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# The formation of economic porphyry copper (-gold) deposits: Constraints from microanalysis of fluid and melt inclusions

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**Abstract**

This paper summarises our current understanding of the formation of porphyry-style Cu ± Au ± Mo deposits, in the light of data obtained by direct analysis of the ore metals in individual fluid and melt inclusions using laser-ablation ICP mass spectrometry. An integrated study of the evolution of the calc-alkaline Farallón Negro Volcanic Complex hosting the Bajo de la Alumbrera porphyry-Cu-Au deposit (Argentina), and supplementary fluid-chemical data from Bingham (Utah) and other examples, permit a quantitative re-assessment of the fundamental processes controlling the key economic parameters of porphyry-style ore deposits. Deposit size (total metal content) is optimised by exsolution of a relatively dense (> 0.3 g/cm$^3$) single-phase fluid or a two-phase brine + vapour mixture from a moderately large hydrous pluton, possibly with an intermediate step involving the scavenging of the ore-forming elements in a magmatic sulphide melt. Emplacement mechanism, magma-chamber dynamics and possibly an additional source of sulphur are probably more decisive for the formation of a large deposit than sheer pluton volume and elevated Cu contents in the melts. Primary bulk ore grade is determined by temperature-controlled precipitation of ore minerals, which is optimised where a large magmatic fluid flux is cooled through 420 – 320°C over a restricted vertical flow distance. Bulk metal ratios of the deposits, exemplified by the economically important Au/Cu ratio in the ore, are primarily controlled by the magmatic source defining the composition of the fluids before they reach the deposit site, although selective precipitation may contribute to metal zoning within orebodies.

## Introduction

Porphyry-style ore deposits constitute our main source of copper and molybdenum and they contribute significant resources of gold and other rare metals such as rhenium. They are the economically most important type of hydrothermal deposits that are related directly to hydrous magmas, through a process that is simple in principle but complex in detail — thus giving rise to many variants in composition, age, tectonic setting, structural style, and dominant host rocks among different porphyry ore deposits (Burnham and Ohmoto, 1980; Titley and Beane, 1981; Hedenquist and Lowenstern, 1994; Sillitoe, 1973, 1997). In broad terms, all porphyry-style deposits owe their origin to hydrous mantle-derived or lower-crustal melts, usually forming near convergent ocean-to-continent plate boundaries, followed by their ascent and emplacement as intermediate-composition magmas in the upper crust. Here, magma crystallisation and decompression drive the exsolution of excess volatiles, in the form of magmatic-hydrothermal fluids composed dominantly of water and chloride salts. This fluid exsolution is a first major step in the selective enrichment of ore metals and sulphur, compared to the parent magma and its melting source region (Candela, 1989; Dilles, 1987; Cline and Bodnar, 1991). For the second metal-enrichment step in the formation of an economic orebody, the magmatic-hydrothermal fluids must be focussed from a large volume of magma into a confined fracture network, which often develops in or above an apophysis or subvolcanic stock in the roof of an upper-crustal intrusion (Titley and Beane, 1981; Proffett and Dilles, 1984; Dilles and Einaudi, 1992). Metals are concentrated by precipitation of ore minerals in a relatively small volume of intensely fractured and chemically altered rock, by a combination of physical and chemical processes that may include fluid decompression and throttling at the lithostatic to hydrostatic transition, phase separation and adiabatic cooling, heat exchange and mixing of magmatic with surface-derived fluids, and chemical reaction of the fluids with the wall-rocks (Burnham and Ohmoto, 1980; Fournier, 1999).

Successive steps of chemical redistribution of ore metals — first from silicate magma to ore fluids, and finally from ore fluids to metallic minerals — are the key to economic ore formation (before supergene upgrading which is important for some deposits but not discussed in this paper). Abundant analytical data about ore-metal concentrations in magmatic source rocks and hydrothermal ore samples exist, but information about the concentration and speciation of metals in the mobile phases (silicate melts, locally occurring igneous sulphide melts, and various types of

hydrothermal fluids) are more limited. A considerable level of understanding of the chemical behaviour of ore metals has been achieved by high-temperature experimental studies of chloride, sulphur and metal partitioning between silicate melts and saline fluids (e.g., Burnham, 1979; Bodnar et al., 1985; Candela, 1989; Carroll and Webster, 1994; Williams et al., 1995), and by measurements of the volatility and solubility of ore minerals at subsolidus temperatures (Zotov et al., 1995; Williams-Jones et al., 2002; Stefánsson and Seward, 2004; Liu et al., 2001).

Only recently, extensive and systematic data are becoming available about the actual concentrations of ore metals in natural magmatic melts and evolving hydrothermal fluids, thanks to technical progress in the development of microanalytical techniques for analysing fluid and melt inclusions. Texturally-controlled analysis of individual inclusions is now possible by micro-PIXE (Ryan et al., 1991), Synchrotron-XRF (Vanko and Mavrogenes, 1998), and especially by laser-ablation ICP mass-spectrometry (LA-ICPMS; Günther et al., 1998; Heinrich et al., 2003), which is currently the most efficient and sensitive technique for studying metal concentrations in single fluid and melt inclusions at parts-per-million or even lower levels (Fig. 1). Following initial application of this technique to a granite-related Sn-W system (Audétat et al., 2000), LA-ICPMS has been used for studying several porphyry-type ore deposits, permitting analysis not only of Cu, Mo and other major and trace-elements, but also of Au in single fluid inclusions (Landtwing et al., 2004; Rusk et al., 2004; Ulrich et al., 2001; Ulrich et al., 1999). Thanks to the ability of representative sampling and effective homogenisation of the bulk element content even of heterogeneous inclusions, LA-ICPMS is suited for quantitative analysis of fluid inclusions with daughter crystals and glassy as well as crystallised melt inclusions (Halter et al., 2002a; Heinrich et al., 2003; Fig. 1).

This paper presents a summary of observations and conclusions obtained from quantitative studies of fluids in porphyry deposits, as well as silicate and sulphide melts in associated magmatic rocks. The main focus is on processes in the Farallón Negro Volcanic Complex in NW Argentina (Fig. 2), where detailed geological data about long-term magma evolution from melt inclusions (Halter et al., 2002b, 2004a, b; Harris et al., 2004) can be combined with mine-scale observations of the geology and compositional evolution of ore fluids in the Bajo de la Alumbrera porphyry-Cu-Au-(Mo) deposit (Sasso and Clark, 1998; Ulrich et al., 2001; Ulrich and Heinrich, 2001; Harris et al., 2003; Proffett, 2003; Fig. 3). These observations are supplemented by cathodoluminescence petrography and fluid inclusion analyses from Bingham (Utah; Redmond et al., 2004; Landtwing et

al., 2004) and reconnaissance studies of other porphyry-style deposits of variable metal proportion (Ulrich et al., 1999; Kehayov et al., 2003; Rusk et al., 2004). Conclusions regarding the basic economic parameters of porphyry-style ore deposits will be discussed in turn: Deposit size or total metal content, bulk ore grade or degree of metal enrichment, and proportion of economic metals such the Au/Cu ratio.

**Magma-chamber evolution and deposit size**

The size of a porphyry-style ore deposit, i.e., the total mass of metal enriched in a mineable orebody volume, varies from typical values of ~ 1 Mt copper, 0.1 Mt molybdenum or 10 t gold in presently operating small to medium-sized mines, to ~100 Mt Cu (El Teniente; Camus and Dilles, 2001), ~ 1.6 Mt Mo (Climax; Carten et al., 1993), or ~ 1000 t Au + 20 Mt Cu (Bingham; Krahulec, 1997) in some of the worlds biggest deposits of their kind. Explaining these variations and the formation of several of the very largest deposits within certain provinces and during short periods of the Earth's history has remained one of the most elusive questions in global metallogeny. For example, how could 9 of the 16 biggest porphyry Cu deposits of the Circumpacific Belt be formed in Chile within two short time periods between 40 – 30 and between 9 – 5 Ma years ago (Camus and Dilles, 2001)? On a global to province-scale, the answer probably lies in the tectonic architecture of interacting lithospheric plates and underlying asthenosphere, enabling the emplacement and evolution of hydrous magma reservoirs in the middle to upper crust (Richards, 2003). The size of a porphyry deposit depends on the dimensions of this magmatic source for fluids and ore-forming components, but also on the efficiency by which ore-metals are extracted into a fluid with the right physical and chemical properties for final concentration in an economic orebody. In a comprehensive study of the Farallón Negro Volcanic Complex of NW-Argentina, we have followed the ore-forming components through the compositional evolution of melt, mineral and fluid phases, to learn more about the processes in the source of porphyry-mineralising fluids and to constrain the metal mass-balance in the formation of the associated Cu-Au deposit of Bajo de la Alumbrera.

