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The Origin of Cu/Au Ratios in Porphyry-Type Ore Deposits

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Microanalysis of major and trace elements in sulfide and silicate melt inclusions by laser-ablation inductively coupled plasma mass spectrometry indicates a direct link between a magmatic sulfide liquid and the composition of porphyry-type ore deposits. Copper (Cu), gold (Au), and iron (Fe) are first concentrated in a sulfide melt during magmatic evolution and then released to an ore-forming hydrothermal fluid exsolved late in the history of a magma chamber. The composition of sulfide liquids depends on the initial composition and source of the magma, but it also changes during the evolution of the magma in the crust. Magmatic sulfide melts may exert the dominant direct control on the economic metal ratios of porphyry-type ore deposits.

Magmatic-hydrothermal ore deposits in porphyry stocks are the world's most important source of Cu and Mo and a significant source of Au, and their profitable exploitation often depends on a combined recovery of several metals. Porphyry deposits form through pervasive veining and alteration of intermediate to acid (that is, silica-rich) intrusions by magmatic-hydrothermal aqueous fluids, exsolved from a subjacent magma reservoir (*1*). This fluid mobilizes metals from several cubic kilometers of magma and transports them to the depositional site within a short period of time. Ore minerals precipitate from the fluid upon cooling and interaction with solidified rock. The relative proportions of ore metals (Cu, Au, and Mo) in porphyry-type deposits are variable, and systematic criteria to explain this variation are difficult to isolate (*2*). Crustal magmatic processes may have an important influence on metal ratios, whereas hydrothermal precipitation within the porphyry vein network appears not to strongly fractionate chemically similar metals such as Cu and Au (*3*, *4*). Therefore, the key to the genesis and composition of economic porphyry-type ore deposits lies in the processes controlling the composition of the magmatic volatile phase.

To understand the exsolution of the mineralizing fluid and the transfer of ore metals from the magma to the volatile phase, we are investigating the igneous history of ore-forming calcalkaline systems. Primary melt inclusions (MIs) in phenocrysts preserve the magmatic record despite pervasive hydrothermal alteration of the rock matrix. MIs are small droplets (5 to 50 μm in diameter) of magmatic liquids trapped during the growth of minerals. Silicate liquid is commonly recorded in MIs, but sulfide liquids were also discovered in certain rocks (Fig. 1). After extensive petrographic study, we used laser-ablation inductively coupled plasma mass spectrometry (LA-ICPMS) to analyze the major and trace element content of entire unexposed MIs (*5*). Integrated analysis of inclusions by laser sampling is essential in the case of sulfide melts, which never quench to a homogeneous glass. Our study focused on the Farallón Negro Volcanic Complex in northwestern Argentina, hosting the large Bajo de la Alumbrera porphyry Cu-Au deposit (*4*, *6*–*9*).

Most major and trace elements in silicate MIs follow the differentiation trend defined by bulk rock compositions, except for Cu, which varies at all stages of magmatic evolution (Fig. 2). Cu concentrations in silicate MIs in phenocrysts from volcanic rocks are one to two orders of magnitude higher [$\sim$100 to 3000 parts per million by weight (ppm)] than in the bulk rocks ($\sim$10 to 50 ppm). This shows that the evolving melt composition was more Cu-rich than common calcalkaline rocks [10 to 150 ppm (*10*)] before the transfer of Cu to the magmatic volatile phase and its dispersion during volcanic eruption (*11*). In the subvolcanic intrusions, MIs with $<$65 weight % (wt %) SiO_2 are depleted in Cu ($\sim$2 to 3 ppm and often below the limit of detection). These silicate MIs are hosted by amphibole and coexist with small (1 to 10 μm in diameter) and irregularly shaped primary sulfide MIs (Fig. 1), documenting the fact that basic to intermediate melts forming the mafic phenocrysts of intrusive rocks had exsolved a sulfide liquid. No sulfide inclusions occur in phenocrysts of the extrusive rocks nor in plagioclase phenocrysts containing silica-rich MIs in the intrusive rocks (Fig. 2).

