Can Economic Porphyry Copper Mineralization be Generated by a Typical Calc-Alkaline Melt?

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Numerical simulation of chlorine and copper partitioning between a crystallizing melt and exsolving aqueous fluids indicates that "typical" calc-alkaline magmas contain sufficient copper, chlorine, and water to produce economic porphyry copper mineralization. Neither an elevated copper content in the magma nor an additional large volume of magma are required to provide metals or volatiles. The most important variables that determine the volume of melt necessary to produce sufficient copper are the degree of compatible behavior displayed by copper, the ratio of initial water in the melt to the water saturation level, and the initial chlorine/water ratio of the melt. The absolute values for initial water in the melt and water content at saturation are relatively unimportant in determining the required melt volume. The bulk salinity of the exsolved fluid may vary from <2.0 wt. % NaCl to saturation levels (84 wt. % NaCl at 700°C) indicating that boiling is not necessary to produce high salinity brines. At appropriate P-T-XNaCl conditions the magmatic aqueous fluid separates into a saline liquid, which transports most of the copper, and a low-salinity vapor. The salinities of the two immiscible phases are governed by the P-T conditions, while the bulk fluid salinity determines the mass fractions of liquid and vapor formed. Pressure quenching causes rapid crystallization of the splittic groundmass in porphyritic rocks associated with copper mineralization and significantly reduces the amount of chlorine and copper partitioning to the aqueous fluid. This results in abrupt and possibly large reductions in fluid salinity and causes copper to become concentrated in the melt. As copper is transported from the melt by the earliest exsolving fluids in deep (2.0 kbar) systems and by late exsolving fluids in shallow (0.5 kbar) systems, the relative timing of pressure quenching/aplite formation and fluid transport of copper from the melt can vary significantly in systems produced under different confining pressures. Model results incorporating petrologic constraints determined for Yerington, Nevada, are in good agreement with observed mineralization.

INTRODUCTION

Porphyry copper mineralization is associated with magmatic aqueous fluids that exsolve from crystallizing silicic melts during the transition from a magmatic to a high temperature, hydrothermal system [Burnham, 1979]. The magmatic/hydrothermal transition occurs in response to decreasing pressure (first boiling) and crystallization (second boiling) as the magma approaches the surface. These factors reduce the capacity of the magma to contain dissolved water and an aqueous fluid exsolves. Repeated episodes of fluid expulsion produce the extensive fracture systems characteristic of productive porphyry copper deposits [Burnham, 1979; Heidrick and Titley, 1982].

The source of copper in porphyry systems continues to be controversial. A variety of models have been proposed, ranging from the orthomagmatic model [Gustafson and Hunt, 1975; Burnham, 1979; Dilles, 1987] which proposes that metals and fluids have a magmatic source, to alternative models [e.g., Norton, 1982] which suggest that metals are leached from wall rocks by circulating non-magmatic fluids and are later precipitated peripheral to the intrusive. The orthomagmatic model suggests that copper is removed from the melt by chlorine-rich aqueous fluids that exsolve under reduced pressure conditions [Burnham, 1979]. At appropriate P-T-XNaCl conditions the exsolved aqueous fluid separates into a high salinity liquid and a low-salinity vapor [Sourirajan and Kennedy, 1962; Khaibullin and Borisov, 1965; Bodnar et al., 1985]. Fluid inclusion evidence [Bodnar and Beane, 1980] and theoretical models for porphyry copper genesis [Henley and McNabb, 1978; Bodnar, 1982] indicate that copper is similarly partitioned between the immiscible aqueous liquid and vapor phases.

Previous models have quantified the mass transfer of copper and chlorine from a silicate melt into exsolving aqueous fluids in deep (2.0 kbar) [Candela, 1989; Cline and Bodnar, 1989] and shallow (0.5 kbar) [Candela, 1989] systems. These models incorporate experimental data which describe partitioning of chlorine [Kilinc and Burnham, 1972; Shinozaki et al., 1984] and copper [Candela and Holland, 1984] between aqueous fluid and melt. Melts under high confining pressures (2 kbar) are capable of dissolving a large amount of water which is exsolved during crystallization [Burnham, 1975]. In these deep or high pressure systems exsolution of a large fraction of water coupled with a high chlorine partition coefficient (aqueous fluid/melt) [Kilinc and Burnham, 1972; Shinozaki et al., 1984, 1989] enables the earliest aqueous fluids which exsolve to deplete the melt of most of the chlorine and chlorine-complexed copper [Candela, 1989; Cline and Bodnar, 1989]. Magmas in shallow systems contain less dissolved water and experimental data [Shinozaki et al., 1984, 1989] indicate the proportion of chlorine partitioning to the aqueous fluid is smaller than at higher pressures. As a result of exsolution of less water and smaller chlorine and copper partition coefficients in shallow systems, these elements become concentrated in the melt as it crystallizes [Candela, 1986, 1989]. Crystallization of the
In this study the physical state of the magmatic aqueous phase exsolved from a typical calc-alkaline magma is considered and optimum conditions for formation of a porphyry copper deposit, assuming an orthomagmatic model, are described. Three examples that simulate intrusion at deep, intermediate, and shallow depths are evaluated and the volume of melt necessary to produce a porphyry copper deposit as initial water and Cl/H2O vary is determined. Parameters incorporated from literature include the solubility of water in a magma, and the partitioning of chlorine and copper between the melt and crystallizing phases prior to water saturation, and between aqueous fluid, melt, and crystallizing phases following water saturation. Water loss to crystallizing hydrous phases is considered and both compatible and incompatible copper behavior prior to water saturation are evaluated. The effect of varying the initial melt water content and Cl/H2O ratio on chlorine and copper partitioning and fluid immiscibility are also determined. Copper precipitation from the liquid and vapor phases at reduced P-T conditions is calculated and the volume of melt necessary to produce a "typical" porphyry copper deposit is determined. Results indicate that average or typical calc-alkaline melts are capable of producing economic porphyry copper deposits. Elevated water, chlorine, and copper contents in the melt are not necessary.

A detailed petrologic study of the Yerington, Nevada, porphyry copper system [Dilles, 1987] has provided important petrologic constraints for an intermediate level (~4.6 km, 1.1 kbar) mineralized system. These constraints are incorporated in order to test the capability of the model to predict mineralization in an economic porphyry system.

THE MODEL

The solubility of water in siliceous melts as a function of pressure has been described by Burnham [1975, 1979]. These data have been regressed to give

$$X_{\text{H}_2\text{O}}^m = -0.11069 + 111.84P - 153.53P^2 + 123.82P^3 - 50.54P^4 + 8.0666P^5$$

(1)

where $X_{\text{H}_2\text{O}}^m$ is the mole percent water soluble in a melt and $P$ is pressure (kbar). This value is converted to wt.% by assuming a rock mass of 275 g/mol [Burnham and Ohimoto, 1980, Figure 2].

