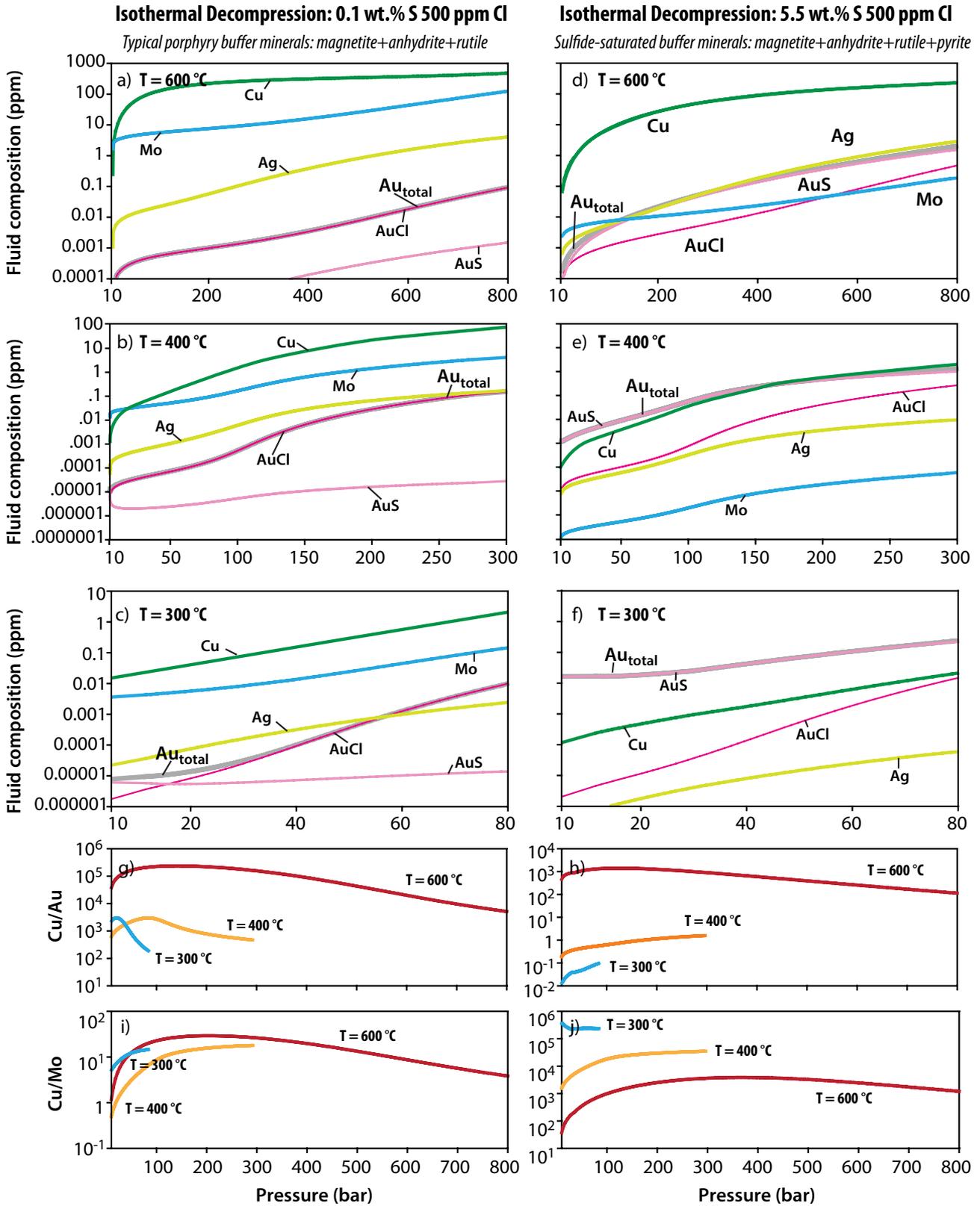


Fig. 9. Results of numerical simulations of metal solubility during isothermal decompression at 600°, 400°, and 300°C at varying S content (0.1 and 5.5 wt %) showing (a-f) metal solubility and (g-j) metal ratios of vapor-like fluids. The attention of readers is drawn to two features in these diagrams. Firstly, there is a strong decrease in the solubility of all the metals with isothermal decompression, and secondly, the path of metal solubility for the different fluid compositions changes markedly with temperature.