Sulfide MIs were analyzed by LA-ICPMS for their Fe, Cu, and Au contents. Analyses and signal quantification were conducted according

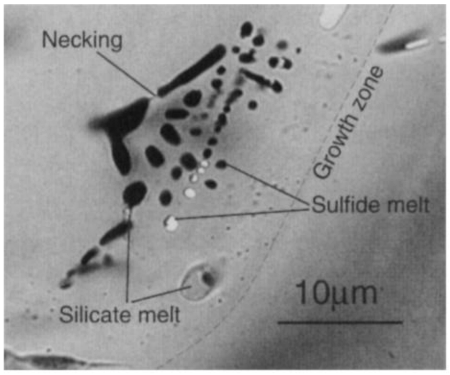

Fig. 1. Microphotograph of MIs, trapped in magmatic amphibole from intrusive rocks. The globular shape and necking of the sulfides are evidence for trapping at a molten stage, in equilibrium with a coexisting silicate melt. The image was taken in transmitted and reflected light, the latter rendering sulfide MIs bright white when exposed to the sample surface. Only entire subsurface inclusions (appearing black) were studied by quantitative LA-ICPMS microanalysis.

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to the procedure of Halter *et al.* (*12*) using our prototype Excimer LA-ICPMS (*13*). All analyses were calibrated with silicate glass standards. Silicate minerals were accurately quantified (<5%) with the National Institute of Standards and Technology SRM 610 glass (*12*). Tests on a chalcopyrite standard yielded Cu/Fe ratios within 10% of the certified value. The maximum calibration uncertainty for sulfide inclusions was closer to 5%, because the ablated material was dominated (>70 wt %) by the silicate host. Overall uncertainties were 5 to 10% for Cu and 10 to 20% for Au concentrations. Concentrations [or upper limits where Au signals were below detection at the 3σ level (*14*)] are shown in Fig. 3. Magmatic sulfides from three weakly altered intrusions were analyzed: (i) the pre-ore 8.5-million-year-old Bajo el Durazno basaltic andesite, (ii) the 8.0-million-year-old Chilca andesite stocks, and (iii) a post-ore 6.7-million-year-old andesite intrusion from the Alumbrera stock. Mineralized intrusions in the composite Alumbrera stock, formed between 7.0 and 6.8 million years ago (Ma), have no magmatic amphibole preserved after pervasive hydrothermal alteration.

Sulfide MIs contain as much as 9 wt % Cu (Fig. 3A) and 0.5 to 4 ppm Au (Fig. 3B) and show systematic compositional variations. Inclusions in the pre-ore stocks have consistent Cu contents, decreasing from ~1.1 wt % in the Durazno to ~0.5 wt. % in the Chilca stock. Au concentrations in these pre-ore inclusions are between 0.3 and 4.3 ppm, clustering around 1 ppm. In the post-ore andesite intrusion, Cu contents in sulfide MIs are variable, between about 30 ppm and 9.4 wt %. Au concentrations in sulfide MIs in this late intrusion show an inverse correlation with Cu (Fig. 3E).

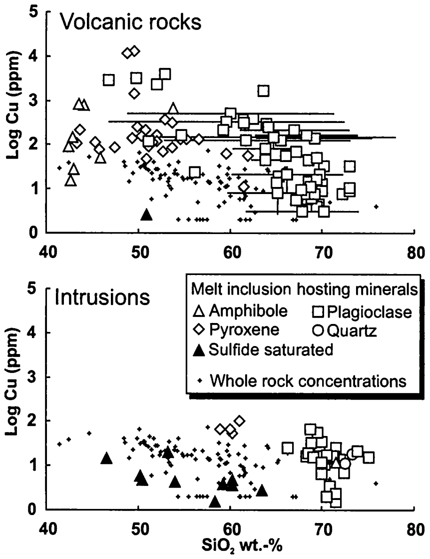

Fig. 2. Cu concentrations in logarithmic scale as a function of the SiO_2 content, in rocks and silicate MIs from (**top**) extrusive and (**bottom**) intrusive rocks. Amphibole from intrusive rocks contains strongly Cu-depleted silicate MIs, coexisting with Cu-Au–rich sulfide liquids (Fig. 3).

The spatial distribution and time-dependent compositional variation of the silicate (*9*) and sulfide MIs can be explained by a protracted magmatic evolution involving four possibly overlapping stages: (i) progressive sulfide exsolution during crystallization of a large differentiating silicate magma; (ii) a possible stage of selective enrichment of chalcophile elements in the sulfide melt by diffusive or advective transport from sulfide-undersaturated portions of the magma chamber; (iii) separation of the sulfide melt into two immiscible melt phases, immediately before or after (iv) bulk destabilization of the sulfide liquid as a result of volatile exsolution throughout the magma chamber.