A crystallizing melt begins to exsolve water when the water dissolved within the melt is concentrated to the saturation level. The mass of water exsolved from a crystallized melt equals the mass of water dissolved in the saturated melt minus the amount incorporated by crystallizing hydrous phases. A typical porphyritic rock associated with copper mineralization has a granodiorite to quartz monzonite composition [Creasy, 1966] and contains an average of 8.5 wt.% hornblende and 12.5 wt.% biotite [Washington and Adams, 1951]. These phases typically contain 1.75 wt.% and 4.3 wt.% water, respectively [Thompson, 1988]. According to experimental data at 2 kbar [Naney, 1983] hornblende does not crystallize from melts which become saturated with less than 4 wt.% water ($M_{\text{H}_2\text{O}}^m < 4$ wt.%). Calculations incorporating these constraints indicate that for those melts which become saturated with less than 4 wt.% water, the water fraction incorporated by hydrous minerals (biotite) constitutes approximately 0.37 wt.% of the melt. In those melts which become saturated with a water content greater than 4 wt.%, water constituting approximately 0.58 wt.% of the melt is incorporated into biotite and hornblende. In order to determine maximum water loss to hydrous minerals in a porphyry-type system, the amount of water lost to rocks containing 25 wt.% biotite, water saturation ($M_{\text{H}_2\text{O}}^m < 4$ wt.%), and 25 wt.% biotite plus 15 wt.% hornblende, water saturation ($M_{\text{H}_2\text{O}}^m > 4$ wt.% was calculated. The amount of water incorporated by hydrous minerals in these two systems would be 1.08 wt.% and 1.34 wt.% respectively.

Chlorine is assumed to be perfectly incompatible with respect to crystallizing phases. Thus, the chlorine concentration in the melt prior to water saturation increases as the melt crystallizes, but the mass of chlorine in the melt remains constant. After water saturation chlorine partitions readily into the exsolving aqueous fluid. Experiments by Shinohara et al. [1984, 1989] have determined the distribution of chlorine between melt and aqueous fluid as a function of pressure and indicate that an increasing proportion of chlorine remains in the melt as pressure decreases. Their results are compatible with earlier data at 2 kbar [Kilinc and Burnham, 1972], and extend these data to higher and lower pressures. Chlorine partitioning between fluid and melt in the quartz-albite-orthoclase-H2O system at 810°C and 0.6 to 2.6 kbar based on experimental data of Shinohara et al. [1989] is given by

$$-\log D_{\text{Cl}}^{m/w} = -0.41288 + 1.8737P - 0.48738P^2 + 4.6511\times10^{-2}P^3$$

(2)

where $D_{\text{Cl}}^{m/w}$ is the melt/water partition coefficient for chlorine and $P$ is pressure (kbar).

To calculate chlorine partitioning between melt and aqueous fluid the crystallization increment, pressure, initial water content, and initial masses of chlorine and melt are selected. The extent of crystallization necessary for the melt to reach saturation is determined based on the ratio of initial water to the water saturation level. After the melt has become saturated in water the mass of chlorine present in the melt (initial chlorine minus that previously partitioned to the aqueous fluid), mass of fluid exsolved (water saturation minus water lost to hydrous minerals), and mass of remaining melt (initial melt minus crystallized melt) are calculated for each increment of melt crystallization. Iterative techniques are then used to calculate the distribution of chlorine between the exsolving fluid and remaining melt ($D_{\text{Cl}}^{m/w} = [M_{\text{Cl}}^{m/w}/M_{\text{Cl}}^{w/e}] / [M_{\text{Cl}}^{m/w}/M_{\text{Cl}}^{m/w}]$), where $M_{\text{Cl}}^{m/w}$ is the mass of Cl partitioned to the aqueous fluid, $M_{\text{Cl}}^{w/e}$ is the mass of exsolving water, $M_{\text{Cl}}^{m/w}$ is the mass of Cl in the remaining melt, and $M_{\text{Cl}}^{m/w}$ is the mass of remaining melt) as the melt crystallizes.

Shinohara et al. [1984] demonstrated that chloride becomes increasingly associated with hydrogen as pressure decreases, significantly reducing the amount of chloride available for complexing with copper in low pressure systems. Candela [1989] described chloride lost by association with hydrogen between 0.6 and 2.3 kbar by the relationship

$$\log_{10} (\text{HCl} / \Sigma \text{Cl}) = -0.11 - 0.47P$$

(3)

where $P$ is pressure in kilobars. Such chloride loss to hydrogen is considered but, loss of chloride to other complexes is not evaluated.
Experimental and field studies indicate that prior to water saturation copper may be distributed between silicate melt, immiscible sulfide melt, and magmatic silicate and oxide phases. Both compatible and incompatible copper behavior prior to water saturation are evaluated because the extent to which these phases form and sequester copper during crystallization of a calc-alkaline melt has not been clearly and consistently established. This treatment is discussed more fully in a later section. Experimental data indicate that when water saturation is reached copper partitions preferentially into the aqueous fluids (E. Ion, personal communication, 1980) [Hilton and Engsler, 1990]. Following water saturation copper is, therefore, assumed to behave incompatibly.

The importance of copper transport as a chloride complex in a hydrothermal fluid has been firmly established [Cerar and Barnes, 1976; Barnes, 1979]. Furthermore, the experimentally determined partition coefficients describing distribution of copper between water and melt is a function of the chloride concentration of the fluid [Candela and Holland, 1984]. To describe partitioning of copper between aqueous fluid and siliceous melt (D Cu\text{Cl} \text{aq}/\text{sil}) the chloride-dependent, Nernst-type partition coefficient determined experimentally by Candela and Holland [1984] at 750°C and 1.4 kbar is used. Their results indicate that the partition coefficient is approximately equal to nine times the chloride concentration of the aqueous fluid (D Cu\text{Cl} \text{aq} = C_{\text{CuCl}} \text{aq}/C_{\text{CuCl}} \text{sil} = 9.1C_{\text{Cl}} \text{aq}). Use of a Nernst-type of partition coefficient rather than an apparent equilibrium constant implies that the model aqueous fluid composition is essentially identical to the experimental fluid composition [Candela and Holland, 1984].

To determine copper partitioning the mass of copper present in the melt during each increment of crystallization is calculated. This is equivalent to the initial copper content of the melt minus that partitioned to crystals prior to water saturation, and minus that partitioned to crystals and exsolved aqueous fluid following water saturation. Iterative techniques, similar to those used for chloride, are used to determine the distribution of copper between crystals and remaining melt (D Cu\text{Cl} = [M Cu\text{Cl} (M Cu\text{Cl})] / [M Cu\text{Cl} (M Cu\text{Cl})] where M Cu\text{Cl} is the mass of copper partitioned to crystals, M Cu\text{Cl} is the mass of crystals, and M Cu\text{Cl} is the mass of copper partitioned to the remaining melt) prior to water saturation, and between water and remaining melt (D Cu\text{Cl} = 9.1C_{\text{Cl}} \text{aq}/[M Cu\text{Cl} (M Cu\text{Cl})] where M Cu\text{Cl} is the mass of copper partitioned to the exsolved aqueous fluid) after water saturation. As the loss of chloride as a complex to other cations is not considered, the amount of copper partitioned into the aqueous fluid should be considered a maximum value.