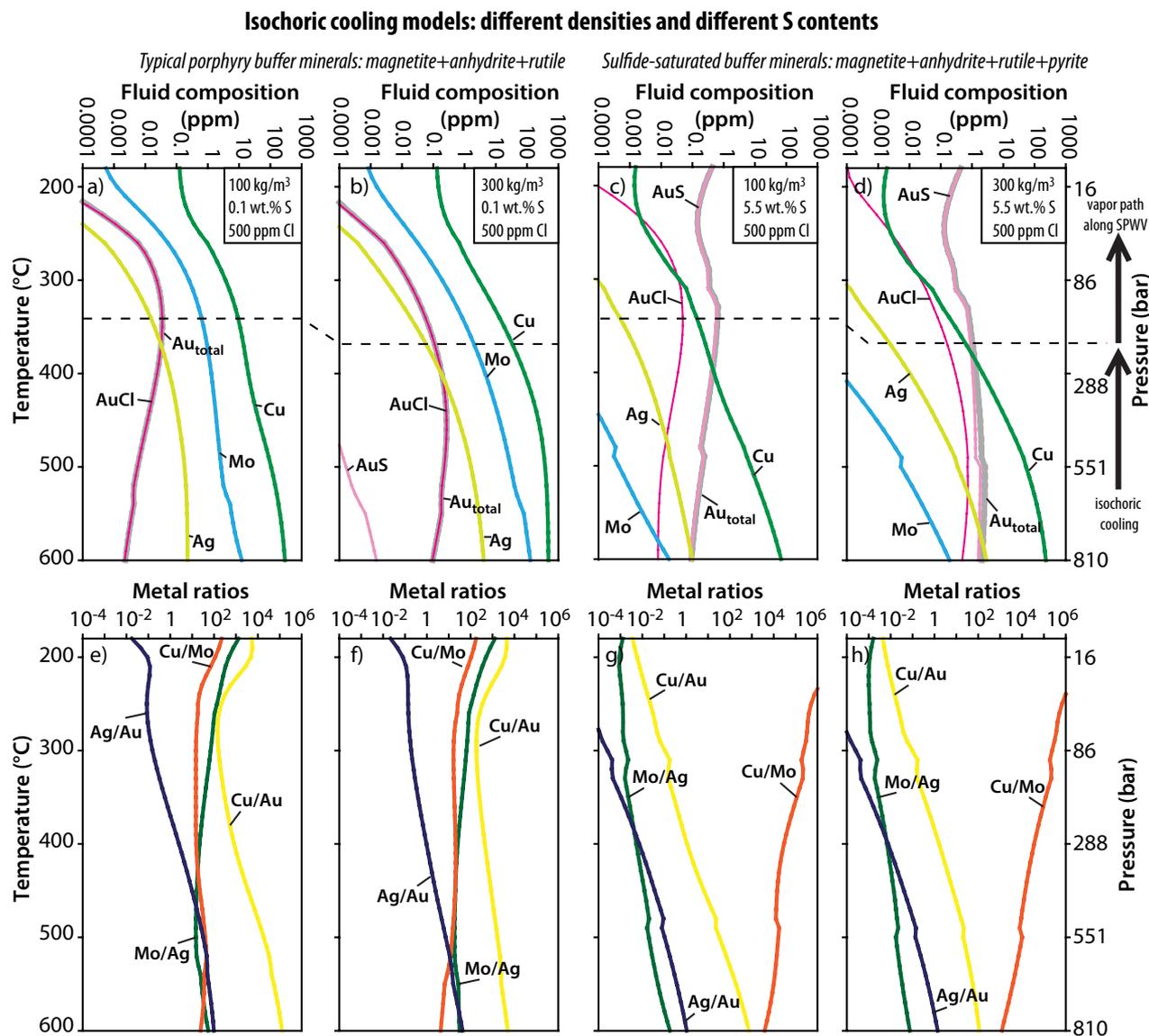


Fig. 10. Results of numerical simulations of metal solubility during isochoric cooling at a density of 100 and 300 kg/m³ (isochoric until phase separation and with further evolution along the saturation pressure water vapor curve, above dashed line). The models were generated for S concentrations of 0.1 and 5.5 wt.%. (a-d) Metal solubility as a function of temperature, with Au solubility maxima at ~330°C in the low-density fluid and at ~450° and ~510°C in the intermediate-density fluid. The solubility of Cu, Mo, and Ag decreases with decreasing temperature. (e-h) Metal ratios as a function of temperature. The trends for the 0.1 wt.% S and the 5.5 wt.% S models differ considerably. SPVV = saturation pressure water vapor curve.

ated for a range of redox conditions, HCl/ΣCl ratios, and S and Cl contents. The P-T path is that of the isochoric cooling model at 300 kg/m³. Initially, the fluids were undersaturated with respect to ore-forming minerals and then became saturated upon cooling and decompression, triggering ore deposition (Table 4). The metal ratios are based on the S, Cl, and redox titration models. The degree of initial ore mineral undersaturation was similar in all precipitation models, except for models presented in Figure 11g and h, in which the excess Cl was increased at constant metal content (that of Fig. 11f). The starting fluid compositions are summarized in Table 4 and are within the range of metal contents reported for fluid inclusions (Table 3). Fluid and mineral compositions for all mineral precipitation models are given in Appendix 1.

We tested a range of starting fluid compositions that fall within the compositional range of a typical porphyry ore fluid (Fig. 11a-c, e, f). The first set of models was performed for 500 ppm Cl and variable S content; the redox conditions were buffered by magnetite-anhydrite-rutile (Fig. 11a-c). These models are specifically designed to evaluate the competition for Cl and S ligands in Au complexation and the effect of S on electrom fineness and Cu/Au and Cu/Mo ratios. The R_H traces for these models vary depending on the S content in the fluid and starting redox buffering assemblage (Fig. 5b). The S-rich model follows a more reduced R_H pathway compared to the low-S model, constraining metal precipitation to higher P-T conditions. At low S content (0.5 wt.%; starting fluid 0.09 ppm Au), Mo precipitated first at ~570°C followed

by bornite and acanthite at 560° to 480°C, chalcopyrite at 510° to 430°C, and electrum at ~390°C ($X_{Au} = 0.73$ –0.69; Fig. 11a). At higher S content (1 wt %; starting fluid 0.14 ppm Au), the amount of precipitated molybdenite was about five times lower than in the low-S model, and the chalcopyrite and electrum zones moved to higher temperature (550°–450° and ~400°C; Fig. 11b). Slightly more electrum with a similar Au content ($X_{Au} = 0.73$ –0.69) precipitated in this model compared to the low-S model. At even higher S content (3

wt % S; 0.74 and 0.47 ppm Au in the starting fluids, respectively), the high-temperature fluid was either buffered by the assemblage anhydrite-magnetite-rutile ($R_H = -3.6$ to -4.1 , common in porphyry deposits) or a reduced assemblage of anhydrite-magnetite-ilmenite-pyrrhotite ($R_H = -2.6$ to -3.6 , representative reduced porphyry deposits). In these models, the amount of Au precipitated exceeded that of Mo, and the Cu/Au ratios were remarkably low (79 and 248, respectively). In the high-S model buffered by anhydrite-magnetite-rutile

