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High Sulfidation and Low Sulfidation Porphyry Copper/Skarn Systems: Characteristics, Continua, and Causes

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In the past decade, multi-disciplinary research on active and fossil hydrothermal systems in volcano-plutonic arcs has resulted in important new information on the physical and chemical evolution of hydrothermal fluids of diverse origin, on the sources of metals, sulfur and other dissolved constituents, and on the possible genetic transitions between different ore-forming environments. Among the most studied magma-hydrothermal systems are those linked to felsic magmatism, whose products extend from plutonic porphyry-Cu deposits to volcanic epithermal-Au deposits. In-between these endmembers can be skarns or massive sulfide replacement bodies and veins of both base- and precious-metals. Here I focus on transitions between ore types in porphyry copper systems and use the the sulfidation state of hydrothermal fluids as a framework. I adopt the sulfidation state as a means of classification of ore-forming environments because this variable spans all deposit types and is independent of host rocks, metals contained, and textures exhibited (in contrast with terms such as "acid-sulfate" which is restricted to quartzo- feldspathic host rocks, or "epithermal" which is restricted to one class of deposit).

Sulfidation State.

McKinstry (1959, 1963) and Barton (1970) applied the terms "sulfur content" and "sulfidation state", respectively, to denote the relative values of the chemical potential of sulfur implied by sulfide mineral assemblages in ore deposits. Both authors noted the general tendency for sulfidation state to increase as unbuffered hydrothermal solutions evolve from high to low temperatures in base- metal veins associated with felsic igneous rocks. The concept of sulfidation state was put on a firm theoretical and experimental base by Skinner and Barton (1967, 1979) and applied to base-metal veins by Meyer and Hemley (1967).

The sulfidation state of hydrothermal fluids can be classified on a continuous scale on the basis of key sulfidation reactions, as defined in [Table 1](#) below (based on Skinner and Barton, 1979). In bold letters

are minerals or assemblages that span only two defined sulfidation states; in *italic bold* are minerals or mineral assemblages that occupy only one defined state.

Only a few minerals or mineral assemblages are diagnostic of a given sulfidation state. For example, although covellite is diagnostic of very high sulfidation states, enargite is less diagnostic, being stable from upper intermediate, through high, and very high sulfidation states. Because of the chemical links between sulfidation, oxidation, and ionization states of hydrothermal fluids (Meyer and Hemley, 1967), covellite would be expected to be associated with acid-sulfate fluids and advanced argillic alteration containing alunite. Enargite, on the other hand, could be deposited from hydrothermal fluids of intermediate oxidation-sulfidation state and be associated with less advanced degrees of base-cation leaching of wall rocks (e.g., sericitic alteration).

Porphyry Copper and Related Deposits: 1940-1980.