Immiscibility of chloride-bearing aqueous fluids occurs over a large region of P-T-XNaCl space. Salinities of coexisting immiscible liquid and vapor phases determined for a wide range of P-T-XNaCl conditions [Sourirajan and Kennedy, 1967; Khatibulin and Borisov, 1965; Bodnar et al., 1985] are controlled by pressure-temperature (P-T) conditions, while the liquid/vapor ratio is governed by the bulk salinity of the exsolved aqueous fluid (liquid plus vapor). Incorporated data includes that presented by Bodnar et al. [1985, Table 1, Figure 13] which give liquid phase salinities at specified pressures and temperatures. NaCl vapor/liquid partition coefficients [Khatibulin and Borisov, 1965] are used to calculate the salinity of the coexisting vapor phase.

A fluid with a bulk salinity between the salinities of the coexisting liquid and vapor phases in equilibrium at a given temperature and pressure will separate into immiscible liquid and vapor phases. As bulk fluid salinity governs the liquid/vapor ratio, the mass of liquid (M L) and vapor (M V) separating from the aqueous fluid exsolved during any increment of crystallization may be described by a mass balance equation.

\[ \text{M Cu}^\text{aq} = (C_{\text{Cu}}^\text{aq}/m^\text{aq}) + (C_{\text{Cu}}^\text{aq}/m^\text{aq}) \]  

where M Cu^aq equals the mass of copper in the aqueous fluid, C Cu^aq is the concentration of chloride in the liquid, and C Cu^aq is the concentration of chloride in the vapor.

Partitioning of copper between immiscible aqueous liquid and vapor phases has not been experimentally determined. The presence of chalcopyrite daughter minerals in vapor-rich fluid inclusions [Bodnar and Beane, 1980] indicates that the vapor phase is capable of transporting significant copper at elevated temperatures and pressures. Copper is assumed to be distributed between the liquid and vapor phases in the same proportions as chloride (C Cu/C Cu = C Cu/C Cu) because copper is transported as a chloride complex. This implies a copper/sodium exchange constant equal to unity for the distribution of copper and sodium between the immiscible aqueous liquid and vapor phases.

The mass of copper partitioned to the fluid in excess of that soluble at 250°C is assumed to precipitate and contribute to mineralization. This temperature is consistent with minimum temperatures observed during fluid inclusion studies of porphyry systems [Bodnar, 1982; Bodnar and Beane, 1980]. Furthermore, Cerar and Barnes [1976] and Barnes [1979] have demonstrated experimentally that copper solubility in fluids typical of porphyry systems drops by 2 orders of magnitude between 350°C and 250°C. Copper remaining in solution at 250°C is assumed to be transported beyond the limit of the deposit where it forms a low grade (subeconomic) copper halo around the ore zone.

Using the experimentally determined log K for 250°C and assuming a pH of 4.75 and log aO2 equal to -36.5, consistent with preferred conditions for copper precipitation at 250°C [Cerar and Barnes, 1976, Figure 8.6; Barnes, 1979], copper solubility as a function of chloride molality (m Cl) is equal to

\[ M_{\text{Cu,sol}} = -1.1286 \times 10^{-5} + 6.6229 \times 10^{-4} m_{\text{Cl}} \]  

where M Cu,sol is the mass (wt.%) soluble copper in equilibrium with chalcopyrite and pyrite at the described conditions. Results calculated for a one molal chloride solution are consistent with copper solubilities determined experimentally for chalcopyrite in a one molal chloride solution buffered by pyrrhotite-pyrite-magnetite (J. J. Hemley, personal communication, 1989).

Initial H\text{2}O, Cl/H\text{2}O, Cu, and Cu Compatibility

Results are presented for three pressures, 2.0, 1.0, and 0.5 kbar, simulating intrusion and crystallization at deep, intermediate, and shallow depths. Crystallization is assumed to occur at constant pressure and constant temperature. While recognizing that systems with similar compositions would crystallize at different temperatures if confined under different pressures, the assumption of isothermal crystallization at a temperature of 700°C for all three systems permits temperature to be eliminated as a variable, and results can be compared as a function of pressure (depth) and copper compatibility.
Burnham [1981] suggested that the water content of intruding magmas in porphyry systems was probably between 2 and 5 wt.%. A minimum of 2 wt.% water is required to provide the energy necessary to cause extensive fracturing during fluid exsolution and vaporization. The presence of greater than 5 wt.% water would cause fluid exsolution and melt crystallization at depths greater than those generally inferred for porphyry deposits. Burnham also noted that the common presence of hornblende and biotite phenocrysts indicates that the water content of the intruding porphyry melt is fairly high. Reported results are based on an initial melt water content of 2.5 wt.%. Use of this value allows evaluation of shallow systems (0.5 kbar) which saturate with less than 3 wt.% water, and comparison with higher pressure systems.

Gill [1981] indicates that the Cl/H$_2$O ratio for andesites varies from 0.03 to 0.10, with orogenic andesites being the most Cl-rich. A Cl/H$_2$O ratio of 0.1 is used and differences which would result from lower ratios are discussed. The copper content in andesites varies from 10 to 150 ppm with a mean equalling about 60 ppm copper [Gill, 1981]. An initial melt content of 50 ppm copper is assumed.

Copper in most andesitic suites decreases irregularly as the silica content in subsequently fractionated rocks increases; however, copper in many suites remains constant [Gill, 1981]. Although copper partitions into magnetite [Evart et al., 1973] and, to a lesser degree, into other mafic silicate or oxide minerals, copper loss to these phases is not extensive enough to account for the decrease in copper content observed in successively fractionated rocks in many systems. This trend has led to suggestions that copper may be lost to an immiscible sulfide phase [Candela, 1986, 1989] or to an exsolving aqueous fluid [Dilles, 1987; Eilenberg and Carr, 1981]. Candela [1986] determined that copper loss to magmatic silicate phases was too small to account for the observed copper decrease in the volcanic Thingmuli suite, Iceland, and concluded that copper was lost to an immiscible sulfide phase. The presence of pyrrhotite in phenocrysts in extrusive rocks equivalent in composition to porphyry-related magmas indicates that porphyry melts may saturate in an immiscible sulfide melt prior to water saturation [Whitney, 1984] providing a sink for copper [Candela, 1989]. In other systems, the lack of any sulfide phases [Eilenberg and Carr, 1981] or the lack of parallel loss of copper and zinc, which would be expected if copper was lost to a sulfide phase [Gill, 1981], indicates copper is most likely lost to an aqueous phase. As the behavior of copper has not been consistently established, copper is modeled as behaving both compatibly ($D_{Cu}^{\text{Cl/m}} = 2.0$) and incompletely ($D_{Cu}^{\text{Cl/m}} = 0.1$) [Candela and Holland, 1984] prior to water saturation.