*Magma evolution and ore fluid generation in the Farallón Negro Volcanic Complex*

The Farallón Negro Volcanic Complex is a Late Miocene stratovolcano that has been eroded almost down to its base above Palaeozoic basement in the interior of the Andes of northwestern Argentina. Geological mapping, isotope geochemistry and geochronology (Llambías, 1972; Sillitoe, 1973; Sasso and Clark, 1998; Proffett, 2003; Halter et al., 2004a; Harris et al., 2004) document a history of dominantly basaltic-andesitic to later dacitic-rhyolitic, extrusive and subvolcanic intrusive activity (Fig. 2). Silicate melt inclusions reveal that the volumetrically predominant high-K andesites are hybrid magmas formed by mixing of a hydrous basaltic to lamprophyric melt (selectively recorded by melt inclusions in amphibole phenocrysts) and a dacitic to rhyolitic melt (recorded by melt inclusions in plagioclase and quartz phenocrysts, often together with amphibole in rocks of intermediate andesitic bulk composition; Fig. 4a; Halter et al., 2004b). The dacitic to rhyolitic melt component becomes more prominent in porphyries emplaced during the later stages of ~ 2.1 Ma of extrusive andesite volcanism. This compositional evolution is interpreted to reflect the gradual build-up of a subvolcanic magma chamber, which is not exposed but was probably internally heterogeneous (Fig. 2). The more mafic melts contain about 200 ppm Cu, and the copper content of all melt inclusions is about 5x higher than the bulk copper content of extrusive or intrusive rocks of similar silica content (Fig. 5; Halter et al., 2002b). All types of phenocrysts, constituting together about 30 vol% of most volcanic rocks, were analysed by LA-ICPMS and found to contain negligible concentrations of copper. These observations and the consistent difference between Cu in melts and in bulk rocks require that 60-80% of the copper initially present in the matrix melt of the andesitic rocks was lost during volcanic eruptions, probably to a low-density volatile phase.

The matrix of all fresh rocks is sulphide free, in contrast to most of the barren subvolcanic intrusions which preserve minute inclusions of iron-rich sulphide melt in amphibole phenocrysts. These sulphide melt inclusions are enriched in copper and gold (~ 0.8% Cu and 1 ppm Au; Halter et al., 2002b, 2004c; see Fig. 8, below), and coexist with almost totally Cu-depleted silicate melt inclusions in the same phenocrysts (Fig. 5, solid triangles). This indicates that Cu and Au were scavenged, at least transiently in some parts of the magma chamber, by sulphide melt droplets exsolving from an initially more Cu and probably Au rich mafic to intermediate silicate melt. Unless protected inside phenocrysts, the sulphide melt droplets in the silicate melt were

decomposed again during extrusive eruption and subvolcanic emplacement, as a result of desulphidation attending fluid saturation (Keith et al., 1997).

The Bajo de la Alumbrera deposit was formed by several pulses of porphyry emplacement and focussed magmatic fluid flow towards the end of this protracted igneous evolution. Ore formation required large-scale fluid saturation of the subvolcanic magma chamber and exsolution of a major quantity of a relatively dense magmatic fluid. This fluid is recorded by brines of ~ 50% NaCl (eq.) and ~ 0.3 wt% Cu, which were trapped in high-temperature inclusions found as widespread and compositionally consistent inclusion assemblages in quartz ± magnetite stockwork veins (Ulrich et al., 2001). Such veins successively cut three distinct porphyry phases, exhibiting decreasing intensities of veining and chalcopyrite ± bornite mineralisation (Fig 4b; Ulrich et al., 2001, based on deposit-scale geology by Proffett, 2003). These 50% salinity fluids were probably trapped initially in the single-phase fluid stability field at >600°C and confining pressures of >1 kb, whereas later brines were entrapped together with vapour inclusions on 'boiling trails', at lower pressures indicated by even higher brine salinities up to 70 wt% NaCl *equivalent* (similar to Fig. 4c). Assuming lithostatic conditions for the earliest brines, a minimum overburden of ~3 km above the deposit is required, irrespective of whether these brines exsolved directly from the underlying magma or were derived from an even deeper fluid precursor of intermediate salinity (cf. Bingham; Redmond et al., 2004). This pressure estimate is consistent with a projected stratigraphic thickness of 2.5-2.8 km at a position located ~ 3 km off the main centre of the preceding volcanic activity (Llambías 1972; Proffett, 2003). Geochronological data by U-Pb on zircons (Harris et al., 2004) and stepwise heating Ar-Ar methods (Sasso and Clark, 1998; Halter et al., 2004a) are consistent with porphyry emplacement and hydrothermal copper introduction some 0.4 Ma after cessation of extrusive volcanism, which had been terminated by dacitic volcanism and an inferred partial caldera collapse (Llambías, 1972; Halter et al., 2004a). This intervening period of volcanic quiescence probably allowed the magma chamber to evolve towards the final event of large-scale fluid saturation, metal extraction, and Cu-Au-mineralisation. Harris et al. (2004) suggested that the first, incompletely preserved but most richly mineralised porphyry event may have occurred ~1 My earlier, but the compositional and petrographic similarity of all mineralised porphyries (Proffett, 2003) and the possibility of zircon growth significantly before magma emplacement (Lowenstern et al., 2000; Oberli et al., 2004) are consisten with the interpretation that all three mineralised

porphyry phases have been emplaced in relatively short succession, after completion of extrusive magmatism (Halter et al., 2004a).

*Fluid source processes controlling the size of porphyry deposits*

The bulk Cu content of the Farallón Negro igneous rocks (Fig. 5) is quite typical for or even lower than that of many calcalkaline basaltic to dacitic rocks worldwide (e.g., Kesler, 1997; Kamenetsky et al., 2001), implying that bulk ore-metal contents even of fresh lavas are not a good indicator for the ore-forming potential of a magmatic complex. The observation that copper contents of the melts are significantly higher than those of the equivalent bulk rocks, without significant incorporation into phenocryst phases, shows that melt inclusions are a much better measure of ore metal availability. Our observations also imply that copper dispersion by low-density fumarolic vapour is probably the norm in calc-alkaline magmatism, consistent with significant copper transport in violently erupted volcanic gases (Taran et al., 1995) and local Cu enrichment in low-density vesicle fillings in lavas and melt inclusions (Lowenstern, 1991, 1993). By contrast, the generation of a sufficiently dense ore fluid (~ 0.3 – 1 g/cm$^3$, depending on salinity) suitable for ore formation requires specific conditions of wholesale volatile saturation in a confined magma source volume at elevated pressures. The analysed copper contents in the silicate melt inclusions imply that quite moderate melt volumes are sufficient to source the copper contained in a large porphyry deposit. For example, ~15 km$^3$ of mixed magma with a density of 2.4 g/cm$^3$, containing 70% melt that loses 120 ppm Cu to an ore fluid upon crystallisation, would be adequate to source the ~ 3 Mt Cu contained in the Alumbrera orebody. This minimum estimate is lower than the actual magma volume involved, because the geological Cu resource is at least twice this value and sourcing the gold may well require a larger magma source (Ulrich et al., 1999). Nevertheless, the required magma volume is only a small fraction of the total quantity of magma produced during the lifetime of the Farallón Negro Volcanic Complex, which is estimated to be on the order of ~ 300 km$^3$ (Halter et al., 2004a). From the total volume of volcanics, about 80 Mt Cu (comparable to the metal content of the giant El Teniente deposit) must have been dispersed in the atmosphere or the local groundwater, prior to the event that formed the Alumbrera deposit.

The complete extraction of Cu from a silicate melt into a sulphide melt containing about 0.8% Cu requires an amount of sulphur that must be ~ 40x higher than the initial Cu content of the silicate melts. The estimated concentration of ~ 5000 ppm S probably exceeds the equilibrium

solubility of sulphur in any upper-crustal silicate melt, be it as sulphide in the mafic melt as sulphate in the felsic mixing component (Halter et al., 2004c). The presence of the Fe-S-rich sulphide melt inclusions associated with almost totally Cu-depleted silicate melts thus requires addition of sulphur to at least some parts of the complex magma chamber, and this unknown process could well be decisive for the formation of a large porphyry copper deposit. Sulphur addition may be effected by an $SO_2$ and/or $H_2S$-rich volatile phase ascending from depth (e.g., from a major volume of underlying mafic magma; cf. Wallace and Gerlach, 1994), or by addition of solid anhydrite from an unusually sulphate-rich felsic magma and its reduction to sulphide + magnetite attending magma mixing with the FeO-rich mafic magma (Halter et al., 2004c; see Fig. 2).

