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New evidence of magmatic-fluid–related phyllic alteration: Implications for the genesis of porphyry Cu deposits

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ABSTRACT

The phyllic alteration in a number of circum-Pacific porphyry Cu-Au deposits is related to high-temperature saline magmatic fluids. This contradicts the widely used genetic models wherein phyllic alteration formed as the result of mixing between magmatic and meteoric fluids. At the Endeavour 26 North porphyry deposit in eastern Australia, the transition from early potassic to the main-stage phyllic alteration is associated with fluids that with time decline in total salinity, NaCl/KCl, and temperature from ~600 to ~550 °C. Calculated and measured δ^{18}O and δD compositions of fluids (5.1‰–8.5‰ δ^{18}O, −57‰ to −73‰ δD) confirm a primary magmatic origin for both the early potassic and main-stage phyllic alteration. These results are consistent with other recent studies (e.g., El Salvador, Chile, Far Southeast, Philippines, and Panguna and Porgera, Papua New Guinea) and suggest that, rather than these results being unusual, a major revision of porphyry Cu genetic models is required.

Keywords: copper, gold, magmatic, ore-forming fluids, porphyry.

INTRODUCTION

Porphyry ore deposits form within and adjacent to porphyritic intrusions that are apophyses to larger stocks that have been water saturated within the upper several kilometers of the crust. The intrusions form huge hydrothermal systems of exsolved magmatic fluids with a carapace of convectively circulating meteoric water. They are important not only because they are the world's largest source of Cu, but also because they provide evidence for how magmas and their hydrothermal systems evolve at shallow depths. Since the appearance of a coherent descriptive model (Lowell and Guilbert, 1970), debate has raged over the role meteoric water plays in the development of alteration assemblages. Hydrothermal alteration is typically zoned from a central potassic (quartz–K-feldspar–biotite) altered core, outward through phyllic (quartz-sericite ± pyrite), argillic (quartz-kaolinite-chlorite), and propylitic (epidote-calcite-chlorite) assemblages. Fluids with high salinities (>35 wt% equivalent NaCl) and temperatures commonly in excess of 450 °C are inferred to cause the earliest potassic alteration (e.g., Gustafson and Hunt, 1975). Calculated fluid δ^{18}O and δD compositions confirm a primary magmatic origin for the responsible fluids. The later, commonly peripheral phyllic alteration has long been thought to form as the result of mixing of lower temperature and salinity magmatic fluids with meteoric water (e.g., Reynolds and Beane, 1985; Taylor, 1997). Evidence for the involvement of meteoric water in phyllic alteration has come from stable isotope studies of some North American porphyry deposits formed at high latitudes (e.g., Butte, Fig. 1). This model has been ingrained in the literature since its inception (Taylor, 1974).

We evaluate the involvement of magmatic fluids in phyllic alteration at several circum-Pacific porphyry Cu-Au deposits, including Endeavour 26 North (E26N), in the Late Ordovician Goonumbla Volcanic Complex, Australia. At E26N we found that mineralized phyllic alteration is largely if not exclusively related to magmatic fluids. Similar observations have been made at El Salvador, El Teniente, and Rio Blanco, Chile; Far Southeast, Philippines; and Panguna and Porgera, Papua New Guinea (e.g., Kusakabe et al., 1990; Hedenquist et al., 1998; Richards et al., 1998). These observations challenge the widely used genetic model in which phyllic alteration in porphyry deposits results from the ingress of meteoric fluids and refocuses attention on the evolution of shallow intrusions, including the timing of saturation and whether metals fractionate to an aqueous phase, and their associated magmatic-hydrothermal systems.

GEOLOGY AND MINERALIZATION OF E26N

E26N is a small, high-grade and relatively gold rich porphyry-related deposit (92.3 × 10^6 t of ore averaging 1.3% Cu and 0.4 g/t Au). Cu-Fe sulfide ore occurs within subparallel sheeted and networked quartz-sericite-anhydrite veins. Heithersay and Walshe (1995) documented 11 stages of veining and alteration spatially related to the emplacement of 2 quartz monzonite porphyry phases at E26N. We have refined the paragenetic sequence to five alteration and veining stages that demonstrate a distinct evolution in vein and alteration mineralogy and fluid characteristics (Table 1). These assemblages developed during the emplacement of four quartz monzonite porphyries. The pervasive and veined K-feldspar–biotite assemblages are the earliest stage of alteration at E26N (potassic, stages 1 and 2). They were overprinted by fracture-controlled, quartz-sericite-anhydrite (phyllic, stage 3) and later pervasive and veined sericite-pyrite-anhydrite and/or gypsum (phyllic, stages 4 and 5) alteration. An annulus of chlorite-epidote-hematite (propylitic) alteration surrounds these assemblages. Sulfide ore is zoned from a bornite-rich core through chalcopyrite-bornite to chalcopyrite-pyrite and an outer pyrite shell. The mineralized zone comprises the core of the deposit, where phyllic alteration overprints potassic alteration.