**RESULTS**

**Chlorine and Copper Partitioning**

The pressure dependence of chlorine partitioning between melt and exsolving aqueous fluid at pressures of 2.0, 1.0, and 0.5 kbar is illustrated in Figure 1. In order to concentrate the original 2.5 wt.% water in the melt to the saturation level at each pressure, 59%, 39%, and 8% of the melt must crystallize at 2.0, 1.0, and 0.5 kbar, respectively (Figure 1). Melts under 2 kbar pressure become saturated when the water comprises 6.0 wt.% of the melt. During subsequent crystallization, approximately 10% of this water (0.6 wt.% of the melt) is incorporated into hydrous minerals (biotite and hornblende). The remaining aqueous fluid (5.4 wt.% of the melt) exsolves. Owing to exsolution of this rather large water fraction and a high partition coefficient for chlorine at 2 kbar ($D_{Cl}^{\text{Cl/m}} = 57$), the first fluids to exsolve are highly saline (53.4 wt.% NaCl) and the exsolving fluid depletes the remaining melt of chlorine. Successively exsolved aliquots of aqueous fluid contain lower chlorine concentrations (Figure 1).

![Fig. 1. Salinity (wt.% NaCl) of the aqueous fluid exsolving from a crystallizing silicic magma at 0.5, 1.0, and 2.0 kbar pressure.](image)

Shallow or low pressure systems (0.5 kbar) become saturated with a water content equivalent to 2.7 wt.% of the melt. During crystallization approximately 13% of this water is incorporated into biotite and the remainder (2.35 wt.% of the melt) exsolves. Owing to a much smaller chlorine partition coefficient ($D_{Cl}^{\text{Cl/m}} = 2.6$) at this lower pressure and exsolution of less water than in deep systems the exsolving aqueous fluid is incapable of removing much chlorine from the melt. The chlorine concentration in the melt increases and successive aliquots of fluid contain higher chlorine concentrations (Figure 1). At 1.0 kbar a crystallizing melt becomes saturated with 4.1 wt.% water; 3.5 wt.% water exsolves, and the remaining is incorporated into biotite. The exsolving aqueous fluid is incapable of transporting significant chlorine. Chlorine becomes concentrated in the melt and successively exsolved aliquots of aqueous fluid contain higher chlorine concentrations (Figure 1).

Copper partitioning generally parallels chlorine partitioning because the copper partition coefficient is a function of the chlorine molality in the fluid. Copper is partitioned into later exsolving fluids in relatively shallow systems (Figures 2a, 2b) and into the first fluids to exsolve in
level and a larger fraction of copper is incorporated by crystallizing phases if copper behaves compatibly. Copper incorporated by mineral phases is not available to the hydrothermal system which develops as water is exsolved from the magma. The extent of copper loss from the hydrothermal system is dependent upon the amount of melt crystallized prior to water saturation and on the degree to which copper is incorporated by crystallizing phases or is lost to an immiscible sulfide melt. As system pressure increases, a larger fraction of copper is incorporated by crystallizing minerals, less copper is available to be partitioned into the aqueous fluid and the difference in the copper concentration of the fluid (compatible versus incompatible behavior) becomes significant (Figures 2a, 2b, 2c). Figure 3 shows the fraction of copper in the melt which is partitioned to the aqueous fluid (\(\Psi\)) at different pressures and illustrates the relative efficiency of the various systems. The fraction of copper partitioned to the fluid varies from approximately 70 to 82% of that initially present in the melt if copper behaves incompatibly prior to water saturation, and varies from 16 to 60% if copper behaves compatibly (Figure 3). Loss of copper to crystallizing minerals in deep systems is responsible for the majority of copper lost from the hydrothermal systems if copper behaves compatibly. These results are consistent with results previously reported for deep [Kilinc and Burnham, 1972; Cline and Bodnar, 1989; Candela, 1989] and shallow systems [Candela, 1989].

Aqueous Fluid Immiscibility

Experimental data [Sourirajan and Kennedy, 1962; Bodnar et al., 1985] indicate that over a wide range of \(P-T-x_{NaCl}\) space the exsolving aqueous fluid separates into immiscible liquid and vapor phases having different salinities. These fluids, upon exsolving from a crystallizing melt, immediately separate into a dense, high-salinity liquid and a low-salinity vapor. Evidence for such immiscibility in natural systems is found in coexisting halite-bearing and vapor-rich fluid inclusions [Bodnar and Beane, 1980; Bodnar et al., 1985].

The first fluids to exsolve from the described melt at 700°C and 0.5 kbar have a bulk salinity of 1.1 wt.% NaCl. At these \(P-T\) conditions the aqueous fluid immediately separates into liquid containing 70 wt.% NaCl and vapor containing 0.2 wt.% NaCl. Mass balance calculations require this fluid to form 1.3 mass % liquid and 98.7 mass % vapor (Figure 4a), reflecting the low bulk fluid salinity. As crystallization proceeds the salinity of the bulk fluid increases (Figure 1). Because the salinities of the immiscible phases are constrained by phase equilibria to remain constant at constant \(P-T\), the liquid to vapor ratio must increase to accommodate the increasing bulk fluid salinity and an increasing proportion of high salinity liquid forms (Figure 4a). The bulk salinity of the fluid produced as the final melt crystallizes exceeds 70 wt.% NaCl (Figure 1). This fluid is stable as a single phase brine (Figure 4a) similar to that associated with granites from the Ascension Islands [Roedder and Coombs, 1967].

At 700°C and 1.0 kbar the first aqueous fluid to exsolve has a bulk salinity of 7 wt.% NaCl. This fluid is unstable in the one-phase field and separates into a high-salinity liquid containing 50 wt.% NaCl and a vapor containing 2.2 wt.% NaCl. The initial relative mass proportions are 10.1% liquid and 89.9% vapor (Figure 4b). As crystallization progresses the salinity of the bulk fluid increases (Figure 1), requiring an increase in
the mass fraction liquid formed (Figure 4b). After 98% of the melt has crystallized, the exsolving fluid has a bulk salinity in excess of 50 wt.% NaCl and is stable as a single-phase liquid. The final fluid to exsolve is saturated in NaCl (84 wt.% NaCl [Sourirajan and Kennedy, 1962]).

![Graph showing mass percent liquid and vapor forming from aqueous fluids exsolved at 700°C](image)

**Fig. 3.** The fraction (wt.%) copper initially present in the melt which is partitioned to the exsolving aqueous fluid (Ψ = [M\text{Cu}]/[\Sigma\text{M}])100) under pressures of (a) 0.5, (b) 1.0, and (c) 2.0 kbar pressure. The melt has an initial water content of 2.5 wt.%, an initial \text{Cl}/H\text{2}O ratio equal to 0.1, and an initial copper concentration of 50 ppm. Copper is modeled as both an incompatible (INC) (D\text{Cu} = 0.1) and compatible (CMP) element (D\text{Cu} = 2.0) prior to water saturation. Total copper partitioned to the fluid varies from approximately 70 to 82% of that initially present in the melt if copper behaves incompatibly prior to water saturation, and varies from 16 to 60% if copper behaves compatibly.