The most basic magmas and silicate MIs are sulfide-undersaturated and have an average Cu content of ~200 ppm. Cu-depleted silicate melts associated with Cu- and Au-enriched sulfide melts demonstrate the selective partitioning upon saturation of the sulfide liquid. The preference of these chalcophile elements for sulfide relative to silicate liquid has been quantified by experiments with solid sulfides (*15*). Our data yield a field-derived partition coefficient of Cu between the sulfide and the silicate liquid of ~10,000, well above experimental values of <1000 between komatiitic melts and sulfide liquid at much higher temperature (*16*). The decrease in Cu concentration [or increase in the Fe/Cu ratio (Fig. 3, A and D)] from the early Durazno to the later Chilca stocks probably reflects an increase in the amount of exsolved sulfide. Fe, Cu, and Au have an increasing affinity for the sulfide phase in that order (*15*), so that the first sulfide liquid segregated from a high-temperature mafic magma will be preferentially enriched in the most chalcophile elements, Cu and Au. With progressive sulfide exsolution, the more differentiated silicate melt becomes correspondingly depleted in Cu relative to Fe (Fig. 3D).

Because of the large partition coefficients, the first sulfide liquid effectively scavenges all locally available Cu and Au; hence, additional exsolution of sulfide from the same magma volume will not increase the total amount of ore metals stored in the sulfide phase. However, the extreme Cu and Au depletion in the sulfide-saturated silicate melt generates a strong chemical gradient from any melt regions in the magma chamber that are still sulfide-undersaturated. Thus, diffusive metal transport through the silicate melt (*17*), plumes of hot new magma or partly fractionated melt rising from the lower boundary layer of the chamber (*18*), or an early-saturating CO_2-SO_2-H_2O–rich volatile phase (*19*) may selectively transport Cu and Au to the existing Fe-rich sulfide melt. This may have happened during continued replenishment of the

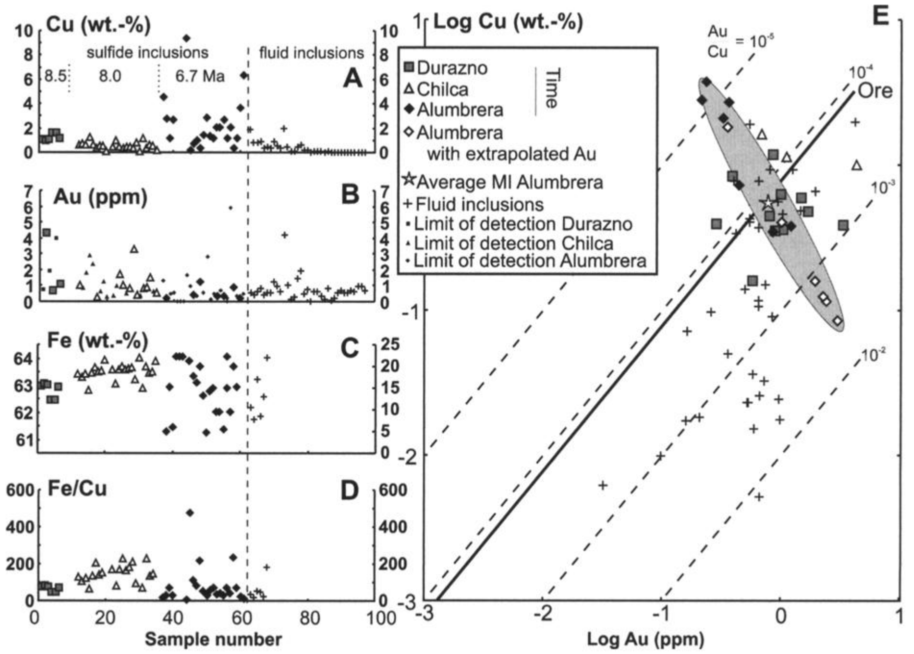

Fig. 3. Element concentrations of sulfide MIs in the premineralization Durazno and Chilca stocks, in the postmineralization andesite of the Alumbrera stock, and in early fluid inclusions of the Alumbrera deposit. (**A**) Cu concentrations. (**B**) Au concentrations (the limits of detection were calculated individually and plotted if analyte signals were nonsignificant). (**C**) Fe concentrations. (**D**) Fe/Cu ratio. (**E**) Cu versus Au concentrations in inclusions of sulfide melt and hydrothermal brine. The gray ellipse shows the negative correlation between Au and Cu in sulfide melts at Alumbrera. In some samples, only Au/Cu ratios were measured (but not Fe) to increase accuracy, and the absolute Au and Cu contents were extrapolated from the Au/Cu correlation. Also shown are the ratio of the average Au and Cu concentrations in the earlier sulfide MIs, the composition of the bulk ore (heavy line), and lines of constant Au/Cu ratio (dashed lines).

magma reservoir between 8.5 Ma and the cessation of volcanism at 7.5 Ma, or during $\sim$0.4 million years of quiescence before emplacement and hydrothermal mineralization of the Alumbrera stock.