Combined observations from the Farallón Negro Volcanic Complex show that the physical and chemical processes of metal extraction from silicate melt into an effective ore fluid, and perhaps the availability of an additional sulphur source, are probably more decisive for the formation of a large porphyry deposit than sheer magma volume and total ore-metal availability. The potential chemical influence of sulphide melts as an intermediate metal scavenger (Spooner, 1993; Keith et al., 1997; Halter et al., 2002b) challenges the interpretation that optimal conditions for direct metal partitioning from the melt to the fluid occur in magmas that are so oxidised to be sulphide undersaturated (Dilles, 1987; Cline and Bodnar 1991; Core and Kesler, 2001; Audétat et al., 2004). Possibly more important than the presence or absence of igneous sulphide are the salinity, density and phase state of the hydrothermal fluid during volatile exsolution (Audétat and Pettke, 2003). Efficient metal partitioning of chloride-complexed metals including Cu, together with volatile sulphur species required for later Cu-Fe-sulphide precipitation, are favoured by initial fluid saturation of a magma with high Cl/OH at elevated pressure (probably >1 kbar in general; cf. Cline and Bodnar, 1991), yet not too deep to prevent efficient focussing into brittle structures by hydraulic fracturing in the upper crust (Burnham and Ohmoto, 1980; Fournier, 1999). Wholesale or convection-driven (Shinohara et al., 1995) fluid-saturation from a significant magma reservoir, at elevated pressures and without continual loss of magmas and low-density volatiles to the surface, seems to be a key physical prerequisite for generating a large volume of relatively dense (> 0.3 $g/cm^3$) fluid able to produce a large porphyry-Cu-(Mo-Au) deposit. Magma ponding, the exsolution of dense magmatic fluids, and transient accumulation of fluids in the top of the magma chamber, are all favoured by a neutral to compressive upper-crustal stress regime (Tosdal and Richards,

2001). As a result, many large porphyry deposits correlate with subduction reversals or tectonic basin inversions, and with the cessation of extrusive activity prior to hydrothermal ore formation (Solomon, 1990; Sillitoe, 1997; Camus and Dilles, 2001; Rohrlach, 2003; Halter et al., 2004a).

**Metal precipitation efficiency and ore grade**

The bulk ore grade of a deposit is defined as the fraction, in wt% Cu for example, of total metal contained in a certain mass of economically mineable ore. Primary ore grades in porphyry-copper deposits are affected by the typical complexity of intrusions containing variable metal concentrations introduced in multiple magma and fluid pulses (Fig. 4b). Commonly, the earliest mineralised porphyry contains the highest metal concentrations, and subsequent less-intensely mineralised porphyries contribute to overall ore dilution rather than to upgrading of copper concentrations, despite additional metal introduction (e.g., Gustafson and Hunt, 1975; Proffett, 2003; Redmond et al., 2004). Thus, Bingham partly owes its exceptionally high grade to a single dominant pulse of hydrothermal activity that mineralised the main Quartz Monzonite Porphyry, followed by volumetrically minor less-mineralised dykes (Redmond et al., 2004). The lower bulk grade of Alumbrera is partly due to the dilution of the most strongly mineralised 'P2' porphyry by volumetrically dominant but somewhat less intensely mineralised later porphyries. Sharp grade differences at intrusive contacts indicate that each mineralising magmatic-hydrothermal pulse was essentially completed before the next one started (Proffett, 2003). For one pulse of hydrothermal copper introduction into a fractured porphyry intrusion and its surrounding and overlying wall rocks, the resulting ore grade is a function of the efficiency of metal deposition within a certain ore volume (Fig. 6). For an approximately cylindrical orebody of any horizontal cross-section, upward focussing of magmatic fluid generates an integrated fluid flux corresponding to the total mass of available fluid ($m_{fluid}$) divided by the cross-section (A) of the mineralised ore zone, as indicated by equation (2) in Figure 6. Ore grade is related to the amount of initially dissolved metal focussed into this orebody volume ($m_{fluid} \cdot C_{Cu}^{fluid}$), and to the efficiency by which the advected metal is trapped within this volume by precipitation of hydrothermal ore minerals (precipitation efficiency, $X_{Cu}$). Equation 2 in Figure 6 further illustrates that ore grade is maximised by high precipitation efficiency over a preferably short flow distance (d), for a given cross-section of the orebody.

*Fluid evolution and Cu-Fe-sulphide precipitation at Alumbrera and Bingham*

LA-ICPMS microanalysis of fluid inclusions has provided extensive data on the initial concentration of Cu (and sometimes Au and Mo) as well as many other element concentrations in porphyry-mineralising fluids of highly variable density and total salinity. Single-phase fluids of near-critical density and a total salinity of 3-4 wt% NaCl eq., trapped in early stockwork quartz veins at Butte (Montana) contain about 1 wt% Cu as one of four dominant cations (Na, K, Fe and Cu; Rusk et al., 2004). Comparable compositions with regard to salinity and major cations including Cu are observed in vapour inclusion assemblages from Grasberg (Ulrich et al., 1999: ~ 1.2 %Cu), Bajo de la Alumbrera (Ulrich et al., 2001: up to 3% Cu), Bingham (Landtwing et al., 2004: Cu/Na ~ 0.8, with absolute concentrations less certain due to the presence of $CO_2$), and Elatsite (Bulgaria; Kehayov et al., 2003; ~ 2% Cu). In all orebodies except Butte, pre-sulphide quartz also contains high-salinity brine inclusions, indicating fluid phase separation well before the onset of ore-mineral precipitation, or introduction of hypersaline brine as an original single-phase fluid (Ulrich et al., 2001). These brines contain higher concentrations of Na, K and Fe in the form of chloride salts, but comparable or slightly lower Cu concentrations compared with coexisting vapour inclusions (average Alumbrera ~ 0.3, Grasberg ~ 0.3, Bingham ~ 0.8, Elatsite ~ 3 wt% Cu, with overlapping ranges; Heinrich et al., 1999). Locally, even higher Cu concentrations up to 10 wt% were measured (see also Harris et al., 2003), but such extreme values probably reflect local re-dissolution of existing copper sulphides by subsequent fluid pulses (Landtwing et al., 2004). Extensive LA-ICPMS data indicate that the input concentration of Cu in porphyry-copper forming ore fluids, of either phase state, is between 0.3 and 3 wt%. The copper content in the fluids is therefore of the same order of magnitude as typical ore grades in porphyry-Cu deposits (both in weight percent), implying that the minimum integrated fluid to rock ratio* attending porphyry mineralisation can be as small as 1 (Ulrich et al., 2001). Similarly modest integrated fluid/rock ratios were estimated for porphyry-related alteration reactions (Ulrich and Heinrich, 2001), which contrasts with the much higher minimum integrated fluid/rock ratios envisaged for metamorphic gold or sediment-hosted base metal deposits where metal concentrations in the fluid are assumed to be lower and therefore quantities of fluid required for ore formation are much higher. The relatively small amount of extremely metal-rich magmatic fluids involved in the formation of

* Mass of fluid required for ore formation, divided by the mass of rock in which all the advected and precipitated metal is trapped ($m_{fluid} / m_{ore} \sim m_{fluid}/r_{ore} \cdot A \cdot d$)

porphyry copper (-Au-Mo) deposits further emphasises the importance of processes at the magmatic source of such compositionally specialised fluids, but it also emphasises that ore formation requires an efficient and possibly quite selective metal-precipitation process.

In conjunction with petrographic and microthermometric data, quantitative LA-ICPMS microanalysis of fluids has helped us to clarify the mechanism and conditions of ore mineral precipitation at Bajo de la Alumbrera (Ulrich et al., 2001) and at Bingham (Landtwing et al., 2004). In both deposits, the precipitation of chalcopyrite and/or bornite with gold occurred after most of the quartz deposition in stockwork veins, as shown most clearly at Bingham thanks to extensive cathodoluminescence petrography (Redmond et al., 2004). Gold and Cu-Fe-sulphide co-precipitation was caused by cooling of a two-phase magmatic fluid (coexisting brine + vapour) within a narrow temperature interval. Sulphide precipitation is recorded by a decrease of two orders of magnitude in the copper concentration, in fluids containing essentially constant concentrations of all other, non-precipitating elements including chloride and Na, K, Rb, Cs, Zn, Pb and others. The variation in Cu content in the fluids trapped at one location is therefore interpreted to reflect the larger-scale evolution of a fluid of essentially constant input composition flowing through the region of ore deposition. While textural relations of the analysed fluids at Alumbrera were somewhat ambiguous due to the complex intrusion history (Ulrich and Heinrich, 2001), more clearcut relations between fluids and minerals are documented at Bingham (Redmond et al., 2004; Landtwing et al., 2004), as summarised in Figure 7.

Cathodoluminescence petrography of main stockwork veins at Bingham (Fig. 7a) reveals a consistent separation of an early bright luminescing quartz generation that predates the deposition of bornite, chalcopyrite and texturally associated gold, from a later generation of dull-luminescing quartz that largely postdates metal precipitation (Fig. 7a), similar to observations in quartz - molybdenite veins at Butte made by Rusk and Reed (2002). A steep decrease in Cu concentration in otherwise identical fluids with falling homogenisation temperatures (Fig 7b) is recorded by numerous assemblages of secondary brine inclusions in the pre-sulphide quartz. A decrease of similar magnitude in copper is also observed among coeval vapour inclusions hosted by the early quartz, and the vapour phase probably represented the dominant ore fluid in terms of absolute mass and metal contribution (Landtwing et al., 2004). The estimated pressure (200-500 bar) and temperature interval in which Cu is extracted from the fluid (410-350°C) corresponds to the P-T

region where quartz solubility is retrograde (i.e., quartz becomes more soluble with cooling; Fournier and Thompson, 1993; Manning, 1994) while Cu-Fe-sulphide solubility steeply decreases with falling temperature (Hezarkhani et al., 1999; Liu et al., 2001 and unpubl. data). Ore deposition was facilitated by textural reactivation of the stockwork veins and the generation of secondary permeability, into which the ore metals were precipitated without the obstruction of co-precipitating gangue minerals. After fluid throughput had waned, post-ore dull-luminescing quartz finally re-cemented the veins by local re-equilibration of pore fluids at slightly lower temperature, with local grain boundary adjustment between quartz crystals and the typically anhedral Cu-Fe-sulphides. Some of these fluids still have variably high copper contents, interpreted to reflect final cooling during occlusion of the remaining pore space, by increasingly acid fluids in contact with Cu-sulphides but isolated from pH buffers in the wall rock (Rusk and Reed, 2002; Redmond et al. 2004; Landtwing et al., 2004).