**Fig. 4.** Mass percent liquid (L) and vapor (V) formed by aqueous fluids exsolved at 700°C and (a) 0.5, (b) 1.0, and (c) 2.0 kbar pressure. The chlorine content of the melt, chlorine partition coefficient, amount of fluid exsolved and extent of melt crystallization determine the salinity of the bulk exsolved fluid while the P-T conditions determine the salinity of each immiscible aqueous phase. (a) The first fluids exsolved at 0.5 kbar and 700°C immediately separate to form 1.3 mass % liquid containing 70 wt.% NaCl and 98.7 mass % vapor containing 0.2 wt.% NaCl. (b) The first fluids exsolving at 1.0 kbar and 700°C separate into 10.1 mass % brine containing 50 wt.% NaCl and 89.9 mass % vapor containing 2.2 weight % NaCl. As crystallization proceeds at 0.5 and 1.0 kbar pressure, the salinity of the bulk exsolving fluid varies (see Figure 1), and, as the salinity of each immiscible phase must remain constant at constant P and T, the liquid to vapor ratio varies to accommodate the changing bulk salinity (Figures 4a, 4b). (c) Fluids exsolving at 2.0 kbar have a bulk salinity equal to 53.4 wt.% NaCl and are stable in the one-phase field. As crystallization proceeds and fluids continue to exsolve, bulk salinity (Figure 1) and fluid density decline and the fluid becomes a vapor (Figure 4c).
The first aqueous fluid to exsolve from the melt at 2.0 kbar and 700°C has a salinity of 53.4 wt.% NaCl. At these P-T conditions, all aqueous fluids that exsolve during crystallization of the melt are stable as a single phase regardless of fluid salinity (Figure 4c). As the density of these fluids is greater than the critical density, these fluids are liquid. As these fluids rise they eventually reach reduced pressure conditions where they are unstable as a single phase and an immiscible vapor phase begins to form. Assuming no temperature change, a small vapor fraction first begins to separate from the liquid at a pressure of approximately 0.9 kbar [Bodnar et al., 1985, Figure 13]. As the salinity of subsequently exsolved fluids decreases, the fluid approaches critical conditions (700°C, 1237 bars, 26.4 wt.% NaCl [Sourirajan and Kennedy, 1962]). Fluids exsolved at 700°C with salinities below 26.4 wt.% NaCl have a density less than the critical density and the exsolved fluid is a vapor (Figure 4c). As this fluid rises, decompresses, and encounters the two-phase field, a fraction of the vapor condenses and a liquid phase forms.

**Copper Precipitation**

Calculations indicate that nearly 99% of the copper partitioned into the aqueous fluid precipitates as the fluid temperature is reduced to 250°C. Most copper precipitates between 350° and 250°C; however, copper does precipitate at higher temperatures from highly saline fluids which transport high copper concentrations, particularly those late fluids saturated in NaCl and produced by shallow, low pressure systems.

Less than 11% of the copper precipitated in the systems evaluated is transported by the vapor phase (Table 1). Factors affecting copper transport and precipitation from the vapor phase are discussed in a later section.

**Table 1. Summary of Copper Precipitation and Volume of Melt Necessary to Produce 250 Million Tons of 0.75 wt.% Copper**

<table>
<thead>
<tr>
<th>Pressure, kbar</th>
<th>% Cu originally in melt</th>
<th>% Cu precipitated from vapor</th>
<th>Vol. melt (km³) necessary</th>
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<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
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<td>Cu Compatible</td>
<td>Cu Incompatible</td>
<td></td>
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<tr>
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Volume of Magma Required to Produce a Typical Porphyry Copper Deposit

In order to evaluate copper productivity in magmatic systems and to compare the productivity of systems at different pressures the minimum volume of magma necessary to produce the mass of copper present in a porphyry copper deposit containing 250 million tons of 0.75 wt.% copper (3.75 x 10⁹ lbs copper) has been determined. Calculations indicate that melts with minimum volumes of 15 to 20 km³, if copper behaves incompatibly, or 20 to 90 km³, if copper behaves compatibly, are required to produce economic deposits at pressures between 0.5 and 2.0 kbar (Table 1). As porphyritic bodies of this size are associated with copper mineralization in porphyry systems, these results indicate that melts containing average concentrations of water, chlorine, and copper are capable of providing the necessary metals to form a typical economic deposit. A significant additional volume of melt is not necessary to provide copper to porphyry systems.

**Varying Initial Water, Cl/H₂O**

Previous studies [Candel and Holland, 1984; Candel, 1986] have emphasized the importance of the ratio of initial water in the melt to the water content at saturation (M_w/m_s) in controlling the amount of copper lost to crystals. These studies also indicate that high Cl/H₂O and increased H₂O in the melt (with fixed Cl/H₂O) enhance the efficiency of copper partitioning to the fluid. Increasing H₂O in a melt with a constant chlorine content slightly reduces the efficiency of copper partitioning to the fluid.

Figure 5 illustrates the volume of melt necessary to deposit the copper (3.75 x 10⁹ lbs) in a system as initial water varies from 2 to 4 wt.% for a 1 kbar system (M_w/m_s = 4.1 wt.% H₂O, Figure 5a), and from 2 to 6 wt.% for a 2 kbar system (M_w/m_s = 6.0 wt.% H₂O, Figure 5b). The nearly flat slope and very

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**Fig. 5.** The volume of melt (km³) required to produce 250 million tons, 0.75 wt.% copper in (a) 1.0 and (b) 2.0 kbar systems as initial water in the melt varies from 2 to 4 wt.% and 2 to 6 wt.%, respectively. See text for explanation of trends.
similar values for the lines illustrating incompatible copper behavior at both 1.0 and 2.0 kbar (Figures 5a, 5b, INC) indicate that if copper behaves incompatibly, the initial water content of the melt, system pressure, and ratio of initial water to water at saturation \( M_{w}^{m,0}/M_{w}^{m,s} \) have a minimal affect on the volume of melt necessary to produce the deposit.

If, however, copper exhibits compatible behavior and is incorporated into crystallizing minerals, the initial water content of the melt and the ratio \( M_{w}^{m,0}/M_{w}^{m,s} \) are highly influential in determining the volume of melt necessary to produce an economic deposit. By comparing compatible copper behavior at different pressures (i.e., water saturation levels) (Figures 5a, 5b, CMP) it is apparent that very similar volumes of melt are necessary, for similar values of \( M_{w}^{m,0}/M_{w}^{m,s} \) (initial water/water saturation) to produce the deposit. For example, systems with initial water/water saturation equal to 0.75 require approximately 29 km\(^3\) of melt to produce the deposit at 1 kbar pressure and approximately 28 km\(^3\) at 2 kbar pressure (Figure 5). This indicates that variations in the water saturation level \( M_{w}^{m,s} \) from 4 wt.% (Figure 5a) to 6 wt.% (Figure 5b), and in pressure from 1 to 2 kbar contribute to only minor differences in results. As \( M_{w}^{m,0}/M_{w}^{m,s} \) approaches 1.0, i.e., less melt crystallizes prior to saturation, the issue of copper compatibility becomes less important. In summary, the \( M_{w}^{m,0}/M_{w}^{m,s} \) ratio is significantly more critical than the initial water or water saturation levels alone in determining the required melt volume. Furthermore, the importance of this ratio is dependent on the degree to which copper behaves incompatibly.