SAMPLING AND ANALYTICAL METHODS

Vein material for stable isotope and fluid-inclusion analysis was sampled from underground workings and drill core at intermediate and shallow levels of the deposit. Water for δD analysis was extracted from sericite and fluid inclusions in quartz by stepwise heating of the sample under vacuum. The extracted water was reduced to hydrogen by reaction with zinc metal at 450 °C (Coleman et al., 1982). Quartz and sericite for δ^{18}O analyses were reacted at 650 °C with BrF_5 in nickel vessels in order to liberate oxygen, which was converted to CO_2 by reaction with an internally heated carbon rod (Clayton and Mayeda, 1963). All isotopic data are reported in per mil relative to Vienna standard mean ocean water.

Fluid inclusions were studied from established vein and alteration generations using polished sections. Room-temperature observations subdivided inclusion populations in terms of the number of daughter crystals, the phase proportions, and the distribution and relative timing of their development. Microthermometric measurements were obtained using a modified Fluid Inc. heating stage, capable of temperatures to 700 °C.

FLUID-INCLUSION RESULTS

Fluid inclusions in veins of most paragenetic stages are divided into three principal categories: (1) vapor + liquid inclusions with small chalcopyrite daughter crystals and variable vapor/liquid ratios; (2) vapor + liquid +

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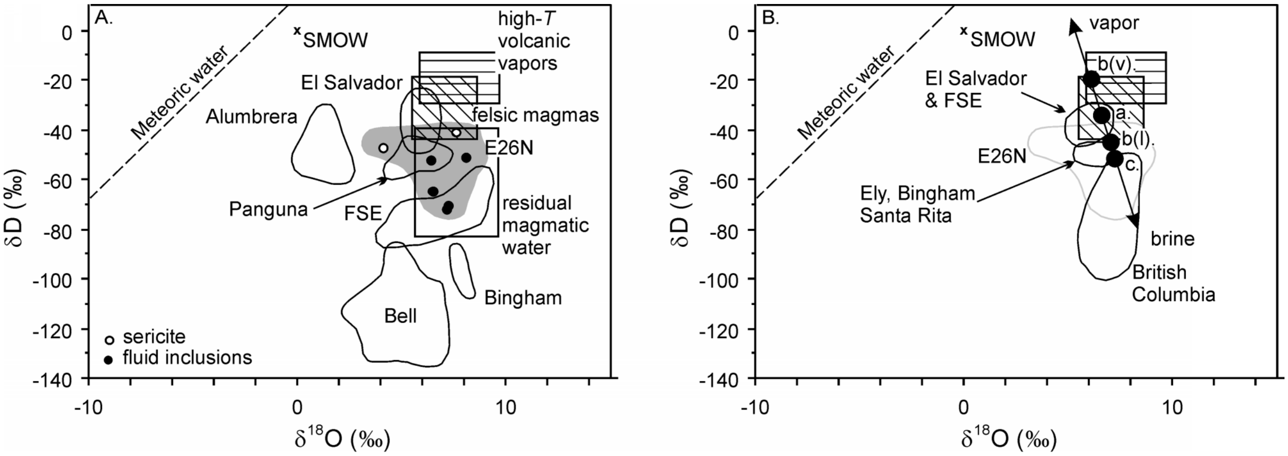

Figure 1. A: Comparison of δD and δ^{18}O values of fluid compositions associated with phyllic alteration in porphyry-related deposits (modified after Taylor, 1997, and references therein; including data from Zaluski et al., 1994; Hedenquist et al., 1998; Ulrich et al., 2001; and this study); E26N data are shaded. Ranges of residual magmatic water, i.e., that remaining in intrusion after degassing and crystallization (Taylor, 1974), compositions of water initially dissolved in felsic melts (Taylor, 1992), and low-salinity vapor discharges from high-temperature (*T*) volcanic fumaroles (Giggenbach, 1992) are also shown and discussed in text. B: Isotopic compositions of fluid associated with potassic alteration (modified after Hedenquist et al., 1998). Refer to text for discussion of marked points (calculated after Shmulovich et al., 1999). Isotopic composition of phyllic alteration for E26N is plotted for comparison.

salt (halite ± sylvite ± unidentified daughter crystal); and (3) vapor + liquid + salt + opaque phase (chalcopyrite and/or hematite).