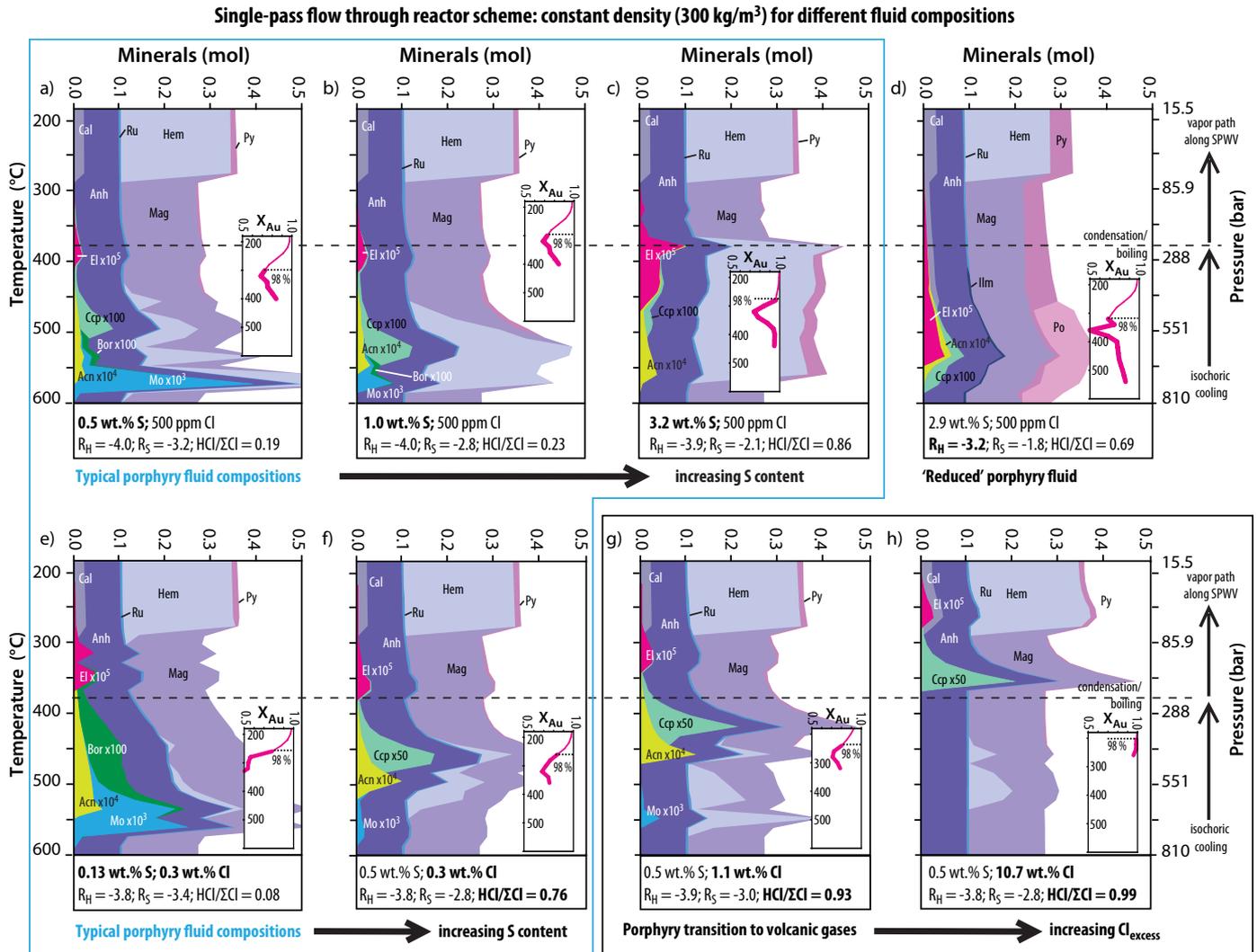


Fig. 11. A single-pass flow-through reactor scheme showing the amounts of ore minerals precipitated during isochoric cooling at a fluid density of 300 kg/m³ and various starting fluid compositions. Metal ratios in the starting fluids (a–f) are based on titration models, and the degree of undersaturation is similar for all models (Table 4). (a–c) Typical fluid compositions for a porphyry ore fluid with a relatively low Cl content (500 ppm) as a function of increasing S content (0.5, 1, and 3 wt % S). With increasing S content, the AuS species becomes more important, promoting Au transport. (d) The fluid is buffered by the reduced assemblage of magnetite-anhydrite-ilmenite-pyrrhotite at 3 wt % S. (e, f) A typical fluid composition for a porphyry ore fluid with a relatively high Cl content (3,000 ppm) and increasing S contents (0.1 and 0.5 wt %). Gold mobility is controlled by the AuCl species, and increasing the S content only has a moderate effect on Au transport. (g, h) The excess Cl content was increased to very high HCl/ΣCl ratios comparable to those in volcanic gases; however, the metal concentration was equal to that used in (f). The models show the sensitivity of metal mobility at a high degree of excess Cl, which promotes ore deposition at lower temperature. Insets show the Au content in electrum ($X_{Au} = \text{mole fraction of Au}$) and the point at which the cumulative precipitation of electrum reaches 98%. The buffer minerals are magnetite (Mag), hematite (Hem), anhydrite (Anh), rutile (Ru), ilmenite (Ilm), calcite (Cal), pyrite (Py), and pyrrhotite (Po). The proportions of the ore minerals are multiplied by a factor to better visualize the ore shells of molybdenite (Mo), acanthite (Acn), bornite (Bor), chalcopyrite (Ccp), and electrum (El). SPWV = saturation pressure water vapor curve.

($R_H = -3.8$), Ag and minor Mo deposited at high temperature ($\sim 560^\circ\text{C}$); the bulk of the chalcopyrite precipitated at 500° to 400°C (Fig. 11c). Electrum precipitated between 560° and 360°C , and its Au content decreased ($X_{\text{Au}} = 0.95\text{--}0.74$) with decreasing temperature and pressure. In the reduced high-S model ($R_H = -3.2$), Cu precipitation was dominated by chalcopyrite, which deposited at higher temperature ($580^\circ\text{--}460^\circ\text{C}$) than in the more oxidized high-S model, overlapping with Ag and Au mineralization (Fig. 11d). The Au content of the electrum was lower ($X_{\text{Au}} = 0.89\text{--}0.50$) and reached a minimum mole fraction of 0.5 at 360°C .

The second set of models was performed for 0.3 wt % Cl and two different S contents to establish a baseline for comparison with models at lower Cl content (Fig. 11e, f) and variable excess Cl, i.e., HCl/ Σ Cl ratio (Fig. 11g, h). The low-S model for 0.3 wt % Cl produced the highest proportion of precipitated Cu minerals, which was expected as the starting fluid contains 2,620 ppm Cu (Table 4; App. 1). Increasing the S content at 0.3 wt % Cl (the starting fluid contained 655 ppm Cu) has a similar effect on metal ratios and the distribution of ore shells to simulations with lower Cl content (the starting fluids contained 65–400 ppm Cu). It is noteworthy that the occurrence of molybdenite and bornite is restricted to the low-S models (Fig. 11e, f). In the high-Cl models, the precipitation of gold is controlled by the Cl complex, and thus increasing the S content has a minimal effect on the amount of electrum precipitated. Models for 1 and 10 wt % Cl (Fig. 11g, h) were performed for the same metal contents as in the model for 0.3 wt % Cl (i.e., 655 ppm Cu, 7 ppm Ag, 0.18 ppm Au, and 6 ppm Mo). Consequently, the HCl/ Σ Cl ratio, which represents the proportion of excess Cl to complexed Cl (0 = all Cl is complexed; 1 = all Cl is excess HCl), is higher in simulations with high Cl content. Generally, but not exclusively, volcanic gases and vapor inclusions have the highest HCl/ Σ Cl ratios (0.7–0.99), whereas high-T intermediate-density fluid inclusions have moderate ratios (0.3–0.7), and brines have the lowest ratios (0.03–0.3). For comparison, the HCl/ Σ Cl ratio was determined to vary between 0.07 and 0.68 in the aqueous phase of experiments involving equilibrium between a silicate melt and an aqueous fluid (Williams et al., 1997).