The effect of varying the Cl/H\(_2\)O ratio on the required volume of melt is shown in Figure 6 for pressures of 0.5, 1.0, and 2.0 kbar, and an initial water content of the melt equal to 2.5 wt.% of the melt. In shallow or intermediate level systems (Figures 6a, 6b) the relatively flat slope of the lines indicates that varying this parameter has a surprisingly small effect and the volume of melt necessary to produce the required amount of copper is reduced by less than 15% as Cl/H\(_2\)O increases from 0.03 to 0.1. In deeper systems (Figure 6c) the effect of varying Cl/H\(_2\)O is more significant and the required melt volume is reduced by approximately 50% as Cl/H\(_2\)O increases from 0.03 to 0.1. These results do not change regardless of initial water content (2.0 to 6.0 wt.% of the melt). This behavior is related to chlorine partitioning which is a function of pressure (Figure 1) [Shinohara et al., 1984, 1989]. Fluids exsolving from melts at pressures less than approximately 1.3 kbar do not deplete the melt of chlorine for the systems described. The chlorine concentration in the melt increases (Figure 1) and the latest fluids to exsolve are, in most instances, saturated in NaCl. Even melts with low initial Cl/H\(_2\)O ratios are capable of concentrating chlorine in the final fluids to saturation levels because minimal chlorine is partitioned to exsolving fluids during much of melt crystallization (Figures 3a, 3b). As a result, the final fluids to exsolve in most moderate to low pressure systems have similar high salinities, transport abundant copper, and require similar volumes of melt to produce the deposit.

At pressures greater than approximately 1.3 kbar, the first fluids to exsolve are the most saline (Figure 1) and the chlorine content in the remaining melt is depleted. The salinities of these early fluids and their ability to transport copper directly reflect the initial Cl/H\(_2\)O ratio of the melt. As this ratio varies the salinity of the first fluids to exsolve varies (Figure 7) and systems with Cl/H\(_2\)O ratios equal to 0.10 are twice as efficient in transporting copper and producing economic deposits as systems with Cl/H\(_2\)O equal to 0.03 (Figure 6c). Note, however, that even fluids with a low initial Cl/H\(_2\)O ratio

Fig. 6. The volume of melt (km\(^3\)) required to produce 250 million tons, 0.75 wt.% copper, at pressures of (a) 0.5, (b) 1.0, and (c) 2.0 kbar as a function of the Cl/H\(_2\)O ratio. The melt has an initial water content of 2.5 wt.% and contains 50 ppm copper. In shallow or intermediate level systems (Figures 6a, 6b) the volume of melt necessary to produce the required amount of copper is reduced by less than 15% as Cl/H\(_2\)O increases from 0.03 to 0.1. In deeper systems (Figure 6c) the required melt volume is reduced by approximately 50% as Cl/H\(_2\)O increases from 0.03 to 0.1. See text for explanation of trends.
crystallization proceeds ($\text{Cl/H}_2\text{O} = 0.07, 0.03$; Figure 8b) and, as a result, late fluids, which transport the highest copper concentrations, have the lowest salinities ($\text{Cl/H}_2\text{O} = 0.03, 95 - 100\%$ crystallization, Figures 8a and 8b).

Fluids exsolving from a melt at 1.4 kbar and 700°C are stable as a single phase, however, decompression to 1.0 kbar would cause immiscibility and the formation of a brine containing 50 wt.% NaCl and a vapor containing 2.2 wt.% NaCl. The salinities of these phases are the same at a given pressure and temperature regardless of the initial $\text{Cl/H}_2\text{O}$ ratio of the melt. Varying liquid/vapor ratios accommodate differences in bulk salinity. In systems with low initial $\text{Cl/H}_2\text{O}$ a larger proportion of vapor forms ($\text{Cl/H}_2\text{O} = 0.03$, Figure 8c). As bulk fluid salinity decreases and a larger vapor fraction forms (Figures 8a, 8c) increasing copper is transported by and precipitated from the vapor phase (Figure 8d). In a melt with a $\text{Cl/H}_2\text{O}$ ratio equal to 0.03, as much as 35 to 50 mass % of the copper in the hydrothermal fluid may be precipitated from the vapor phase.

**COMPARISON WITH THE YERINGTON, NEVADA, PORPHYRY COPPER SYSTEM**

A detailed study of the Yerington batholith in the vicinity of the Ann-Mason porphyry copper deposit [Dilles, 1987] provides important constraints for the petrogenesis of this porphyry copper system. Following intrusion of a quartz monzonodiorite magma, differentiation of the batholith proceeded by inward and downward crystallization and was twice interrupted by intrusion of differentiated quartz monzonite and granite magma. Copper mineralization is associated with the final intrusive event which produced the Luhr Hill porphyritic granite and related granite porphyry dikes. Post mineral tilting has exposed the batholith and ore deposits in cross section and has permitted estimation of a formation paleodepth of 4.6 km for the Luhr Hill porphyritic granite. Approximately 65 km$^3$ of porphyritic granite (6 vol.% of the batholith) are exposed. Phase petrology and mineral compositions indicate the Luhr Hill granitic magma was within 1% of water saturation when emplaced and that crystallization and cooling to about 750°C at 1.1 kbar led to water saturation and exsolution. The presence of abundant aplite and pegmatite dikes in the granite indicates water saturation throughout the Luhr Hill granite as it crystallized. The early crystallization of hornblende requires a high initial water content [Naney, 1983] and an initial $M_w^{1.0}/M_w^{1.0}$ ratio near 1.0 is suggested. A 1:1 ratio of phenocrysts to aplite groundmass indicates that after 50% of the melt crystallized the system was significantly undercooled, probably as a result of pressure quenching to hydrostatic conditions, and a fine-grained groundmass rapidly crystallized. The average copper content of the early quartz monzonodiorite and quartz monzonite intrusions is ~ 62 ppm [Dilles, 1987].

Dilles [1987] indicates that crystal fractionation was probably responsible for the evolution of the Yerington batholith from quartz monzonodiorite to granite composition. The copper content is nearly constant or increases slightly as the silica content of the plutonic rocks increases from 58 to 66 wt.% SiO$_2$ (quartz monzonodiorite to quartz monzonite), but drops sharply as SiO$_2$ increases from 66 to 68 wt.% (quartz monzonite to granite) [Dilles, 1987, and personal communication, 1989]. These trends are interpreted as indicating that copper exhibited mildly incompatible behavior (Figure 6c) can produce a deposit from a fairly small volume of melt if copper behaves incompatibly. If copper behaves compatibly and the initial $\text{Cl/H}_2\text{O}$ ratio is low, much copper is lost to crystallizing phases and a large volume of melt is required to produce the deposit (Figure 6c). These results demonstrate that fluids with fairly low salinities are capable of transporting sufficient copper to form a deposit if copper has not been lost to crystallizing phases. Competition for chlorine by other cations reduces the amount of chlorine available to complex and transport copper.