*Fluid cooling as the first-order factor controlling ore grade*

The recent results from Bingham confirm the original conclusion from Bajo de la Alumbrera (Ulrich et al., 2001) and reconnaissance data from Elatsite (Kehayov et al., 2003), indicating that fluid cooling through a small interval at relatively low temperatures is the main driving force for copper ± gold deposition in porphyry deposits. This is in agreement with experimental evidence, which is reliable at least with regard to the steep temperature dependence of Cu-Fe-sulphide solubility. Experimental solubility data would have to be wrong by many orders of magnitude to permit Cu-Fe-sulphide saturation at temperatures above 700°C, as suggested by Harris et al. (2004) on the basis of a few high-temperature inclusions with highly variable copper contents. At Butte, single-phase fluids of intermediate density precipitated chalcopyrite + pyrite at somewhat higher pressures, prior to phase separation into brine and vapour. Ore deposition was associated with sericite alteration of plagioclase-rich rocks, which is indicated by an antithetic correlation between Na and Cu in the ore-depositing fluids (Rusk et al., 2004). Temperatures are less well-defined in the single-phase field and may be a little higher than 420°C, but fluid cooling is again likely to drive acid-consuming alteration reactions, which in turn are likely to drive Cu-precipitation by $H^+$ neutralisation (Rusk and Reed, 2002; cf. Hemley et al., 1992). None of the deposits studied so far show any evidence for fluid mixing by incursion of meteoric water into the forming orebody, before or during Cu-Fe-sulphide and gold precipitation.

Evidence for temperature-controlled sulphide precipitation and the principles defined in Figure 6 lead to the conclusion that ore grade is maximised, to a first order, by steep temperature gradients ($\Delta T/\Delta d$) along the pathway of the focussed magmatic fluids. This conclusion is based on observed fluid-compositional constraints and locally recorded temperature variations alone, and therefore does not say anything about the physical mechanism by which fluid cooling is effected at the scale of the ore-forming fluid system. Fluid cooling in a region of focussed magmatic fluid flow is severely limited by the slow rate of heat transfer to surrounding rocks of low thermal conductivity (Barton and Toulmin, 1961; Hayba and Ingebritsen, 1997). Efficient metal precipitation thus requires a sensitive balance between solution chemistry and physical processes. Mechanisms contributing to fluid cooling include adiabatic expansion in the two-phase fluid stability field and heat exchange with externally convecting, but probably not admixing meteoric water. Our fluid-chemical findings imply more generally that the hydrology and thermal structure of the magmatic fluid plume flowing through the porphyry-style vein network has a primary influence on ore grade. This will be strongly influenced by the actual geometry of the system (e.g. cylindrical or dyke-shaped; vein permeability within, surrounding and above the magmatic feeder intrusion) and by the hydraulic characteristics of the surrounding country rocks. Geological situations permitting highly efficient cooling of a large but chemically isolated flux of magmatic fluid over a short flow distance along the vein network will maximise ore grade. Fluid and rock dynamics modelling including two-phase hydrosaline fluid convection is in progress (Geiger et al., 2004; Heinrich et al., 2004b), to investigate the key physical parameters including rate of fluid flow from the pluton, initial fluid salinity, depth of mineralisation, and the pressure evolution from lithostatic to hydrostatic conditions.

**Bulk metal ratios in porphyry deposits**

We have investigated the causes leading to variable metal ratios, in particular the economically important and geologically intriguing Au/Cu ratio of porphyry-style ore deposits, by studies of mine- to grain-scale ore metal distribution, and by comparing metal ratios in the ore with microanalyses of Au/Cu in fluid and melt inclusions. Extensive fluid-chemical data from Alumbrera (Ulrich et al., 2001) and reconnaissance data from Grasberg (Ulrich et al., 1999), Bingham (Landtwing, unpublished data) and Elatsite (Kehayov et al., 2003), consistently indicate that the bulk Au/Cu ratio of each ore deposit is similar to the average Au/Cu ratio of the incoming

ore fluids, trapped at high temperature prior to ore mineral saturation. Figure 8 shows the close correspondence between the bulk Au/Cu ratio in the Bajo de la Alumbrera orebody (Au/Cu $= 1.2 \cdot 10^{-4}$; Proffett, 2003) together with the highly correlated element ratios in individual assay samples from one drill section (Ulrich and Heinrich, 2001) and the Au/Cu concentrations in the interpreted pre-precipitation ore brines analysed by LA-ICPMS (Ulrich et al., 2001). In conjunction with the fluid-chemical evidence for copper sulphide precipitation at relatively low temperatures discussed above (Fig. 7b), this correlation between metal ratios in fluid and ore indicates that the magmatic source of the ore fluid is the first-order factor determining the metal ratios of the deposit. Fluid inclusion analyses indicating relatively low precipitation temperatures for copper (and by inference also of the texturally associated gold; Fig. 8) in the Alumbrera and Bingham porphyry-Cu-Au deposits do not support the suggestion of Kesler et al. (2002), that systematically higher ore-deposition temperatures are the main cause for the formation of gold-rich porphyry deposits, by incorporation of gold into chalocopyrite and particularly into bornite solid solution at higher temperatures (Simon et al., 2000). Selective precipitation can lead to zoning of mineralogy and Au/Cu ratios within porphyry orebodies (e.g., Redmond et al, 2004), but the overall gold-rich or gold-poor nature of porphyry deposits is determined by processes in the magmatic source of the fluids.

This conclusion from fluid inclusion analyses at the deposit scale, and published evidence for a first-order source control on metal ratios in magmatic-hydrothermal ore deposits at the province scale (e. g., Kesler, 1997), was one of the motivations for our study of the evolution of the Farallón Negro Volcanic Complex at the scale of an entire magmatic-hydrothermal system. The discovery by Halter et al. (2002b), that sulphide melt inclusions in barren porphyries pre- and postdating hydrothermal mineralization in this magmatic complex also contain Au and Cu in the same proportions as the ore fluids and as the bulk ore at Bajo de la Alumbrera (Fig. 7), clearly confirms that magmatic source processes, operating at the scale of the subvolcanic magma chamber, are the first-order control the Au/Cu ratio of porphyry-style ore deposits.

Irrespective of whether igneous sulphide saturation contributes an essential intermediate metal enrichment step for economic ore formation or not, LA-ICPMS analysis of magmatic sulphide inclusions in phenocrysts of barren porphyries and dykes can be applied as a practical exploration indicator, for predicting the potential Au/Cu ratio of undiscovered porphyry deposits in a magmatic complex (Halter at al., 2004c).

## Summary and conclusions

Laser ablation ICPMS microanalysis has proven to be not only sensitive but also efficient enough for the systematic study of ore metal concentrations in assemblages of fluid and melt inclusions preserved in porphyry-mineralising magmatic-hydrothermal systems. Sample selection and interpretation of microanalytical results in petrographic context has been further improved with the recent use of SEM cathodoluminescence mapping of inclusion generations. Results have allowed the first documentations of spatial variability and temporal evolution of interacting fluids and melts in selected porphyry-mineralising hydrothermal systems, at scales from individual crystals to entire magmatic complexes. Much work remains to be done before we understand the processes of mixing and unmixing of up to four mobile phases in subvolcanic magma chambers — silicate melt, sulphide melt, brine and vapour — as well as their interaction with non-magmatic fluids.

Physical processes in an evolving magma chamber, generating a large transient flux of relatively dense single- or two-phase magmatic fluid — without gradual loss of metals to low-density volatiles attending volcanic eruption — is the key to generating economic deposits of *large metal content*; dispersed loss of volatiles and metals is probably the norm in calcalkaline magmatism. The mechanism of metal extraction into a relatively dense volatile phase is probably more important for generating large deposits than the sheer volume of magma, which can be smaller than previously thought in light of the high Cu content of un-devolatilised, mafic to intermediate hydrous melts.