There is no difference in the distribution of the different inclusion types between the early potassic alteration and the quartz-sericite-anhydrite alteration. However, there is a general decrease in the total salinity (from ~80 to 70 wt%) and NaCl/KCl ratio (from 1.05 to 0.92) with evolution of the hydrothermal system. The wide range of salinities for individual alteration assemblages may correspond to phase separation (>650 °C), which led to local increases in the total salinity of the magmatic brines.

Homogenization temperatures range from 550 to 640 °C for the early potassic alteration and from 370 to 560 °C for quartz-sericite veining (Table 1). As with most porphyry Cu and Cu-Au deposits (Beane and Bodnar, 1995), early potassic alteration at E26N is characterized by high-temperature, high-salinity inclusions (42 wt% NaCl; 40 wt% KCl; 18 wt% H_2O) derived from magmatic fluids. However, the occurrence of high-temperature and high-salinity inclusions (35 wt% NaCl; 38 wt% KCl; 27 wt% H_2O) in the quartz-sericite veins is not considered to be typical for porphyry deposits, and may also suggest a magmatic origin for such phyllic alteration. This differs from the previous thinking that the sericite stage formed as the result of meteoric water overprinting of the early magmatic system (Taylor, 1997). Phyllic alteration along faults and fractures at E26N is characterized by secondary fluid-inclusion populations that are low temperature (240–320 °C), low salinity, and liquid rich, more characteristic of mixing between meteoric and magmatic fluids (Beane and Titley, 1981) or just the thermal collapse of the magmatic-hydrothermal system (Shinohara and Hedenquist, 1997).

TABLE 1. STABLE ISOTOPE RESULTS FOR VEINING AND ALTERATION STAGES AT E26N

Vein and alteration stage	Th (°C)	Tmd* (°C)	Mineral	Measured† δ^{18}O (‰)	Measured† δD (‰)	Calculated fluid compositions# δ^{18}O (‰)	Calculated fluid compositions# δD (‰)
1. Early K-silicate alteration Kfps + Bt ± Mag ± Ser ± Bn	N.D.			N.D.	N.D.		
2. K-silicate alteration and veining Qtz + Kfps ± Bt ± Mag ± Anhy ± Bn	550–640	600–640	Qtz	9.2	N.D.	8.1–8.5	N.D.
3. Main stage phyllic alteration and veining Qtz + Anhy + Ser + Cpy ± Gyp	370–560	470–500	Qtz	8.4	N.D.	5.7–6.1	N.D.
			Ser	4.7	−66	4.3–4.6	−45 to −48
			Ser	7.8	−62	7.5–7.8	−41 to −44
			Qtz	9.9	−57	7.2–7.6	−57
		530–560	Qtz	8.3	−58	6.4–6.8	−58
			Qtz	8.9	−73	7.0–7.4	−73
		460–480	Qtz	8.4	−63	5.5–5.8	−63
			Qtz	8.0	N.D.	5.1–5.4	N.D.
4. Late stage phyllic alteration Py ± Anhy/Gyp + Ser ± Gn ± Sp	240–320	300–320	Qtz	9.5	N.D.	1.9–3.4	N.D.
5. Anhy/Gyp + Ser fracture fills	N.D.			N.D	N.D.		

*Model temperature range, taken as the mean to maximum of the sample fluid inclusion homogenization temperatures.

†Analytical uncertainties are < ±0.2‰ (1 standard deviation) for silicate oxygen isotope analyses and ±3‰ (1 standard deviation) for silicate and inclusion hydrogen isotope analyses.

#Calculated δ^{18}O fluid composition from quartz is determined using Matsuhisa et al. (1979) mineral-fluid fractionation factor, while δ^{18}O and δD for sericite are determined using O'Neil and Taylor (1969) and Suzuoki and Epstein (1976), respectively.

Abbreviations: Qtz = quartz, Kfsp = K-feldspar, Ser = sericite, Gyp = gypsum, Anhy = anhydrite, Py = pyrite, Bn = bornite, Cpy = chalcopyrite, Gn = galena, Sp = sphalerite, N.D. = no data.