Water loss to crystallizing hydrous phases increases the $\text{Cl/H}_2\text{O}$ ratio of the fluid. Such water loss improves the capacity of the fluid to transport copper from the melt and produce an economic deposit as long as the amount of exsolving water is not reduced below 2 wt.%. Calculations assume an average of 0.37 wt.% water lost to biotite in melts which saturate with less than 4.0 wt.%, and 0.58 wt.% water lost to biotite and hornblende in melts which saturate with greater than 4.0 wt.% water. As much as 1.34 wt.% water may be lost to hydrous phases in mafic-rich rocks (25% biotite, 15% hornblende). The ubiquitous presence of biotite and common presence of hornblende in porphyry systems indicate that sufficient water is present and that the initial $\text{Cl/H}_2\text{O}$ ratio has probably been enhanced in most porphyry copper systems by crystallization of these phases. Results discussed previously indicate that increasing fluid salinity has the greatest influence on copper transport and precipitation in high pressure systems which produce the highest salinity fluids immediately following water saturation (Figure 6c).

**Copper Transport by the Vapor Phase**

At intermediate pressures the salinity of the exsolving fluid remains relatively constant during crystallization of much of the melt (1.4 kbar, Figure 8a), rather than being highly saline immediately following saturation or during crystallization of the last bit of melt (Figure 1). At pressures slightly greater than ~ 1.3 kbar, exsolving fluids gradually deplete the melt of chlorine (Figure 8a) and, for $\text{Cl/H}_2\text{O}$ equal to 0.1, fluid salinity is sufficient to deplete the melt of copper (Figure 8b). In systems with low initial $\text{Cl/H}_2\text{O}$ ratios, fluid salinity is low (Figure 8a) and the fluid is less effective in removing copper from the melt. Copper becomes concentrated in the melt as
prior to water saturation and, upon saturation, fluid exsolution was responsible for depletting the granitic magma in copper [Dilles, 1987, and personal communication, 1989]. Significant copper may also be lost to a sulfide phase prior to water saturation. Therefore, copper is modeled as behaving both moderately incompatibly ($D_{Cu} \times m = 0.5$) and compatibly ($D_{Cu} \times m = 2.0$) prior to water saturation.

Model calculations incorporating the above constraints indicate crystallization of 13% of the melt is necessary to achieve water saturation and the first fluid to exsolve contains 8.2 wt.% NaCl (Figure 9a). The exsolving fluid does not deplete the melt of chlorine and, during the first 50% crystallization, successively exsolved fluids contain slightly greater chlorine concentrations (Figure 9a). Copper partitioning (Figure 9b) and precipitation parallel chlorine partitioning. At initial conditions of 750°C and 1.1 kbar the exsolving fluid separates into immiscible liquid and vapor phases with salinities of 50 wt.% and 2.2 wt.% NaCl, respectively. Because of the relatively low bulk fluid salinity (8.2 wt.% NaCl), a small saline liquid fraction (15.4 mass %) forms initially (Figure 9c). As the melt crystallizes and bulk fluid salinity increases, the liquid fraction increases.

After 50% of the melt crystallized the system was subjected to a sudden pressure drop to ~400 bars, simulating a change from lithostatic to hydrostatic conditions. Water solubility in the melt was instantaneously decreased and the system was flooded with the exsolving aqueous fluid. The chlorine partition coefficient ($D_{Cl} \times m$), a function of pressure, decreased abruptly from 13 to 2 and the bulk salinity of the exsolving fluid dropped from 10.7 wt.% to 1.5 wt.% NaCl. As copper partitioning to the aqueous fluid is a function of the chlorine molality of the fluid, the mass of copper partitioning to the fluid was also immediately reduced (Figure 9b) and less copper was subsequently available for precipitation. The salinity reduction coupled with the pressure reduction caused vaporization of 98% of the fluid (Figure 9c). These results indicate that while boiling may be an excellent mechanism for precipitation of metals already in transport by an aqueous fluid, decompression and boiling serve to concentrate chlorine and metals in the melt rather than to partition metal-bearing chloride complexes into the large mass of exsolving aqueous fluid. In response to greatly reduced partition coefficients for both chlorine and copper, both elements are concentrated in the melt as the remaining 50% of the melt crystallizes. High concentrations of both chlorine and copper are forced into the final fluids to exsolve as the last of the melt crystallizes (Figures 9a, 9b).

Results were calculated for Yerington assuming both compatible and incompatible copper behavior prior to water saturation (Table 2). If copper behaves incompatibly, 69% of the copper initially present in the melt is partitioned into the exsolving aqueous fluid and 31% is lost to crystallizing minerals. Approximately 99% of the copper transported by

Fig. 8. Effect of varying the Cl/H$_2$O ratio in a melt crystallizing at intermediate pressure (1.4 kbar). The melt initially contains 50 ppm copper and copper behaves incompatibly. (a) Bulk salinity (wt.% NaCl) of the exsolving aqueous fluid, (b) mass copper (wt.% ) in the fluid, (c) mass % vapor formed as pressure declines from 1.4 to 1.0 kbar, and (d) mass % copper precipitated from the vapor phase at 1.0 kbar pressure for Cl/H$_2$O = 0.10, 0.07, and 0.03. See text for explanation of trends.
partitioned into the exsolving aqueous fluid and 43% is lost to crystallizing minerals. Ninety-nine percent of the copper exsolved from the magma precipitates as the aqueous fluids cool to 250°C and at least 58 km³ of magma are necessary to produce the orebody present at Yerington. These results are in good agreement with the exposed (minimum) 65 km³ of Leu Hill granite.

**CONCLUSIONS**

Results indicate that "average" plutons of the size typically associated with porphyry copper systems and with very "typical" volatile, chlorine, and copper contents, are capable of producing an economic porphyry copper deposit. Neither nongenetic sources nor additional magma are necessary to provide copper to the system and an elevated initial copper concentration in the melt is not necessary. Model results, incorporating constraints determined for the Ann Mason deposit at Yerington, Nevada, indicate that the Leu Hill granite was capable of providing the mass of copper concentrated in the deposit.