Lastly, the third set of models tests the sensitivity of ore mineral precipitation as a function of Au, Ag, and Cu undersaturation by increasing the Cl content from 0.3 wt % (Fig. 11f) to 1 and 10 wt % (Fig. 11g, h). At a Cl content of 1.1 wt % and a HCl/ Σ Cl ratio of 0.93, the Cu, Ag, and Au ore shells form at lower P-T conditions compared to the model for 0.3 wt % Cl and 0.76 HCl/ Σ Cl. For the same starting metal contents, the sequence of metal zoning did not change with increasing Cl content, i.e., the degree of Au, Ag, and Cu undersaturation. The molybdenum solubility (7 ppm in the starting fluid) is controlled by the $\text{MoO}_3(\text{H}_2\text{O})_y$ species; thus, it is not affected by increasing the amount of Cl in this model and formed its ore shell at similar P-T conditions. At an even higher Cl content of 10 wt % (0.99 HCl/ Σ Cl), the Cu and Au ore zones form below the critical point of water (Fig. 11h). At these conditions, the gaseous hydrated silver species (~ 7 ppm Ag) remain stable in the vapor-like fluid leading to the highest electrum fineness. The Mo content decreased to 0.09 ppm in the starting fluid because of the increased stability of solid molybdenum oxychloride, which limited the solubility of Mo.

Discussion

Comparison of the metal contents and ratios of simulated and natural fluids in porphyry deposits

To evaluate the importance of vapor-like fluids for porphyry ore formation, we compare the simulated metal solubility and metal ratios to metal contents measured in vapor-like and intermediate-density fluid inclusions (Fig. 4) and metal ratios of ores in porphyry deposits (Fig. 12). The simulated metal solubility and metal ratios change as a function of the fluid composition at 600°C and 810 bar, i.e., a density of 300 kg/m^3 (Table 5; Figs. 6–8), isothermal decompression (Fig. 9), and isochoric cooling (Fig. 10). We evaluated the metal solubility for R_H values ranging between -4.6 and -1.5 . Importantly, we consider simulations buffered by the assemblage magnetite-anhydrite-rutile to be representative of the deep barren stockwork zone in porphyry ore deposits (Fig. 1a; Macdonald and Arnold, 1994; Audétat et al., 2004; Reed et al., 2013) and simulations buffered by pyrite-anhydrite-rutile(-magnetite) to be representative of sulfide-saturated silicate melts in porphyry ore deposits (Halter et al., 2002, 2005; Wilkinson, 2013; Richards, 2014; Rottier et al., 2019).

At elevated Cl contents (>700 ppm) and high temperature, the solvated Cu species $\text{CuCl}(\text{HCl})(\text{H}_2\text{O})_y$ is dominant; at lower temperature ($<400^\circ\text{C}$) the $\text{CuCl}(\text{H}_2\text{O})_y$ species becomes dominant. The high-temperature species comprises two Cl molecules, resulting in a stronger positive correlation of Cu solubility with increasing Cl content compared to other species containing a single Cl atom, i.e., $\text{AuCl}(\text{H}_2\text{O})_y$ and $\text{AgCl}(\text{H}_2\text{O})_y$. The potential role of Cu-S species could not be evaluated, because the required thermodynamic data were not available. A recent in situ XAS and Raman spectroscopic study (Louvel et al., 2017) designed to investigate the effect of S on Cu transport in water vapor failed to detect the presence of Cu-S complexes at temperatures between 300° and 600°C . We therefore conclude that such species are not relevant for the simulated fluid compositions in this study.

The highest Cu solubility (7,533–8,817 ppm) was predicted for fluids in which the Cl content was highest (Fig. 6; Table 5). For comparison, in Reed et al. (2013) copper concentrations ranged from 10 to 6,000 ppm in simulations using the HKF model for liquid-like fluids assuming a starting fluid composition of 8 wt % S, 2 wt % Cl (~ 4 wt % NaCl equiv), and 3 wt % C. Copper concentrations in vapor-like and intermediate-density fluid inclusions range from 10 ppm to 3.3 wt %; however, the highest Cu values were shown to be affected by postentrapment Cu diffusion into quartz-hosted fluid inclusion (Lerchbaumer and Audétat, 2012). Subsequently, Cu was also measured in topaz- and garnet-hosted vapor inclusions yielding concentrations of 56 to 160 ppm (Seo and Heinrich, 2013). To constrain the Cu content in natural fluid inclusions to realistic values, we used P-T- C_{Cu} correlations and removed elevated Cu values that did not follow the systematic P-T trends (App. 1). Here, we suggest that a concentration range of 10 to 4,300 ppm Cu with a median concentration of 850 ppm is realistic for vapor-like porphyry fluids based on fluid inclusion data (Table 3). The redox titration models provide a comparable range of 163 to 2,785 ppm Cu for vapor-like fluids buffered by magnetite-anhydrite-rutile. In volcanic gas condensates, Cu contents range from 3 ppb to 60 ppm and have a

median content of 0.3 ppm, which makes Cu the most abundant metal compared to Au, Ag, and Mo in very low density vapors (Table 3). Copper solubility at the lowest pressure (~8 bar) from decompression models ranges from 0.07 to 2.5 ppm at 600°C, from 0.08 to 1.9 ppb at 400°C, and from 0.22 to 21 ppb at 300°C.

Silver is transported as $\text{AgCl}(\text{H}_2\text{O})_y$ in vapor-like fluids and is predicted to dissolve in concentrations up to 22 ppm for a Cl concentration of 1 wt %. This Ag solubility is an order of magnitude lower than that reported in Hurtig and Williams-Jones (2015) for the same Cl concentrations and reflects the strong competition for the chloride ion by Cu species, which were not considered in the earlier study. By comparison, vapor-like and intermediate-density fluid inclusions have been reported to contain up to 190 ppm Ag with a median of 23 ppm (Table 3; Fig. 4g). The lower Ag contents predicted by our current model could reflect the presence of a high-temperature gaseous AgS species, as suggested by the experiments of Yin and Zajacz (2018), which showed that the Ag concentration in vapor-like hydrothermal fluids increases with increasing H_2S concentration. In the absence of thermodynamic data for gaseous solvated AgS species, however, we were unable to evaluate the potential contribution of AgS species to the transport of Ag in vapor-like fluids. Decompression models at 600°C predict 0.7 to 3.5 ppb Ag at the lowest pressure (~8 bar); at lower temperature and ~8 bar, Ag concentrations are generally below 1 ppb. For comparison, the Ag contents of volcanic gases are 3 to 14 ppb; however, only 12 of the 136 measurements in our compilation showed detectable Ag contents, indicating that Ag contents are likely lower than the limit of detection.