The temporal change from hypersaline fluids associated with early potassic alteration to lower salinity fluids and associated phyllic alteration in most porphyry Cu deposits has been attributed to dilution of the magmatic fluids with meteoric water (Henley and McNabb, 1978). As an alternative to this model, Shinohara and Hedenquist (1997) proposed that the early crystallization of a magma chamber releases a hypersaline brine and low-salinity vapor that form potassic and advanced argillic alteration, respectively. Subsequent crystallization leads to the escape of lesser amounts of low-salinity aqueous magmatic fluids. As these fluids ascend and cool they may travel along a pressure-temperature path that does not intersect their solvus, and in doing so retain the bulk salinity of the original magmatic fluid (Shinohara and Hedenquist, 1997). These low-salinity magmatic fluids will not only result in phyllic alteration through K-metasomatism as the fluids cool, but they may also carry significant concentration of metals (Hedenquist and Richards, 1998).

OXYGEN AND HYDROGEN ISOTOPE RESULTS

The δ^{18}O and δD of sericite and δ^{18}O of quartz and δD of fluid inclusions in quartz range from 4.7‰ to 9.9‰ and from −57‰ to −73‰ (Table 1), respectively, in veins from main-stage, mineralized phyllic (quartz-sericite-anhydrite) alteration (stage 3). Calculated isotopic fluid compositions of the alteration minerals are most similar to K-silicate alteration of other porphyry Cu and Cu-Au deposits, in that the bulk of the samples plot within the magmatic water box (Fig. 1A).

Hedenquist et al. (1998) argued that magmatic water as defined by Taylor (1974) is more appropriately termed residual magmatic water, because it is the water left in a magma upon complete crystallization, i.e., after the majority of the water has exsolved. A simple mass balance demonstrates this. Magmatic fluid that discharges from volcanic fumaroles has a relatively enriched δD composition, ∼−20‰ ± 10‰ (Giggenbach, 1992), and the initial melt compositions are between −20‰ and −45‰ (Taylor, 1992). If the typical aqueous fluid-melt fractionation factor (∼20‰; Suzuki and Epstein, 1976) is appropriate, clearly an isotopically depleted fluid remains in the crystallizing magma (Taylor, 1986). The residual, depleted δD fluid will be incorporated in hydroxyl-bearing minerals and/or degassed at a later stage (e.g., Taylor et al., 1983). Continued magma degassing may explain large variations and/or strong depletion of δD (Taylor, 1988) in potassic and phyllic alteration of some porphyry Cu-Au deposits (Fig. 1).

If the exsolved magmatic fluid intersects its solvus, hypersaline liquid and vapor form. Further isotopic fractionation occurs during such boiling (e.g., Horita et al., 1995). We demonstrate this through modeling the evolution of an originally single-phase magmatic fluid with an initial fluid composition of 6.5‰ $\delta^{18}O$ and −35‰ δD, and ∼10 wt% NaCl at 550 °C (point a in Fig. 1B). As the fluid reaches its solvus, the fluid becomes immiscible and vapor-liquid separation occurs. The vapor has an isotopic composition similar to that exsolved from volcanic fumaroles (Shmulovich et al., 1999). The formation of hydrous minerals through reaction with this vapor will produce mineral assemblages that are enriched in D and depleted in ^{18}O [b(v) in Fig. 1B], whereas reactions with the separated brine would give the opposite effect [b(l) in Fig. 1B]. Subsequent cooling of the brine will result in further depletion of D and ^{16}O as the solvus closes (c in Fig. 1B; e.g., Shmulovich et al., 1999). However, wall-rock interaction and finite reservoir effects will tend to deplete the $\delta^{18}O$ fluid composition (Pollard et al., 1991). These competing mechanisms for isotopic fractionation can explain many of the calculated fluid D and ^{18}O compositions in porphyry-related phyllic alteration (Fig. 1B).

OTHER EXAMPLES OF MAGMATIC-FLUID–RELATED PHYLLIC ALTERATION

In their study of the Rio Blanco, El Teniente, and El Salvador deposits of the central Andes, Kusakabe et al. (1990) found that the transition from early potassic into phyllic alteration was accompanied by an enriched δD isotopic composition of the alteration minerals (∼−53‰ to −30‰ δD). They concluded that the phyllic alteration minerals formed through reaction with an evolved magmatic fluid enriched in D as a result of the previous formation of a hydrous potassic alteration assemblage (Kusakabe et al., 1990). Alternatively, these enriched δD values could occur through interaction with an exsolved magmatic vapor.