Sulfide MIs in amphibole phenocrysts of the intrusion emplaced immediately after Cu ore formation at Alumbrera have mean Au/Cu/Fe ratios similar to those of the earlier sulfide phases and are interpreted as the closest record of the magmatic state of the ore metals during hydrothermal fluid generation (*9*). Their greater variation in Cu content (Fig. 3, A and D) and inverse correlation between Cu and Au (Fig. 3E) may result from the separation of the sulfide melts into two phases, one enriched in Cu and the other close to FeS but rich in Au. Both phases may be liquid, as shown by experimental phase relations suggesting unmixing of a homogeneous sulfide melt into Cu-rich and FeS-rich melts around 1000°C (*20*).

The mean Au/Cu ratio of each population of sulfide MIs overlaps, within a factor of 2, with the bulk Au/Cu ratio of the large Bajo de la Alumbrera ore body, which in turn is identical to the average Au/Cu ratio in fluid inclusions of the earliest hydrothermal brine before ore mineral saturation in the deposit (*3*) (Fig. 3E). We conclude that the ore-forming hydrothermal fluid acquired its high metal content and characteristic Au/Cu ratio by bulk destabilization of magmatic sulfides with similar metal ratios. Bulk resorption of the sulfide liquid is expected to result from the exsolution of a volatile phase, which causes oxidation through H_2 loss and removal of sulfur as SO_2 and H_2S (*21*, *22*). A link between wholesale destabilization of sulfide melt and the generation of the ore fluid is substantiated by similar Fe/Cu ratios (Fig. 3D), despite the contrasting chemical behavior of these two elements in sulfide and volatile phases. In addition to ore metals and Fe, most of the S in the ore fluid is probably derived from the magmatic sulfide liquid. Preliminary results from the Elatsite porphyry deposit in Bulgaria, which has a lower Au/Cu ratio in the bulk ore and in the magmatic sulfide, are consistent with this interpretation.

Our data indicate that magmatic sulfide melts can act as intermediate metal hosts contributing to metal enrichment in large hydrothermal porphyry-Cu-Au deposits. Sulfide melts have previously been proposed (*22*, *23*) as a key factor in the genesis of the giant porphyry deposit at Bingham (Utah). It remains to be tested whether exsolution of sulfide liquid is a ubiquitous and essential prerequisite for ore formation, but it is probably a favorable step in the genesis of extensive porphyry-type ore deposits, by preconcentrating Cu and Au during the evolution of the magmatic system before volatile saturation. During later exsolution of a chloride-rich volatile phase, the sulfide liquid can be instantaneously destabilized, leading to bulk transfer of metals and sulfur to the hydrothermal ore fluid. Although the availability of ore metals ultimately depends on the contribution from the mantle and the history of interaction with the crust, sulfide melts may exert an immediate control on the metal composition of magmatic-hydrothermal ore deposits.

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^{40}Ar/^{39}Ar Dates from the West Siberian Basin: Siberian Flood Basalt Province Doubled

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Widespread basaltic volcanism occurred in the region of the West Siberian Basin in central Russia during Permo-Triassic times. New ^{40}Ar/^{39}Ar age determinations on plagioclase grains from deep boreholes in the basin reveal that the basalts were erupted 249.4 ± 0.5 million years ago. This is synchronous with the bulk of the Siberian Traps, erupted further east on the Siberian Platform. The age and geochemical data confirm that the West Siberian Basin basalts are part of the Siberian Traps and at least double the confirmed area of the volcanic province as a whole. The larger area of volcanism strengthens the link between the volcanism and the end-Permian mass extinction.

Basaltic magma that erupted simultaneously over large areas of Earth's surface—so-called flood basalts—may have released prodigious volumes of SO_2, CO_2, HF, and other gases; hence, it is argued, such an event would trigger climatic disruption and a destabilization of major ecosystems, leading to mass extinction (*1*). The Siberian Traps (Fig. 1) are the largest Phanerozoic continental flood basalt province. They were erupted at the end of the Permian, about 250 million years ago (Ma) (*2*, *3*), coincident with the largest known mass extinction event, the Permo-Triassic (P-Tr) crisis (*4*–*6*). Several authors have proposed that the flood volcanism triggered the mass extinction event (*4*–*6*), although the precise causal links are not understood (*7*, *8*).