Molybdenum, which dissolves as $\text{MoO}_3(\text{H}_2\text{O})_y$, had its highest solubility of 230 ppm Mo in oxidizing low-S (0.1 wt %) fluids buffered by magnetite-anhydrite-rutile. Molybdenum solubility correlates positively with increasing f_{O_2} (i.e., degreasing R_{H}) and correlates negatively with S because of the formation of molybdenite (MoS_2), the main Mo ore-forming mineral. Vapor-like and intermediate-density fluid inclusions in porphyry ore deposits have comparable Mo contents of 1.2 to 290 ppm with a median of 50 ppm (Fig. 4a, b). Some systems, notably Rito del Medio (Zajacz et al., 2008; Audéat, 2019) and Cave Peak (Audéat, 2010), report consistently higher Mo concentrations than those predicted (80–230 ppm) for simulations at 0.1 wt % S buffered by magnetite-anhy-

drite-rutile. This could be because NaCl-bearing fluid inclusions in these deposits are of higher density (~350–500 kg/m^3) than the density considered in our models (300 kg/m^3). These higher-density fluids also have a higher salinity, which could promote the formation of molybdenum oxychloride species (Rempel et al., 2008; Ulrich and Mavrogenes, 2008; Borg et al., 2012) or $\text{H}_{(2-x)}\text{Na}_x\text{MoO}_4$ species (Cao, 1989; Kudrin, 1989; Shang et al., 2020) that were not considered in our simulations. Several studies have evaluated the solubility of MoS_2 in hydrothermal liquid-like fluids; however, with the exception of Zhang et al. (2012), these studies attributed Mo transport to molybdate or molybdenum oxychloride (Wood et al., 1987; Kudrin, 1989) or HNaMoO_4 species (Shang et al., 2020). Im-

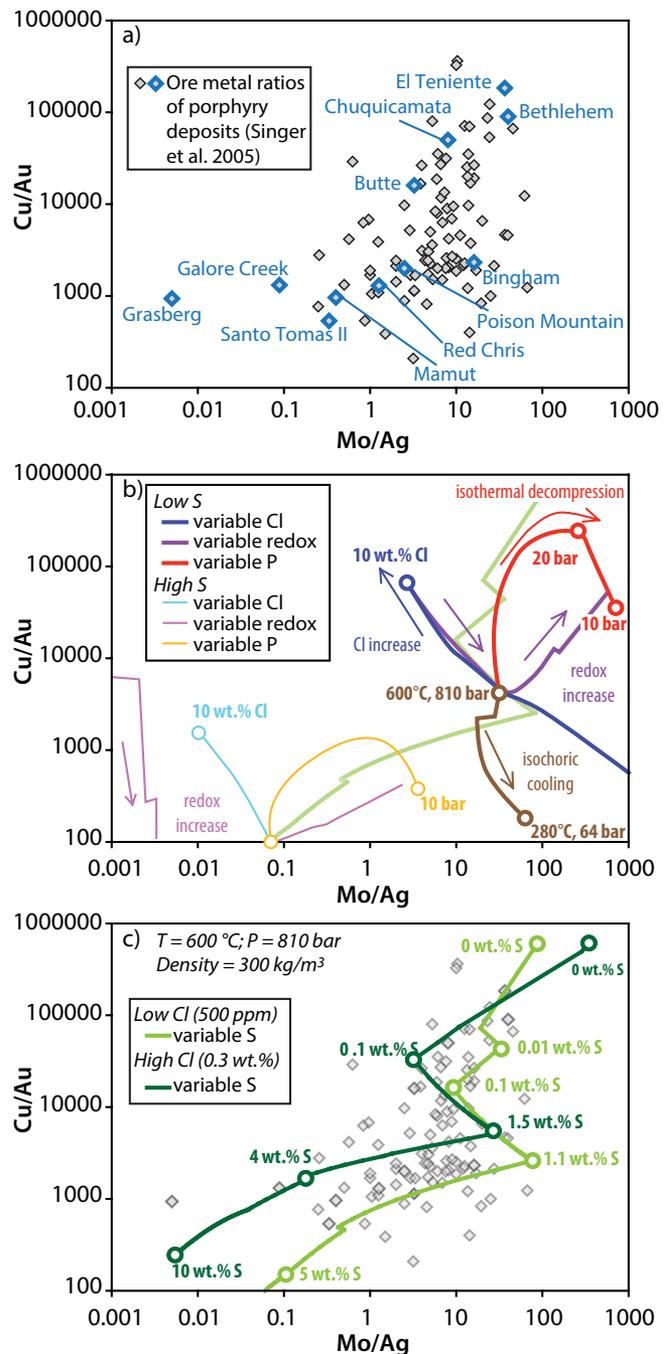


Fig. 12. The Cu/Au and Mo/Ag ratios of (a) porphyry ore deposits (Singer et al., 2005) compared to (b, c) the simulated metal ratio evolutionary paths from the equilibrium models discussed in the sections “Effect of fluid composition on ore metal solubility and metal ratios” and “Isothermal decompression.” The simulated metal ratios are determined by metal solubility and represent the capacity of a hydrothermal vapor-like fluid to transport and precipitate metals in a porphyry setting. (b) Metal ratio evolutionary paths from Cl and redox titration models, isothermal decompression, and isochoric cooling solubility models do not reproduce the general trends of porphyry ore deposits. (c) Metal ratio evolutionary metal paths from equilibrium models for variable S content (0–10 wt %), 500 ppm Cl, and 0.3 wt % Cl. At low S content (0–1 wt %), the data follow a vertical trend characterized by decreasing Cu/Au ratios with increasing S content, whereas at elevated S content (1–10 wt %) there is a horizontal trend in which the Mo/Ag ratio decreases with increasing S content. This indicates that the composition of the ore fluid imposes an important control on the ore metal ratios and metal enrichment in porphyry systems.

portantly, Mo shows a strong negative correlation with S content in the experiments of Zhang et al. (2012), and contrary to their interpretation the occurrence of Mo-S complexes is unlikely and not predicted by the hard-soft acid-base concept (Pearson, 1963), because Mo(IV) qualifies as a hard metal, which would not easily bond with soft ligands such as reduced sulfur. In decompression models, Mo contents range from 4 ppb to 2.5 ppm with increasing temperature (300°–600°C) at the lowest pressure (~8 bar) and low S contents and decrease to below 2.4 ppb below 600°C and high S content (5.5 wt %). In volcanic gases, the Mo content ranges between 2 ppb and 2.8 ppm Mo (Table 3), which is comparable to the values predicted using the hydration models.