Stable isotope and fluid-inclusion data for the Panguna porphyry Cu-Au deposit, Bougainville Island (Ford and Green, 1977; Eastoe, 1978), indicate that early potassic alteration resulted from high-temperature (≥500 °C) and high-salinity magmatic fluids. A decline in temperature (500–380 °C), salinity, and the NaCl/KCl ratio of the hydrothermal fluids led to the onset of main-stage quartz veining and Cu-Au mineralization. Associated chlorite-sericite alteration is inferred to be either synchronous with or immediately postdate potassic alteration. Calculated fluid compositions (5‰–8.2‰ $\delta^{18}O$, −39‰ to −53‰ δD) indicate that this alteration probably developed from magmatic, not meteoric, fluids (Fig. 1). Ford and Green (1977) also emphasized this point, stating that they felt it was highly optimistic to propose a meteoric-hydrothermal source for the main-stage phyllic alteration.

At the Far Southeast porphyry Cu-Au deposit, Philippines, Hedenquist et al. (1998) proposed that the isotopic composition of fluid responsible for phyllic alteration (7.7‰–8.8‰ $\delta^{18}O$, −58‰ to −75‰ δD) was the result of late degassed magmatic fluid, which was depleted in D relative to that responsible for potassic alteration. The potassic to phyllic transition was marked by a sharp decline in temperature (≥500 °C to <350 °C), salinity (∼50 to <7 wt% NaCl), and pressure from lithostatic to hydrostatic, interpreted to reflect a lower rate of fluid advection from the magma that precluded phase separation (Shinohara and Hedenquist, 1997).

IMPLICATION FOR THE GENESIS OF PORPHYRY Cu-Au DEPOSITS

We have documented that high-temperature and hypersaline fluids are responsible for both the early K-feldspar-biotite (potassic) and overprinting quartz-sericite-anhydrite (phyllic) alteration at E26N porphyry Cu-Au deposit. Although this differs from the traditional porphyry model, where phyllic alteration is peripheral to mineralized potassic alteration (Beane and Bodnar, 1995), it is not unique. Cu-Fe sulfide- and Au-bearing phyllic alteration (sericite-quartz-anhydrite ± illite-chlorite) within and not peripheral to the potassic (biotite ± K-feldspar) altered core has been documented at Alumbrera (Ulrich et al., 2001), Panguna (Ford and Green, 1977), Granisle and Bell (Wilson et al., 1980), El Teniente and Rio Blanco (Kusakabe et al., 1990), Far Southeast (Hedenquist et al., 1998), and Chuquicamata (Ossandon et al., 2001).

At E26N and other porphyry Cu-Au deposits, the transition from early potassic to the main-stage phyllic alteration is associated with fluids that with time declined in total salinity, NaCl/KCl, and temperatures from 700 °C to those <550 °C and as low as 250 °C. Quartz saturation occurred at temperatures above 600 °C, with sufficiently high $a(K^+)/a(H^+)$ to initially stabilize K-feldspar. A decline in temperature and $a(K^+)/a(H^+)$ of the magmatic fluid led to sericite becoming the predominant K-silicate phase during subsequent veining events (e.g., Hemley and Hunt, 1992). At these high temperatures (350 to >700 °C), in relatively oxidized (fO_2 ∼NNO to HM buffer) hydrothermal brines, Cu may be transported as an aqueous chloride complex ($CuCl^0$) (Williams et al., 1995, and references therein). Any changes in temperature, pH, and/or oxygen fugacity will result in deposition of Cu-Fe sulfides and Au (e.g., Hezarkhani and Williams-Jones, 1998; Ulrich et al., 2001). The presence of economic levels of Cu-Fe sulfides and Au in phyllic alteration from a number of porphyry deposits would imply that ore metals are exsolved from the magma, rather than sequestered from the wall rock it overprints.

We conclude that mineralization during phyllic alteration in porphyry-related deposits can be generated solely from cooling of exsolved magmatic brines. Furthermore, the thermal and pH conditions required for feldspar destructive alteration need not be a result of meteoric and magmatic fluid mixing, but simply reflect cooling of these exsolved magmatic brines. Although meteoric fluid may mix with magmatic fluids, major incursion occurs only after the advection of magmatic fluid has largely waned. That phyllic alteration in porphyry deposits may be produced from magmatic fluids was long overlooked in genetic models. This was in part due to the voluminous literature published on North American porphyry Cu deposits, where it has been demonstrated that meteoric waters may play a major role (Taylor, 1997, and references therein). However, globally there is increasing evidence relating phyllic alteration predominately to magmatic fluids (e.g., Hedenquist et al., 1998; Richards et al., 1998). This supports a continuum between high-temperature magmatic and lower temperature meteoric water–dominated hydrothermal systems in the formation of phyllic alteration. The recognition of high-temperature phyllic alteration during exploration is important because it means that the distribution of alteration zones and mineralization may not fit the expected alteration pattern so often used to focus drilling programs in porphyry environments.

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