The key to accumulating *high ore grade* in a restricted volume of rock is the high metal content of magmatic ore fluids (in the order of 1% Cu and 1ppm Au), and the precipitation of these metals by efficient cooling of a focussed fluid flux over a relatively small vertical flow distance. Ore deposition ideally happens at relatively low temperature (~400°C) and low pressure where Cu-Fe-sulphide solubility decreases exponentially while quartz solubility increases with cooling, leading to vein reactivation and the generation of secondary permeability in previously formed quartz veins. The physical mechanism of efficiently cooling a focussed fluid flux is a key to high ore grade, but remains poorly understood until hydrodynamic modelling of two-phase fluid flow can be applied to realistic geological scenarios.

Microanalytical results show that *Au/Cu ratios* in porphyry ores are determined by the metal ratio in the ore fluids entering the forming orebody, and therefore by the magmatic fluid source, but brine/vapour phase separation and selective mineral precipitation may lead to spatial zoning of metal ratios within porphyry orebodies or between porphyry-style and associated epithermal deposits (Heinrich et al., 2004a). A similar magmatic source control is indicated for Sn/W ratios in granite-related vein deposits (Audétat et al., 2000) but other element ratios including Mo/Cu remain to be investigated. Metal ratios in upper-crustal magma reservoirs are in turn controlled by the sources of contributing melts and fluids in the mantle and crust, and the new microanalytical techniques should ultimately lead to an understanding of transport processes and ore-metal variations at the scale of global metallogenic provinces.

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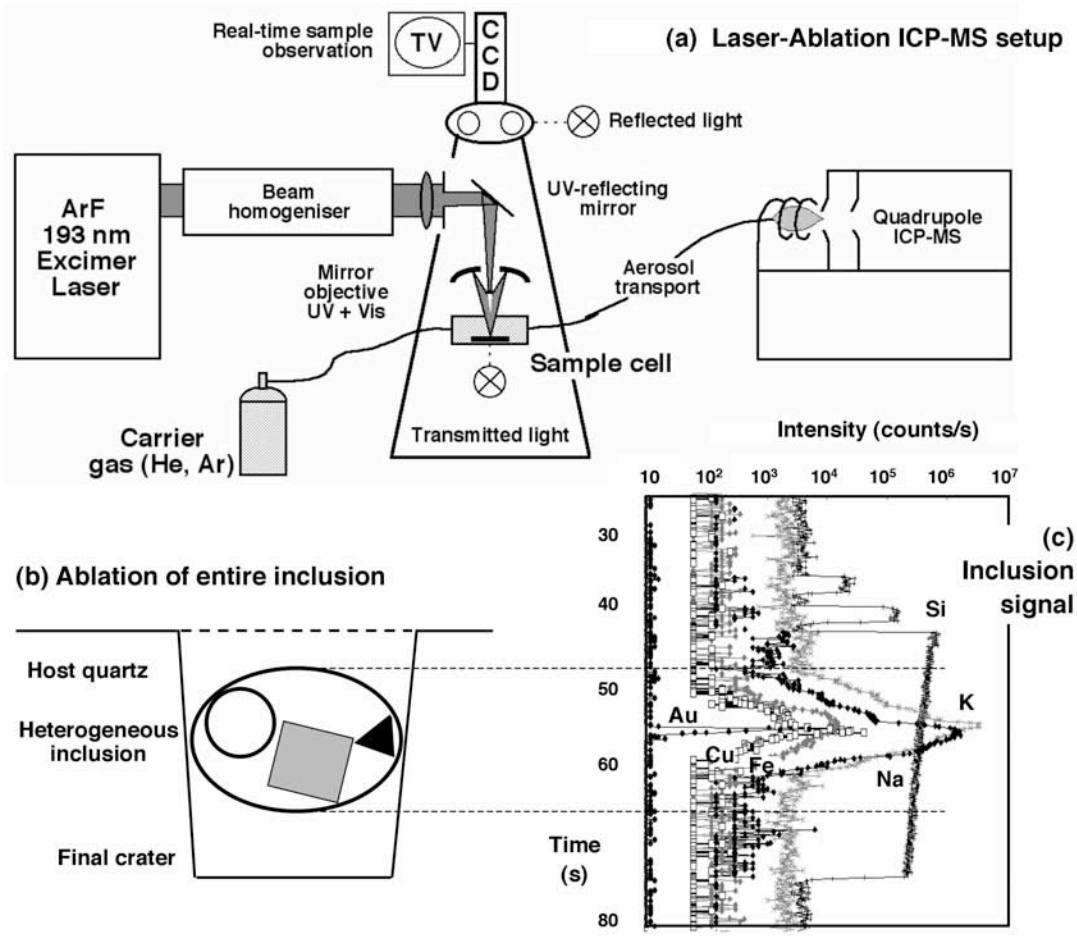


***Fig. 1***. *The principle of laser-ablation ICP mass spectrometric analysis of microscopic fluid and melt inclusions. (a) Schematic representation of experimental setup, using a UV laser whose high-energy photon beam (193 nm wavelength) is imaged onto the sample surface, using a mirror-optical microscope that allows concurrent observation of the sample in the visible wavelength range (a). The sample is a small mineral plate containing fluid or melt inclusions a few tens of microns under its polished surface (b). The circular ablation spot can be adjusted in size to that of the inclusion, typically between 8 and 40 microns in diameter. Successive ablation from a circular, flat-bottomed crater generates an aerosol in the small sample chamber, which is continually flushed by a carrier gas stream (pure He and/ or Ar) to the inductively-coupled plasma torch of a commercial quadrupole ICP mass spectrometer, where the multielement composition of the arerosol is recorded. Successive ablation of host mineral and inclusion from the deepening crater thus generates a time-resolved record of element intensities (c), starting with the pure host mineral (quartz in this case) followed by ablation of the inclusion contents. The inclusion represented by (c) contained a vapour bubble, a saline liquid phase and at least two daughter crystals that were precipitated internally during cooling from magmatic-hydrothermal temperatures (like the brine inclusions in Figure 4c, below). Although the halite (Na peak) and the Au-bearing copper sulphide daughter crystals (overlapping Au and Cu spikes) are clearly resolved from the broader Na and Cu signals originating from the elements dissolved in the aqueous liquid, time integration of element intensities and calibration using an external standard yields consistent element ratios in an assemblage of several coeval inclusions. Absolute element concentrations are calculated by combination of these ratios with the NaCl (wt% equivalent) salinity determined by microthermometry prior to ablation of the inclusion (modified from Heinrich et al., 2003).*