Gold solubility is controlled by hydrated AuCl ($\text{AuCl}(\text{H}_2\text{O})_y$) and solvated AuS species ($\text{AuS}(\text{H}_2\text{S})_{x-1}(\text{H}_2\text{O})_y$) and thus exhibits a more complex behavior than Cu, Ag, or Mo (Figs. 6–8). The highest Au solubility was predicted for models simulated at the highest S content of 10 wt %. The Au concentrations in these models were 7.6 ppm for a Cl concentration of 500 ppm and 8.2 ppm for a Cl concentration of 0.3 wt %. Gold solubility increased with increasing Cl and S concentrations and reached a maximum at intermediate redox conditions; the latter is more pronounced for AuS than AuCl. The modeled Au concentrations are comparable to concentrations of 0.05 to 10 ppm Au measured in vapor-like and intermediate-density fluid inclusions (Table 3; Fig. 4e, f). Most vapor-like and intermediate-density fluid inclusions have Au contents below the limit of detection: note that the compilation consists of only 16 data points. Therefore, accurately predicting Au contents in porphyry ore fluids is challenging, and simulations presented in this study provide a new opportunity to evaluate reasonable Au contents for vapor-like fluids. Numerical values for simulated Au solubility are listed in Table 5 and Appendix 1 for a wide range of conditions. In volcanic gases Au contents range from 7 ppt to 5 ppb (Table 3; Fig. 4e, f). In comparison, simulated Au solubilities predicted at 8 bar in decompression models are 9 to 73 ppt in the low-S models and 0.2 to 16 ppb in the sulfide-saturated models. The highest value of 16 ppb Au was predicted for a fluid composed of 4.8 wt % S, 2 wt % C, and 500 ppm Cl at 300°C; at these conditions the AuS species dominates.

Fluid evolution pathways: Metal mobility and precipitation

Numerical simulations of metal solubility in vapor-like fluids provide a means for evaluating the effects of pressure, temperature, and composition on metal solubility and the formation of ore shells in porphyry deposits. Ore mineral precipitation in porphyry deposits is commonly zoned with a high-temperature Mo shell partially overlapped by a telescoped Cu shell and a narrow shallow Au shell (Fig. 1a; Lowell and Guilbert, 1970; Dilles, 1987; Landtwing et al., 2005; Rusk et al., 2008; Gruen et al., 2010). However, it is also common that several events of mineralizing fluid produce overlapping ore shells not only in space but also in time (Seedorff and Einaudi, 2004; Gruen et al., 2010).

In Figure 11, we present simulated ore precipitation models that illustrate a single pulse of fluid during isochoric cooling at a density of 300 kg/m³ (see “Isochoric cooling” section). The Cu/Au (~4,300) and Cu/Mo ratios (~6) predicted by the model with the lowest S content (0.5 wt %) at 500 ppm Cl are

similar to the metal ratios observed in porphyry deposits such as Bingham (Singer et al., 2005). Obviously, the timing of ore formation and subsequent mineralizing pulses are much more complex in natural systems than in the simplified models presented here. A somewhat lower Cu/Au ratio and higher Cu/Mo ratio is predicted by the model for 1 wt % S, namely ~2,800 and ~30, respectively; these ratios are comparable to those for the Boneng Lobo and Nevados del Famatina porphyry deposits (Singer et al., 2005). In contrast, the predicted Cu/Au and the Cu/Mo ratios for the highest S content (3 wt %), are ~90 and ~300 at the redox conditions commonly interpreted for porphyry deposits and ~300 and ~8,200 for the subset of reduced porphyry deposits (Rowins, 2000; Tarkian et al., 2003), respectively. These ratios are also similar to those observed, for example, in the Dizon and Santo Thomas II porphyry deposits (Singer et al., 2005). These two deposits are not part of the reduced porphyry subclass as they do not contain pyrrhotite and/or ilmenite (Imai, 2001, 2005). Instead, the presence of high-temperature iron and rounded sulfide inclusions (Imai, 2001, 2005) indicate sulfide-saturated silicate melts in these deposits. As pointed out in the S titration models, the observed Cu/Au and Cu/Mo ratios also depend on the S content of the vapor-like fluid and are indicative of sulfide-saturated systems (>4.8 wt % S). At high Cl and low S contents (0.3 wt % Cl, 0.1 wt % S), the Cu/Au increases to ~16,600 and the Cu/Mo ratio is ~30. Increasing the S content to 0.5 wt % in the high-Cl model decreases the Cu/Au ratio to ~3,700 and increases the Cu/Mo ratio to 104, showing that S strongly affects metal ratios also at higher Cl contents. Increasing the HCl/ΣCl ratio does not affect the Cu/Au and Cu/Mo ratios, because the metal contents were kept constant at the same level as in the models presented in Figure 11f. However, at the highest Cl content of 10 wt % solid $\text{MoO}_2\text{Cl}_{2(s)}$ starts buffering the Mo content at high T and thus the Cu/Mo ratio increases to ~7,400. This indicates that Au-rich porphyry deposits are favored at reduced redox conditions and high S content and that the interplay between the S content and redox conditions is an important control on the Cu/Au and Cu/Mo ratios in porphyry ore fluids (Fig. 11a-f). In addition to the compositional controls changing, the P-T pathway of the fluid will also affect the shape and distribution of the ore shells. An important conclusion that can be drawn from the numerical precipitation models (Fig. 11) is that the locations and extent of overlap of the Cu, Mo, Au, and Ag ore shells vary with the major fluid chemistry (i.e., S, Cl, and redox condition) for similar degrees of ore mineral undersaturation. Compositional parameters (S, Cl content, redox conditions) exercise a particularly important control on metal ratios and the capacity of magmatic fluids to transport metals. Thus, magma evolution during cooling and crystallization and continued fluid exsolution (Giggenbach, 1996; Webster, 1997; Webster et al., 2009; Webster and Botcharnikov, 2011) may result in variable metal solubility and metal ratios in vapor-like fluids throughout the lifetime of magmatic-hydrothermal systems, not captured by the simplified simulations presented in this study.