The first detailed studies of advanced argillic (including acid-sulfate) and sericitic alteration associated with relatively high sulfidation state sulfide assemblages were focussed on enargite-bearing veins associated with felsic igneous rocks at Cerro de Pasco, Peru, and Butte, Montana (Graton and Bowditch, 1936; Sales and Meyer, 1948; 1949). Field documentation that enargite-bearing veins with acid-sulfate alteration commonly were superimposed on the upper portions of porphyry copper deposits (Meyer and Hemley, 1967; Meyer et al., 1968; Taylor, 1933), systematization of naturally occurring sulfide mineral assemblages as a function of "sulfur content" (McKinstry, 19xx, 19xx), and experimental definition of mineral equilibria as a function of temperature and fluid compositions (Barton et al., 1963; Hemley and Jones, 1964; Hemley et al., 1969;), led to increased understanding of the geologic and geochemical factors that control the formation of very high- to high- sulfidation enargite-covellite ores versus low-sulfidation (magnetite-bornite) to intermediate-sulfidation (chalcopyrite-pyrite) ores in porphyry-related systems (Hemley and Jones, 1964; Meyer and Hemley, 1967; Hemley et al. 1969; Gustafson and Hunt, 1975; Einaudi, 1977; Knight, 1977; Brimhall, 1977, 1979). At the same time, there was increasing field evidence that some epithermal high-sulfidation deposits are somehow linked to deeper porphyry systems (Sillitoe, 1973; Wallace, 1979). Combined with an enlarging base of descriptive models of porphyry copper deposits (Titley and Hicks, 1966; Lowell and Guilbert, 1970; Rose, 1970; Guilbert and Lowell, 1974; Sutherland-Brown, 1976; Titley, 1975), data on temperature-salinity (Roedder, 1971; Moore and Nash, 1974; Eastoe, 1978) and sources of water in hydrothermal fluids (Sheppard et al., 1969, 1971; Sheppard and Taylor, 1974; Taylor, 1974), and models of the physical and chemical nature of the magma-hydrothermal transition and of overlying vapor-dominated systems (Burnham, 1967, 1979; White et al., 1971; Holland, 1972; Phillips, 1973; Whitney, 1975; Henley and McNabb, 1978), an evolutionary theme for porphyry copper and closely related deposits emerged. Although this evolutionary model was briefly swayed from its magmatic roots (Norton, 1972; Norton and Cathles, 1976), by 1980 the magmatists prevailed.

Porphyry Copper Systems - Characteristics

The evolutionary framework for porphyry- related deposits formed at depths of 2 to 4 km, established by workers cited above and further refined in the early 1980's (Brimhall, 1980; Burnham and Ohmoto, 1980; Titley and Beane, 1981; Einaudi, 1981, 1982; Eastoe, 1982; Sillitoe, 1983a, 1983b) can be cast

in terms of the observed space-time distribution of two ore-forming environments, as illustrated in [Figure 1](#) (A & C) and summarized in [Table 2](#).

Low- to intermediate sulfidation environment (A): Early and/or deep stages are characterized by potassic alteration and anhydrous skarn with disseminated/veinlet chalcopyrite-bornite-(magnetite) related to refluxing magmatic brines (saline, and hypersaline if a vapor plume is released) at 600-400 C, lithostatic pressure, and intermediate sulfidation-oxidation states (arrow 2, Fig. 1). This early stage is succeeded by late, superimposed and high-level sericitic alteration of porphyry and retrograde alteration of skarn, accompanied by pyrite-chalcopyrite- (hematite), in through-going veins. Late fluids are dominantly meteoric, boiling at 350-250 C under hydrostatic pressures, and are characterized by moderate acidity, low-salinity, and high sulfidation-oxidation states (arrows 5, Fig. 1). The degree of development of sericitic alteration varies significantly at present levels of exposure in porphyry copper districts (e.g., minor at Bingham, Utah; major at Ely (Robinson), Nevada).

High- to very high-sulfidation environment (C): Some porphyry deposits contain very late, high-level advanced argillic alteration (encased in sericitic) with pyrite-alunite, in some cases accompanied by digenite, covellite, and/or enargite (e.g., Butte, Montana; Chuquicamata, Chile), in other cases barren of copper (e.g., El Salvador, Chile). Acid-sulfate alteration is localized in faults, hydrothermal breccias and around pebble dikes. Acid-sulfate fluids are of meteoric water (arrow 7) and/or magmatic-vapor plume origin (arrow 6), at 350-200 C, near-hydrostatic pressure, and high to very high sulfidation-oxidation states (arrow 8). In skarn or carbonate wall-rocks, these fluids generate silica-pyrite Cu-(Au) fissures and replacement bodies (e.g., Bisbee, Arizona; Yauricocha, Peru).