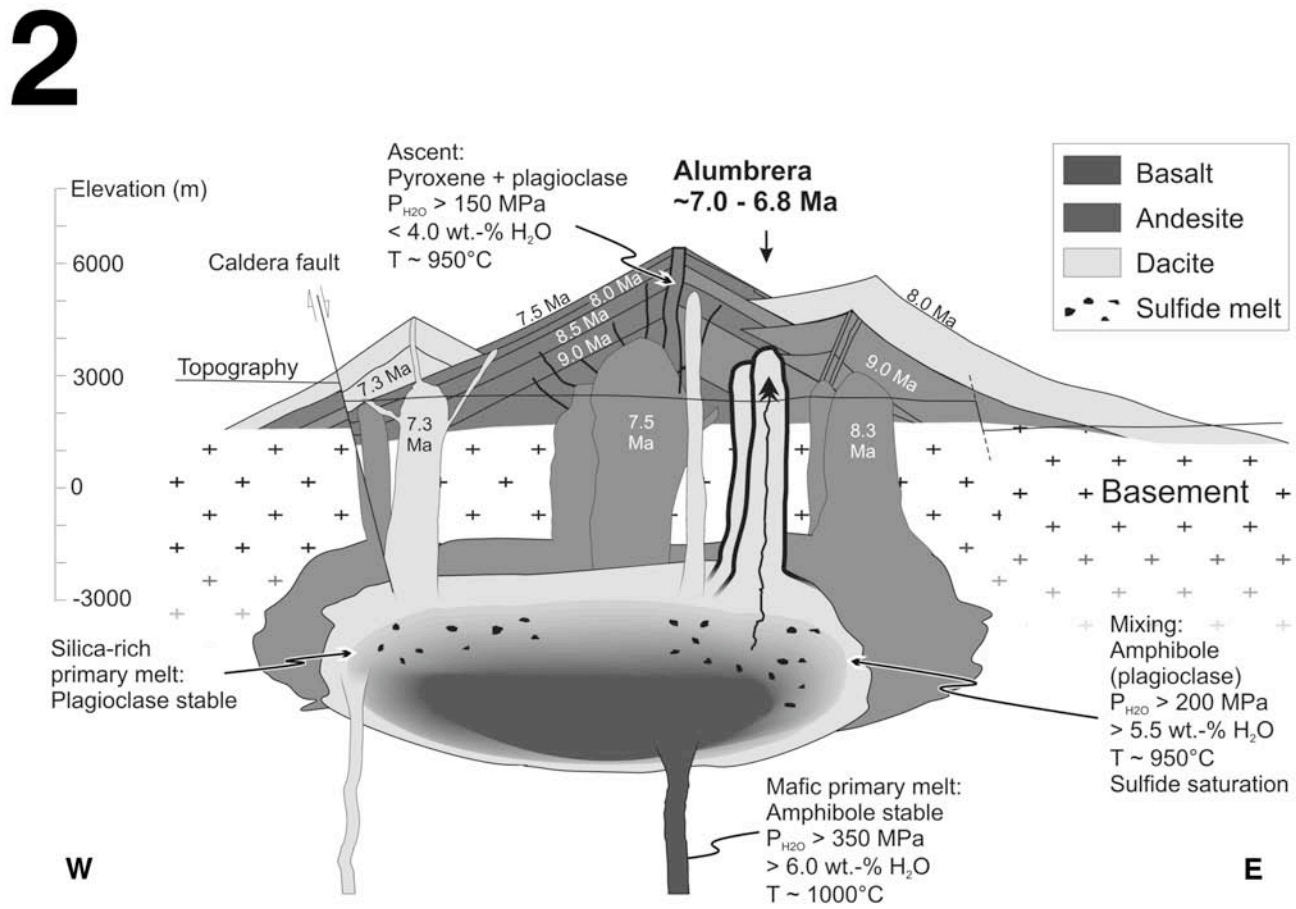


***Fig. 2.*** *Reconstructed cross-section of the Farallón Negro Volcanic Complex at the time of porphyry-Cu-Au mineralisation at Bajo de la Alumbrera, interpreted from stratigraphic mapping relations and geochronological constraints among extrusive and subvolcanic intrusive stocks. Bulk-rock and melt-inclusion compositional evidence indicates generation of andesitic rocks (grey) during magma ascent through an evolving, compositionally structured reservoirs in which dacitic (white) and hydrous basaltic magmas (black) mixed in variable proportions. A complex stratovolcano, whose main feeder had been west of Alumbrera during preceding volcanic activity, generated an estimated lithostatic fluid pressure of ~ 1 kb for pre-sulphide quartz – magnetite veining and potassic alteration, and variably lower temperatures during subsequent Cu-Fe-sulphide precipitation at hydrostatic or even vapourstatic conditions (Ulrich et al., 2001). The approximate size and location of the subvolcanic magma chamber at the time of mineralisation is inferred from petrologic and mass-balance constraints, and from field indications for a partial caldera collapse which terminated extrusive activity some 0.4 Ma before porphyry-Cu-Au formation (after Halter et al., 2004a, modified according to new drilling evidence for crystalline basement ~500 m below Bajo de la Alumbrera; S. Brown, pers. comm, 2004).*

***Fig 3.*** *View of the Bajo de la Alumbrera deposit in 1994, before mining started. The centre of intense quartz – magnetite veining, potassic alteration and high-grade Cu-Au mineralisation stands out as reddish-brown hills, surrounded by a wide halo of later feldspar-destructive alteration (phyllic-argillic; cream white). Bedded andesites, intruded and propylitically altered by the polyphase porphyry stock, crop out in the ring of dark hills around the Alumbrera depression. In the background, stratigraphically higher volcanics dip away towards the northern flank of the former stratovolcano.*

# 4

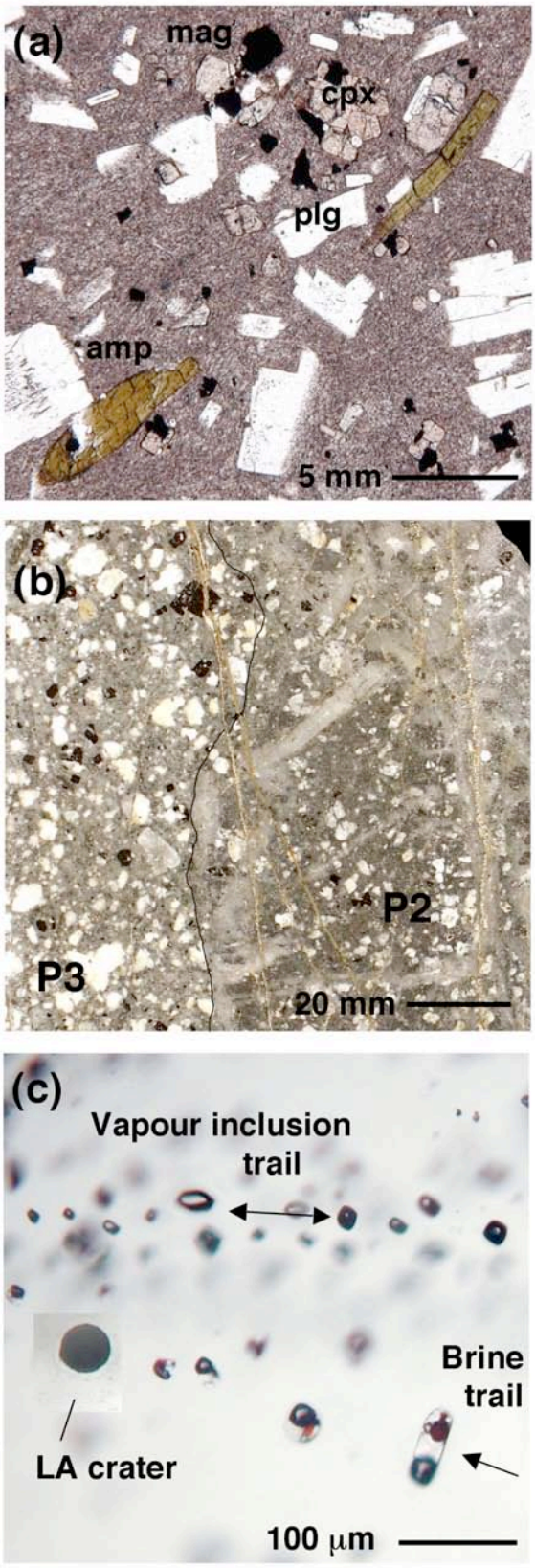


***Fig 4**. Typical rock, mineral and fluid inclusion relationships observed in porphyry copper systems: (a) thin section of a barren subvolcanic andesite porphyry from the Farallón Negro Volcanic Complex, containing plagioclase (plg) and amphibole (amp) phenocrysts that are effective 'xenocrysts', because they grew from different melts prior to magma mixing: amphibole contains basaltic-andesite melt inclusions, plagioclase contains dacitic melt inclusions; only clinopyroxene (cpx) contains intermediate-composition andesite melts similar to the bulk rock composition because it crystallised after magma mixing (Halter et al., 2004b). (b) Two generations of successively intersecting magmatic intrusions and stockwork veins from the Bajo de la Alumbrera deposit; quartz - magnetite ± bornite ± chalcopyrite veins mineralising the earlier P2 porphyry are truncated by a later P3 porphyry intrusion (left side of photo, emphasised by thin black line) affected by less intense alteration and veining with chalcopyrite + pyrite + minor quartz that cuts the igneous contact; in both vein generations, Cu-Fe-sulphides precipitated late compared with most of the quartz. (c) Typical association of high-temperature fluid inclusions in porphyry stockwork veins (Rosia Montana, Romania): brine inclusions (containing liquid, a gas bubble, a halite cube, a red hematite crystal and a smaller Cu-rich opaque daughter crystal), and vapour inclusions (large dark bubble and a small invisible fraction of liquid phase wetting the inclusion wall, reflecting the lower density of the high-temperature vapour phase). One of the brine inclusions has been 'drilled out' for quantitative laser-ablation ICP-MS microanalysis (dark crater with a diameter of 40 μm; inset photographed with image plane on the sample surface).*