The depth of fluid exsolution and fluid pressure fluctuations within magmatic-hydrothermal plumes are important features that need to be considered in order to fully understand the metal zoning. Numerical simulations of physical processes in magmatic-hydrothermal plumes indicate that they are self-

organizing systems, establishing themselves above the magmatic heat source with a stable temperature front and fluctuations between hydrostatic and lithostatic pressure regimes (Weis et al., 2012, 2014). Thus, depressurization events occur frequently and consequently have been identified in detailed studies investigating vein distribution and vein density in stockwork zones (Gruen et al., 2010). As the stability of hydrated gaseous metal species is highly dependent on pressure and temperature, understanding their behavior in evolving magmatic-hydrothermal systems is a prerequisite for predicting the formation of ore shells and the metal endowment of porphyry deposits. The isothermal decompression models at 600°, 400°, and 300°C show that the solubility of Mo, Ag, and Au is strongly dependent on pressure at high temperature (600°C) and that this solubility decreases by about three to four orders of magnitude as pressure decreases from 800 to 10 bar. In contrast, the Cu solubility remains constant for a wide range of pressure (800–100 bar) but decreases by about two orders of magnitude below ~100 bar (100–10 bar). The behavior of hydrated Cu, Au, Ag, and Mo species with pressure depends on the number of water molecules in the hydrated species and their stability at elevated temperature; species with high hydration numbers are more sensitive to pressure changes. In natural systems, the concentration of Mo correlates strongly with pressure (Fig. 4b), as is the case for Cu concentrations below ~4,300 ppm (Fig. 4d). In contrast, Au concentrations do not display a clear positive correlation with pressure and may also reach a solubility maximum (Fig. 4f). The higher metal concentrations of fluids entrapped at elevated pressures (100–1,600 bar) compared to those of volcanic gases at atmospheric pressure (~1 bar) are predicted by pressure-dependent simulations at high temperature (600°C; Fig. 9a, b). At lower temperature (400° and 300°C), the concentrations of all the metals considered in this study decreased by two to three orders of magnitude as pressure decreased from 300 to 80 bar and then to 10 bar, respectively (Fig. 9b, e). In the sulfide-saturated model, the Au solubility governed by the AuS species shows the least dependence on pressure and only decreased by about one order of magnitude as pressure decreased from 80 to 10 bar at 300°C, thereby demonstrating the mobility of Au in S-rich vapors at low pressure and temperature.

Comparing results from isothermal decompression and isochoric cooling simulations allows for independent analysis of the effects of pressure (i.e., density) at constant T and of temperature at constant density on metal ratios in porphyry ore fluids. The isothermal decompression models show that the Cu/Au ratio varies little with pressure, and thus depth, at 600°C (Fig. 9a, b). By contrast, in the isochoric cooling models, gold solubility reaches a maximum between 340° and 510°C, depending on the fluid density and S content (Fig. 10). These models show that there is a considerable potential for Au remobilization during the cooling of magmatic-hydrothermal systems. In the sulfide-saturated simulations, the Au solubility even exceeds that of Cu at low Cl content and a temperature below 300°C. This could be potentially important for the formation of anomalous Au-rich porphyry deposits at very shallow depth, such as in the Maricunga belt (Vila and Sillitoe, 1991; Muntean and Einaudi, 2000, 2001), and transport of Au to epithermal environments (Heinrich et al., 2004).

Simulated metal ratio trends compared to ore metal ratios in porphyry deposits

The predictive power of the numerical simulations and their applicability to natural systems is illustrated in Figure 12. In this figure, we compare the simulated metal ratio evolution paths for titration (“Effect of fluid composition on ore metal solubility and metal ratios” section), isothermal decompression (see “Isothermal decompression” section), and isochoric cooling (see “Isochoric cooling” section) to metal ratios trends for porphyry deposits (Singer et al., 2005; Fig. 12a). The simulated metal ratios are controlled by ore mineral solubility and thus are considered representative of the relative capacity of the magmatic-hydrothermal plume to transport and precipitate metals in a porphyry setting. These models do not consider potential vapor-melt metal partitioning or the degree of undersaturation of ore-forming constituents in magmatic vapors, which have been shown to be important in controlling metal ratios of porphyry ore fluids (Richards, 2013; Wilkinson, 2013).

The trends for Cl and redox titration, isothermal decompression, and isochoric cooling (Fig. 12b) fail to predict the general trend of ore metal ratios in porphyry deposits, which is vertical at high Mo/Ag ratios with decreasing Cu/Au and horizontal at low Cu/Au ratios with decreasing Mo/Ag ratios (Fig. 12a). Trends for isothermal decompression show an increase in Cu/Au ratios at 600°C with decreasing pressure between 810 and 20 bar, whereas trends for isochoric cooling show decreasing Cu/Au ratios between 600°C and 810 bar and 280°C and 64 bar. The Cu/Au ratio in porphyry ore deposits has been shown to decrease with decreasing pressure (Murakami et al., 2010). In this study, we show that isothermal decompression at high T is not responsible for decreasing Cu/Au ratios. However, the Au solubility maximum during isochoric cooling exercises an important control on the Cu/Au ratio and promotes Au mobility at lower temperature and pressure, i.e., in shallow porphyry systems. The behavior of Cu and Au in vapor-like fluids is governed by the interaction of gaseous metal molecules with water molecules (see the section “A Hydration Model for Predicting Gaseous Metallic Speciation”).

It is quite remarkable that the predicted metal ratio evolutionary paths for S titration models broadly follow the ore metal ratios of porphyry deposits along a vertical trend between 0 and 1 wt % S and a horizontal trend between 1 and 10 wt % S (Fig. 12c). The kinks in the vertical part of the model represent variations in the buffering mineral assemblages controlling the redox potential and metal solubility, which mainly affects the Mo/Ag ratio (see the section “Effect of fluid composition on ore metal solubility and metal ratios”). Increasing the Cl concentration displaces the modeled S simulation path to a higher Cu/Au ratio. The S titration models might thus provide an explanation for why some of these deposits (e.g., Bethlehem, Chuquicamata) have high Cu/Au and Mo/Ag ratios, whereas others (e.g., Grasberg, Galore Creek) have relatively low Cu/Au and Mo/Ag ratios.