Continua and Causes

Variations on the degree of development of low sulfidation (A) versus high-sulfidation (C) fluids in porphyry-related copper deposits, as exhibited by localities summarized in Table 2, are controlled by local tectonic, magmatic, and hydrodynamic conditions. Formation of a "classic" low sulfidation porphyry copper deposit (environment A, Fig. 1) would be favored by relatively deep emplacement of multiple, non-venting, intrusions into anhydrous, unfractured rocks in a relatively stable tectonic environment. In contrast, formation of a high-sulfidation "Cordilleran lode" deposit (environment C, Fig. 1) consisting of massive pyritic copper ores encased in advanced argillic and sericitic alteration would be favored by relatively shallow subvolcanic emplacement of isolated stocks and plugs into fractured rocks saturated with meteoric water in an active tectonic environment. Abrupt superposition of high-sulfidation veins (environment C) on to low-sulfidation disseminated ores (environment A) could result from "tectonic quenching", such as pressure release and incursion of meteoric water due to large-scale crustal faulting (Gustafson and Hunt, 1975; Einaudi, 1977; Brimhall, 1980; Einaudi, 1982), or by removal of overlying rocks by erosion during rapid uplift or mass-wasting of volcanic edifices (Sillitoe and Gappe, 1984). In some cases, tectonic quenching could effectively suppress the development of disseminated porphyry copper deposits at (A), resulting in a lode deposit without porphyry roots (Einaudi, 1977, 1982).

Porphyry Copper - Epithermal Gold Systems: The View from Above, 1990

With increased interest in precious metals during the 1980s, research in ore deposits shifted to gold-

rich porphyry copper deposits, epithermal systems and other environments of precious-metal deposition. The result is important new information on: (1) geologic settings of high-sulfidation epithermal deposits and their links to deeper magma-hydrothermal systems (Sillitoe, 1988, 1989, 1992; Heald et al., 1987; White, 1991); and (2) case studies of high-sulfidation epithermal districts that integrate geology, geochemistry, fluid inclusions, and light stable isotopes (Bethke, 1984; Stoffregen, 1987; Bove, 1988; Arribas et al., 1989; Deen, 1990; Bove et al., 1990; Muntean et al., 1990; Rye et al., 1992; Vennemann et al., 1993; Hedenquist et al., 1994). These studies have lent further support to the idea that high-sulfidation epithermal deposits have a magmatic fingerprint and that some are closely linked to deeper porphyry systems

The present conceptual model that ties porphyries with high-sulfidation epithermal systems (in contrast with high-sulfidation copper lodes), based on the studies cited above, is paraphrased here from Sillitoe (1989, Fig. 9) and Rye (1993, Figs. 1 & 33). The porphyry copper environment that occupies a position between the water-rich carapace of the magma and the overlying transition from plastic to brittle rock, also may be of critical importance to epithermal deposits. This volume, characterized by the presence of saline magmatic water, quasiplastic behaviour, and low water:rock ratios, and by the absence of long-lived fractures and of meteoric water, may be the reservoir for evolved magmatic fluids that generate epithermal ores. At the ductile-brittle transition, saline magmatic fluids encounter open fractures and hydrostatic pressures; boiling of these fluids results in a hypersaline brine that remains at the ductile-brittle transition (arrow 2, Fig. 1) and a vapor plume (arrow 1, Fig. 1) that rises to high levels where it generates barren acid-sulfate alteration following condensation (arrow 3, Fig. 1). As the ductile-brittle transition withdraws to deeper levels with time, metal-bearing saline and hypersaline liquid-phase fluids that have been refluxing within the stock (arrow 2) are tapped (arrow 4) and may ascend rapidly to high levels. These are the epithermal ore fluids (environment B, Fig. 1). If the deep environment (A, Fig. 1) fails to evolve to environment (C), then the high-sulfidation deposit (B) is separated from its roots (A) by a rock volume with little or no signs of hydrothermal activity.

The present challenge to students of porphyry systems is to distinguish, within individual districts, between the model endmember processes that generate acid-sulfate fluids (vapor plume or liquid-phase mixing?), the causes of mineralized versus barren acid-sulfate zones, and the potential continuum between copper-rich and gold-rich high-sulfidation deposits.

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