5

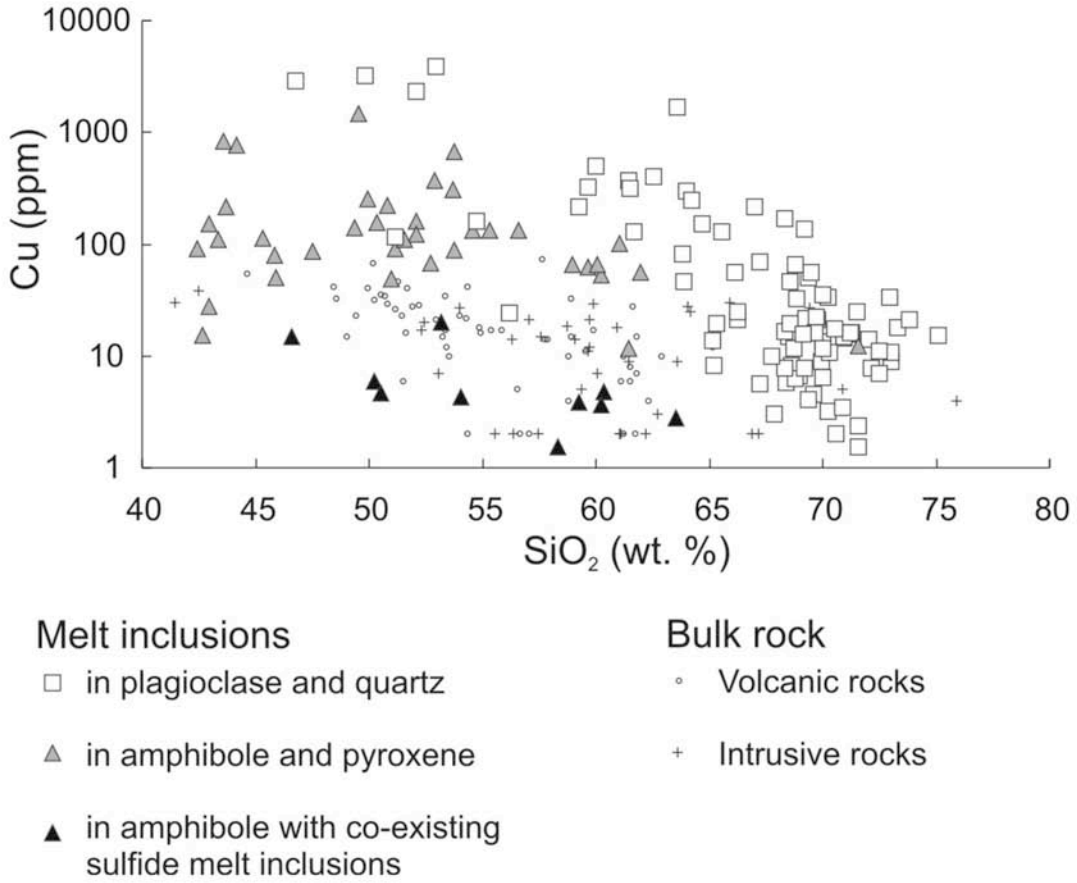


***Fig. 5*** *Cu concentration (on a logarithmic scale) against silica content, comparing bulk rocks and silicate melt inclusions from the Farallón Negro Volcanic Complex. For a given $SiO_2$ content, bulk magmatic rocks (small symbols for volcanics and subvolcanic intrusives) typically contain 3-10x lower Cu concentrations than silicate melt inclusions in amphibole and pyroxene (big triangles) and quartz or plagioclase (big squares). By contrast, silicate melts in amphiboles from barren intrusions, associated with igneous sulphide inclusions in the same phenocrysts (black triangles), are almost totally depleted in Cu, due to ore-metal extraction into a sulphide melt prior to fluid saturation (Halter et al., 2002b, 2004b).*

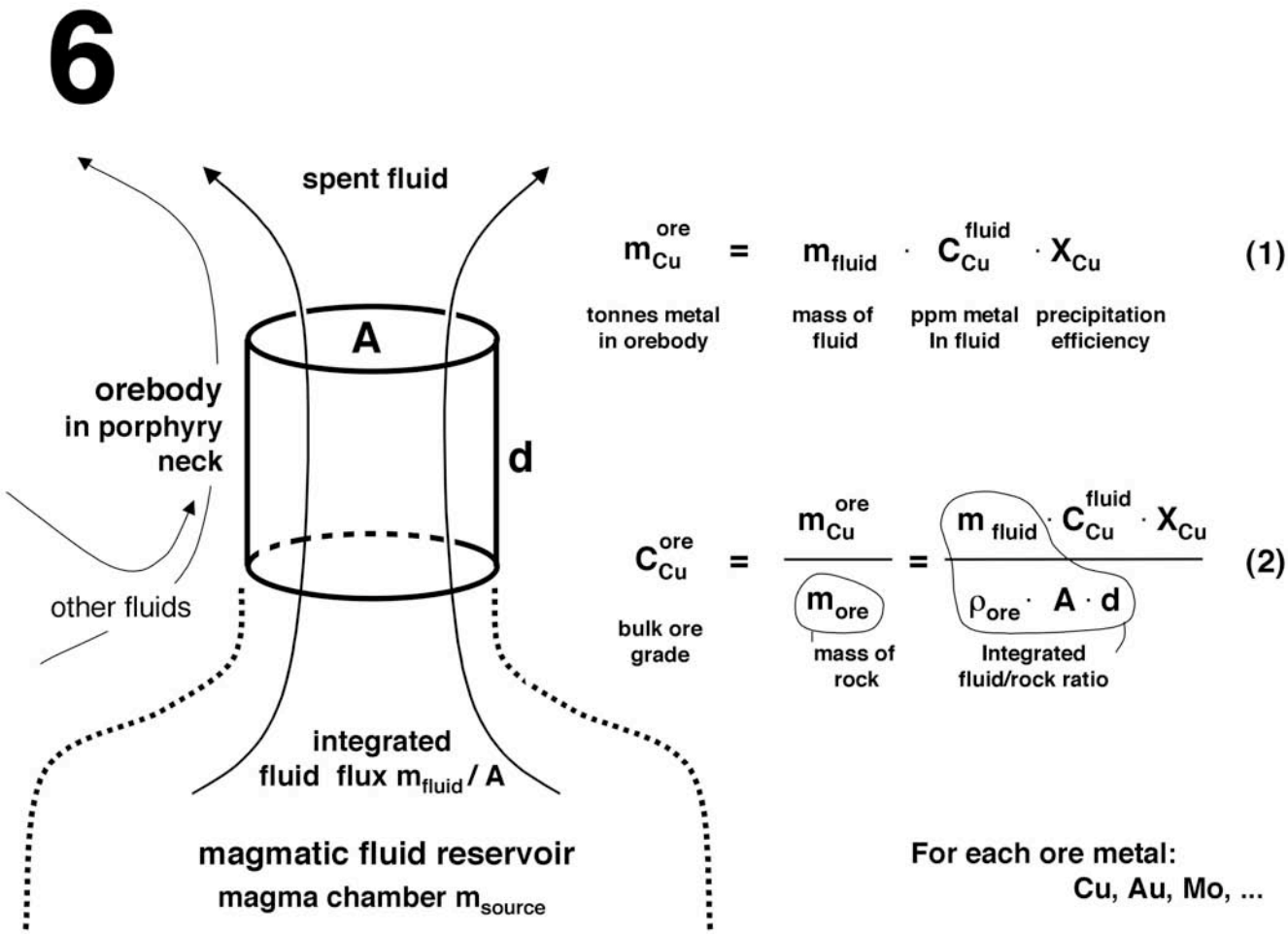


***Fig. 6*** *Schematic cartoon of a cylindrical porphyry copper orebody forming in a zone of intensely hydrofractured rocks above a larger pluton, illustrating the basic proportionalities relating the size (metal tonnage $m_{Cu}$; eq.1) and the metal grade of an ore deposit ($C_{Cu,ore}$; eq.2) to the key parameters of ore formation: ore-fluid composition (e.g. copper concentration in the incoming fluid, $C_{Cu}^{fluid}$), metal extraction efficiency by ore-mineral precipitation ($X_{Cu}$) and the dimension of the orebody in terms of horizontal cross-section (A) and vertical extent along the flow distance (d) of the fluids transporting the metals into the orebody. Equations relate to mass-balance only and fundamentally apply irrespective of orebody shape, which commonly is not a circular cylinder and has lateral boundaries that may or may not coincide with intrusive contacts of a porphyry stock.*