Ultimately, the composition of the exsolved magmatic fluid depends on the composition of the magma and the aqueous fluid-melt element partition coefficients. However, the relative solubility of metals in vapor-like fluids controls their transport and precipitation and thus the formation of ore shells. For example, the high-S models (>4.8 wt %) are repre-

sentative of sulfide-saturated conditions, at which H_2O and H_2S are stable. The presence of magmatic sulfides has been linked to variable sequestration of Cu and Au affecting the Cu/Au ratio of silicate melts during magma evolution, and under conditions where H_2O acts as a temporary sink for Au (releasing it into the ore-forming fluid upon fluid exsolution). It has been argued that this favors the formation of Au-rich porphyry deposits (Halter et al., 2002, 2005; Nadeau et al., 2010, 2016; Wilkinson, 2013; Richards, 2014; Rottier et al., 2019). By extension, the high S content of vapor-like fluids is likely the result of a higher S content in the magma or even the presence of an immiscible sulfide melt. Thus, it is reasonable to argue that the positive feedback from an elevated S content in the magma and the vapor-like fluid on the Cu/Au ratio results in the observed trends seen in Figure 12.

Finally, we emphasize that these models need to be refined to accurately predict the metal endowment/ratios for individual deposits by also considering the effects of T, P, and redox conditions as well as the Cl and S contents of the fluid and potential undersaturation by considering vapor-melt metal partitioning data and the potential presence of magmatic sulfides.

Limitations of the numerical simulations

There are several limitations to the numerical simulation approach employed in this study. Firstly, all gases, except $\text{H}_2\text{O}_{(g)}$, are treated as ideal. This limitation is a result of introducing thermodynamic properties of gaseous metal species in the form of temperature-dependent logarithmic equilibrium constants of hydration reactions. The fugacity of major gas species is calculated manually after mineral-gas equilibrium calculations have been performed using fugacity coefficients where necessary. Gaseous metal species are linked to water fugacity, i.e., the nonideal behavior of water, by employing a set of hydration reactions for implementation of thermodynamic properties into GEM-Selektor (App. 2). Thus, simulations had to be performed at water fugacity and not at total pressure for correct consideration of the experimentally fitted thermodynamic properties of gaseous metal species (see App. 2 for further detail). Partial pressures of major gases, such as SO_2 , H_2S , CO_2 , and HCl , do not exceed ~5 mol % and are less than 2 mol % in most simulations; their effect on the total pressure/water fugacity was assumed to be negligible. Secondly, the vapor density is limited to that of pure water, whereas magmatic-hydrothermal fluids are commonly NaCl bearing with a higher density than that of pure water. This limitation restricted the P-T path to the water vapor saturation point and the critical density of pure water. Intermediate-density fluids in the NaCl- H_2O system displaying critical behavior (homogenization by meniscus disappearance) commonly have a higher density than can be modeled in the pure water system, which is limited to 322 kg/m³.

Finally, below the critical point of water the simulations in this study only follow the vapor path, and vapor-liquid metal partitioning was not considered. The potential contribution of liquids (i.e., hypersaline brines) to the metal budget was neglected. Therefore, simulated metal solubility below the critical point of water represents the minimum metal mobility, and ore mineral precipitation is maximized. In porphyry ore-forming systems, however, hypersaline brines are typically present and commonly have high metal concentrations

(Lerchbaumer and Audétat, 2012; Seo et al., 2012). They could therefore play an important and even dominant role in metal transport after phase separation. Whether hypersaline brines contribute significantly to the metal budget depends on the mole fraction of vapor to liquid in the two-phase mixture (Fig. 1b), the relative mobility of the hypersaline liquid in the magmatic-hydrothermal plume (Weis et al., 2012; Weis, 2015; Afanasyev et al., 2018), and the efficiency of cooling and ore mineral precipitation from the liquid. As magmatic-hydrothermal plumes vary considerably in their P-T paths (Heinrich, 2005; Williams-Jones and Heinrich, 2005; Driesner and Heinrich, 2007; Audétat, 2019), it follows that there are systems that will be liquid-dominated and others of the type represented by our simulations, which will be vapor dominated.

Conclusions

Numerical simulations based on metal solubility experiments in vapors provide important insights into the participation of compressible fluids in the formation of magmatic-hydrothermal Cu-Au-Mo-(Ag) deposits. These simulations represent an independent test of the validity of the hypothesis that vapor-like magmatic-hydrothermal fluids carry sufficient Au, Cu, Ag, and Mo to be viable ore-forming fluids. This idea has recently been challenged through experimental studies showing that Cu and Au may diffuse in and out of quartz-hosted fluid inclusions, thus questioning the reliability of LA-ICP-MS data obtained from natural vapor-rich fluid inclusions (Lerchbaumer and Audétat, 2012).

A key finding of this study is that metal mobility in vapor-like fluids depends strongly on pressure and temperature. As a result, vapor-like fluids can easily deposit large amounts of metals without undergoing phase separation upon decompression thereby connecting low metal contents found in volcanic gases at the surface to orders of magnitude higher metal contents found in fluid inclusions at depth. This observation is critical when considering the efficiency of mineral precipitation from vapor-like fluids compared to that of brines, where cooling and/or fluid-rock reaction would be the driving mechanisms for mineral precipitation. The S content of the fluid was found to exert an important control on metal solubility and metal ratios in vapor-like fluids, which in turn may control the metal endowments and metal ratios in porphyry ore deposits. The major element composition of the vapor-like fluids (SO_2 , H_2S , HCl , CO_2) provides the link between aqueous fluids and silicate melts; thus, the observed trends may be extended to include melt-vapor processes.

The fact that gold solubility reaches a maximum at 340° to 510°C, whereas this is not the case for the other gaseous metallic species considered in this study, argues strongly for the hypothesis that Au is preferentially remobilized to shallow, cooler environments such as those of epithermal systems (Gammons and Williams-Jones, 1997; Heinrich et al., 2004; Williams-Jones and Heinrich, 2005; Henley and Berger, 2011; Hurlig and Williams-Jones, 2015). The Au solubility maximum was also identified as a likely key control on decreasing Cu/Au ratios in shallow porphyry deposits (Murakami et al., 2010).

Our numerical simulations have shown that the P-T distribution of ore shells in porphyry ore deposits is controlled by the fluid composition and the P-T paths of the cooling ascending fluids. Recognition of these systematic controls on metal

ratios and the formation of ore shells is a discovery that could lead to new strategies for the exploration of porphyry and related ore deposits.

Acknowledgments

Alexander Gysi and Dmitrii Kulik are thanked for their help in implementing experimental data to the GEM-Selektor code package and discussion of numerical simulations. We are grateful for the constructive comments by Associate Editor Andreas Audétat and reviewers Thomas Wagner and Christoph Heinrich, which helped improve this manuscript. The funding for this research was provided in part by a Natural Sciences and Engineering Research Council (NSERC) Discovery grant to AEW-J.

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