Copper is transported most efficiently by the latest fluids to exsolve in shallow (low pressure) systems. Melts with initial water concentrations of at least 2.5 wt.% water and Cl/H₂O as low as 0.03 can produce economic deposits with volumes of 50 km³ or less, regardless of copper compatibility. In deeper systems the earliest fluids to exsolve are the most saline and may, with Cl/H₂O ratios as low as 0.03, produce deposits from melts of less than 30 km³ if copper behaves incompatibly prior to water saturation, or if the initial intruding melt is water-rich and requires only minor crystallization to achieve water saturation. If copper behaves compatibly and if significant crystallization is necessary to concentrate the initial water content to the melt saturation level, melts well in excess of 100 km³ are required to produce a deposit owing to copper loss to crystallizing phases. In this case the ratio \( M_w^{m,0} / M_w^{m,s} \) is the principal variable in determining the volume of melt necessary to produce economic copper mineralization. This variable is much less significant if copper behaves incompatibly and is not extensively incorporated by crystallizing minerals. The absolute values of both initial water in the melt (\( M_w^{m,0} \)) and the water saturation level (\( M_w^{m,s} \)) are relatively unimportant as long as the mass of exsolved water is greater than 2 wt.%, i.e., large enough to generate sufficient force during vaporization to fracture the confining rocks.

The Cl/H₂O ratio of the intruding melt may also affect the efficiency with which a system produces a deposit. In deep or high pressure systems the salinity of the early fluids to exsolve from the melt directly reflects the initial Cl/H₂O ratio of the melt. These initial saline fluids remove most of the copper from the melt. Melts with high Cl/H₂O ratios (0.10) are more efficient by approximately half an order of magnitude.
in producing copper mineralization than systems with low ratios (0.30). In shallow or low pressure systems, early fluids to exsolve have very low salinities and chlorine becomes concentrated in the melt. Melts with quite low initial chlorine can concentrate chlorine to NaCl saturation levels in the final fluids exsolved. As a result the final fluids to exsolve in most of these moderate to low pressure systems have similar high salinities, transport similar masses of copper, and similar volumes of melt are required to produce a deposit. The initial Cl/H$_2$O ratio in the melt in low pressure systems has, therefore, a much smaller effect on the efficiency with which a system produces a copper deposit.

Water incorporated by hydrous phases effectively increases the Cl/H$_2$O ratio in the melt and, particularly in deep systems, improves the efficiency of the fluid in transporting copper from the melt. Hydrous minerals probably secrete less than 0.6 wt.% water in most systems, but have the potential to remove as much as 1.3 wt.% water in mafic-rich porphyries. A minimum of approximately 2 wt.% exsolved water is necessary to provide the mechanical energy required to fracture the system and water incorporated by crystals should not reduce the exsolving fluid below this value. The ubiquitous presence of biotite and common presence of hornblende in most porphyries indicate that water loss to hydrous phases and enhancement of the Cl/H$_2$O ratio occurs in all productive systems.

Exsolving aqueous fluids are unstable as a single-phase fluid over much of P-T space. These fluids may separate into immiscible liquid and vapor phases and the salinities of these phases are dependent upon the system pressure and temperature. The masses of the liquid and vapor phases are a function of the bulk fluid salinity. At low and intermediate pressures the first fluids to exsolve have moderately low salinities and a large mass fraction of vapor forms. As the melt crystallizes the salinity of the bulk fluid increases and the vapor to liquid ratio decreases. The final fluids to exsolve are frequently 100% liquid and saturated in NaCl. The first fluids to exsolve under high pressures are highly saline and are commonly stable as a single-phase. As the melt crystallizes fluid salinity and density decrease and the exsolving liquid becomes a vapor. As these fluids rise and decompress they become unstable and separate into immiscible liquid and vapor phases.

Depending on the temperature, confining pressure, initial water content, and the extent of crystallization of the melt, the bulk salinity of the aqueous fluids exsolved from a melt may vary from < 2.0 wt.% NaCl to saturation levels (84 wt.% NaCl at 700°C) (Figure 4), indicating that boiling is not necessary to produce the high salinities observed in some systems. When immiscible liquid and vapor phases do form the salinities of these phases are controlled by the system P-T conditions and are generally very different from the bulk fluid salinity. Therefore, fluid inclusions trapping immiscible aqueous phases will almost never reflect the bulk salinity of the exsolved fluid.

The fluids transporting most of the chlorine and copper in high and low pressure systems are generally liquid. Melts crystallizing at intermediate pressures may, however, if the initial melt Cl/H$_2$O ratio is low, become depleted in chlorine while becoming enriched in copper (Figures 8a, 8b) and late, low-salinity fluids exsolving from the melt transport a significant fraction of the copper originally present in the melt. If these fluids decompress, or are stable in the two-phase field, a large mass fraction of low-salinity vapor forms and may transport as much as 50% of the copper present in the fluid.

Pressure quenching caused rapid crystallization of the aplite groundmass in the Luhr Hill porphyry at Yerington and also significantly reduced the chlorine partition coefficient, reducing the mass of chlorine and copper partitioned to the aqueous fluid. This behavior demonstrates that while boiling may be an excellent mechanism for precipitating metals from an aqueous fluid, decompression and boiling serve to increase the concentration of chlorine and metals in the melt rather than partitioning them into the mass of exsolving aqueous fluid. As pressure quenching abruptly reduces the salinity of the exsolving fluid, fluid inclusions trapping fluids present before and after pressure quenching should display discrete populations with significantly different salinities.

Finally, crystallization under shallow (low pressure) conditions promotes significantly different behavior than crystallization under deep (high pressure) conditions. In shallow systems ( < 1.3 kbar) the latest fluids to exsolve transport most of the chlorine and copper from the melt. Pressure quenching at ≈ 50% crystallization, which produces the aplite groundmass of the porphyritic phase, occurs prior to removal of copper from the melt. Pressure quenching decreases the amount of chlorine and copper partitioning to the fluid, the melt becomes saturated in chlorine and copper, and only the very latest fluids to exsolve would contain high chlorine and copper concentrations. In deep systems (> 1.3 kbar) the relative timing of pressure quenching/aplite formation and copper transport from the melt is dependent on the initial water content of the melt. If the ratio of initial water to water saturation ($M_{w,m}^{0,0}/M_{w,m}^{0,0}$) is high, the melt becomes saturated early during crystallization, the first fluids to exsolve transport and remove most of the copper from the melt, and pressure quenching and formation of the aplite groundmass occur after copper is removed from the melt. Pressure quenching causes fluid immiscibility and copper precipitation. If, however, the ratio of initial water to water saturation ($M_{w,m}^{0,0}/M_{w,m}^{0,0}$) is low, much of the melt must crystallize before water saturation is achieved. Pressure quenching causes both rapid crystallization of the aplite groundmass and initial aqueous fluid exsolution. As the partition coefficients for both chlorine and copper are reduced during pressure quenching, the rate at which both elements are removed from or are concentrated in the melt is dependent upon the new system pressure.

**NOTATION**

$C_i^l$ concentration of element $i$ in the liquid phase (mass %)

$C_i^m$ concentration of element $i$ in the melt (mass %)

$C_i^v$ concentration of element $i$ in the vapor (mass %)

$C_i^{aq}$ concentration of element $i$ in the aqueous fluid (mass %)

$D_i^{w/m}$ partition coefficient indicating the ratio of the concentration of $i$ between aqueous fluid and melt

$D_i^{x/l,m}$ partition coefficient indicating the ratio of the concentration of $i$ between crystals and melt
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