# 7a

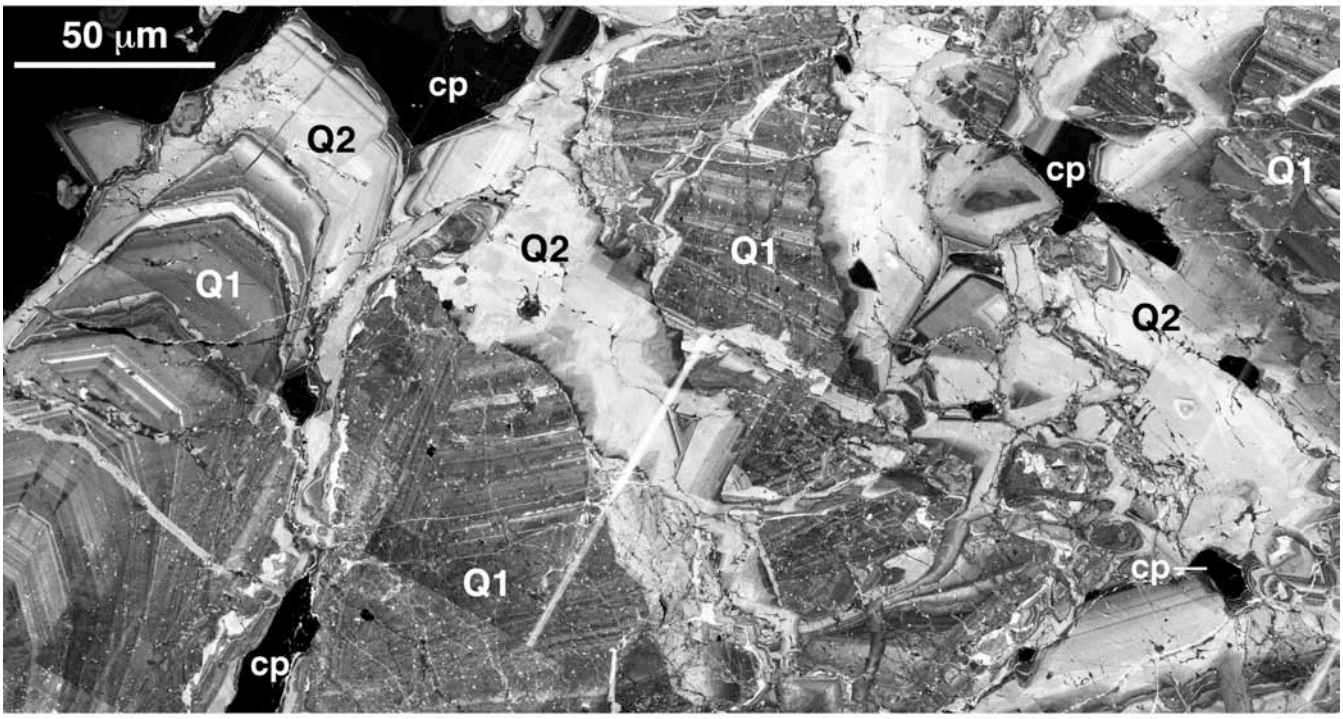


***Fig. 7*** *(a) Cathodoluminescence (SEM-CL) image of quartz crystals in a main-stage stockwork vein in the Bingham Cu-Au orebody (Utah), differentiating an otherwise invisible early generation of vein quartz (Q1) from and a later generation of quartz Q2 overgrowing the Cu-Fe sulphide grains, which precipitated during an intervening time of vein fracturing and secondary permeability creation by quartz dissolution. Cu precipitation and quartz dissolution can occur simultaneously by fluid cooling through the 410 to 350°C temperature interval at near-hydrostatic pressures below ~ 500 bar, as recorded by secondary inclusions trapped in the earlier Q1 quartz*

7b

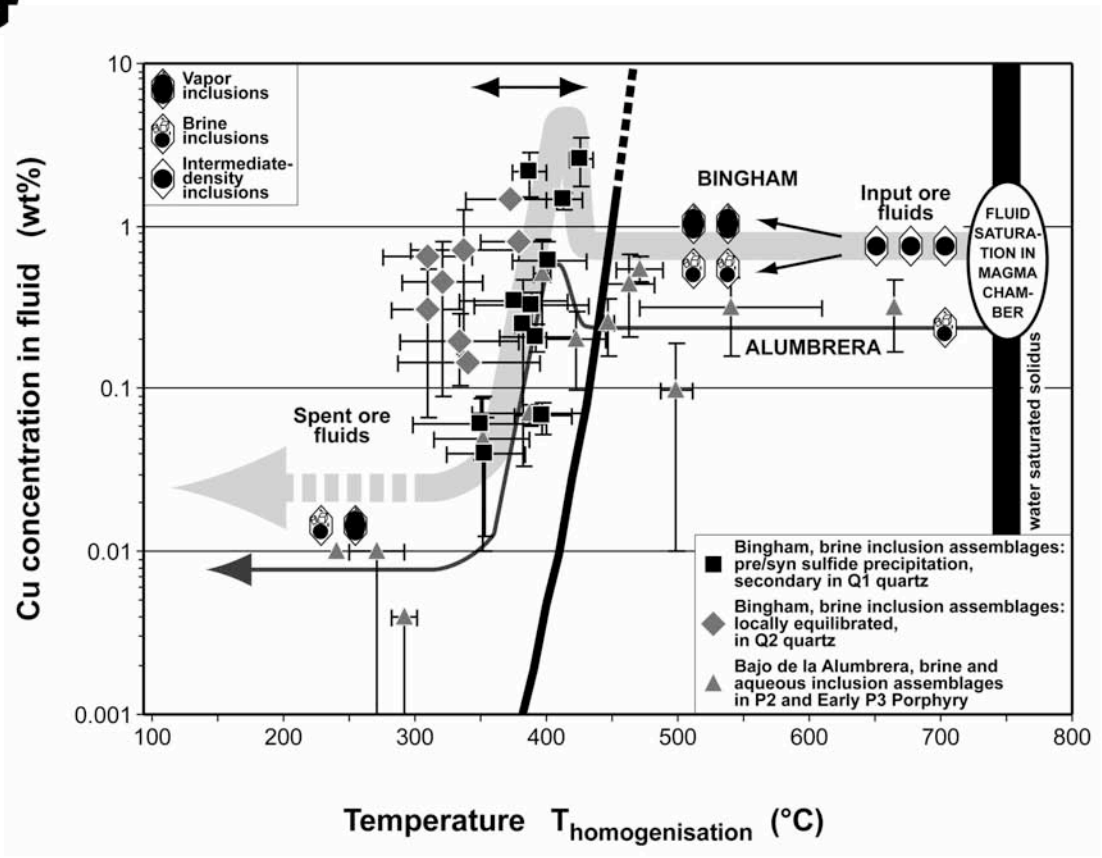


***Figure 7 (b)*** *Concentrations of Cu in brine inclusions in main-stage stockwork vein from the high-grade centre of the Bingham orebody, as a function of homogenisation temperature T (closely corresponding to trapping temperature as indicated by locally coexisting vapour inclusions). Symbols subdivided according to host quartz generation Q1 and Q2 mapped using CL petrography (see a), with error bars denoting standard deviation of several inclusions in one assemblage. Similar data from Alumbrera (without CL-petrographic control; Ulrich et al., 2001) are shown by small triangles and the black trendline with arrow. The heavy steep line parallel to Q1-hosted inclusion trend marks the strong temperature dependence of calculated chalcopyrite + bornite solubility (absolute position depending on assumptions about Cl, S and $O_2$ activities; Hezarkhani et al., 1999).*

# 8

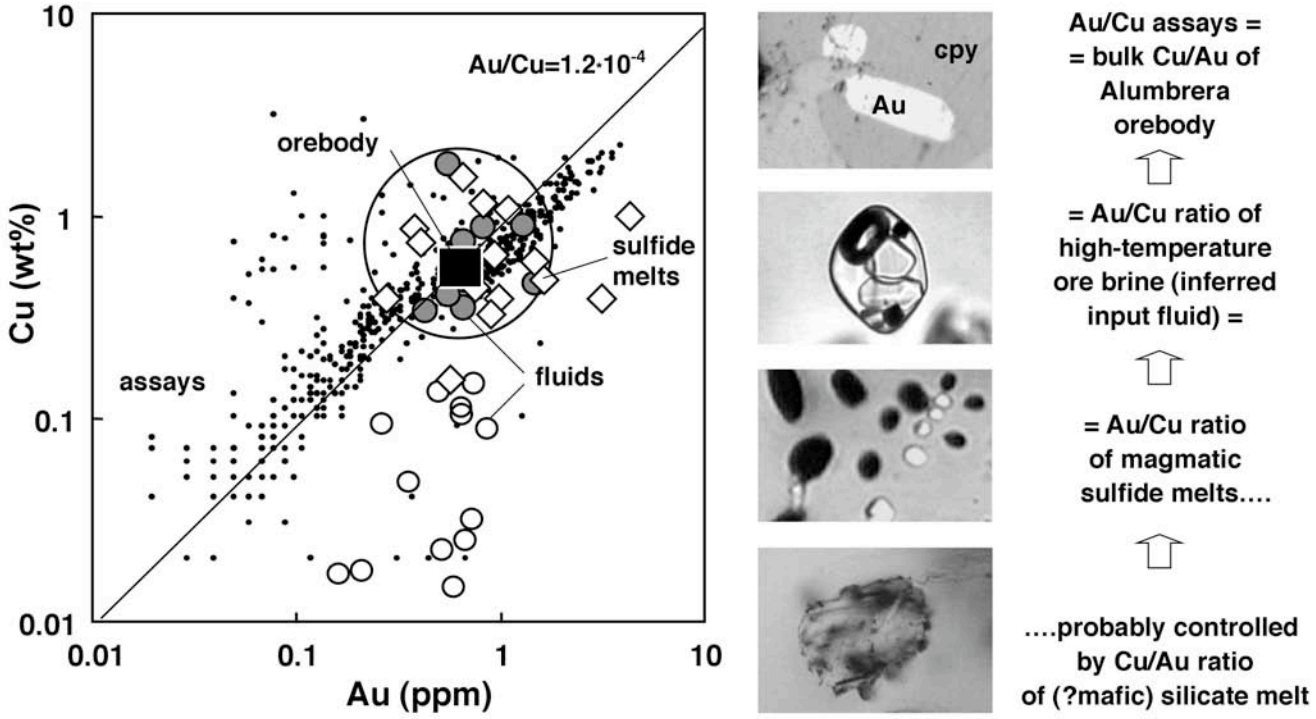


***Fig. 8*** *Log-log plot (a) comparing the Cu and Au concentrations in successively generated melts, fluids and ore in the Farallón Negro Volcanic Complex, shown by small polished thin section micrographs on the right of the diagram, summarising the major steps in the magmatic control leading to the bulk Cu/Au ratio of the Bajo del la Alumbrera deposit (data from Ulrich et al., 1999, 2001, and Halter et al., 2002a).*

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