PGC
PUBLISHING

Barton, M.D.and Johnson, D.A., 2000 - Alternative Brine Sources for Fe-Oxide (-Cu-Au) Systems: Implications for Hydrothermal Alteration and Metals ; *in* Porter, T.M. (Ed.), Hydrothermal Iron Oxide Copper-Gold and Related Deposits: A Global Perspective, Volume 1; *PGC Publishing, Adelaide*, pp 43-60

ALTERNATIVE BRINE SOURCES FOR Fe-OXIDE(-Cu-Au) SYSTEMS: IMPLICATIONS FOR HYDROTHERMAL ALTERATION AND METALS

Mark D. Barton and David A. Johnson

Centre for Mineral Resources, Department of Geosciences
University of Arizona, Tucson, AZ 85721 USA

Abstract – No single model satisfactorily accounts for the diverse characteristic of Fe-oxide-rich hydrothermal systems. Consideration of a spectrum of geologically reasonable models gives insight into the origins of variability among these deposits. Key features that need to be rationalised by any model are the abundance of hydrothermal magnetite and/or hematite, the chemically distinct suite of elements (REE-Cu-Co-Au-Ag-U), the variability of associated magmas, the distributions and volumes of associated hydrothermal alteration, and the broader geologic setting(s).

Geologic and geochemical evidence show that the ore-forming fluids are brines, but the source of the brines is controversial. Multiple sources are possible, indeed likely. The identity and consequences of alternative sources – magmatic and non-magmatic are considered: First, by a review of plausible fluids and general consequences, second, by examination of the system characteristics, third, by specific consideration of the consequences of alternative models, and fourth, by consideration of selected systems where non-magmatic brines must play a major role.

We review some of the key characteristics of different types of hydrothermal Fe-oxide-rich(-Cu-Au) systems. Some are economic; many are only geochemically anomalous. Two end-members and several variants on these end members are proposed. One group is typified by relatively high-temperature mineralisation, and relatively high K/Na and Si/Fe in the alteration. We suggest that these features (and others) are distinctive of magmatic fluid sources and that this group overlaps with porphyry Cu-Au and related deposit types. A second, broad group is typified by more oxide-rich, sulphide-poor mineralisation, low Si/Fe ratios, and voluminous alkali-rich alteration where sodic types commonly exceed K-rich varieties. We suggest that the key features of this group reflect involvement of non-magmatic brines and that ore grades are less common as the metals are less easily trapped. Hybrid examples, where fluids of both types are involved, are expected (and known).

Conceptual and quantitative models of magmatic and non-magmatic fluid sources yield insight into the expected differences, the source and distribution of metals within these systems, and possible controls on ore deposition. These models highlight the difference between magma-sourced fluids and non-magmatic fluids. The former tend to be focused at the tops of magma chambers and have a built-in depositional mechanism – cooling. The latter require a different type of focusing mechanism – structural or stratigraphic, and different traps – mixing, specialised host rocks, and/or boiling. These models predict consistent differences in mineral assemblages, metal contents, alteration volumes, zoning, paragenesis, and geochemistry. For magmatic fluid sources, the models reproduce the key characteristics of that group, notably the porphyry-related systems. For non-magmatic brine sources, predicted characteristics match well with observations of Fe-oxide-rich systems in environments where these fluids are known to dominate, including mafic igneous systems and modern analogs such as the Salton Sea. These cases show that Fe-oxide (-Cu-Au-REE-Co) enrichments can result from non-magmatic sources. In other environments (e.g., with intermediate to felsic igneous rocks; settings deeper than ~5 km) the relative importance of various fluid sources and their consequences for mineralisation remain to be fully explored. Young systems in the American Cordillera and elsewhere can help unravel the many threads that relate these enigmatic mineral deposits.

Introduction

Iron-oxide-rich hydrothermal deposits with accessory copper and gold comprise a large group with geochemical similarities but also important differences. Some systems, such as magnetite-rich porphyry-type deposits are reasonably well understood, but those dominated by iron-oxide remain controversial. Two key themes are:

- *Characterisation*: What constitutes this class? Are these different breeds – i.e., variations on a theme – or different species, with fundamentally different origins? How are they similar and how do they differ – at all scales?
- *Interpretation:* How did they form? What are implications of different (possible) mechanisms? Why are there so many "barren" examples?

This paper poses the question of different sources, briefly reviews characteristics of the broad group, and then focuses on the latter theme: alternative origins for fluids and their geologic implications. This synthesis is founded on field-based studies in the United States and Mexico, on comparison of many systems worldwide through field visits and literature review, and on theoretical modeling of saline hydrothermal systems of several types.

Why Alternative Fluid Sources?

Magmatic, metamorphic, sedimentary and surface sources all contribute fluids to hydrothermal systems – ore-forming and otherwise. In igneous-related systems, magmatic aqueous fluids commonly dominate, but in some settings other fluids can be very important. For example, in many modern and ancient geothermal systems, dilute meteoric waters (surface or ground waters) contributed much, if not most, of the fluid present (Criss and Taylor, 1986; Hedenquist and Lowenstern, 1994; Field and Fifarek, 1985). Likewise, in marine hydrothermal systems seawater is the key fluid, although in some systems supplemented from other sources (Franklin *et al.*, 1993; Sillitoe *et al.*, 1996; Scott, 1997). In contrast, the circulation of more concentrated brines of non-magmatic origin has received relatively little attention in igneous-centred systems, even though their importance is widely recognised in sedimentary and basinal environments. In the latter settings, they are key in the genesis of many Cu-U-Au-Ag-Co-bearing systems such as sediment-hosted Cu(-Co-Ag) systems and unconformity U(-Cu-Au) systems (Komninou and Sverjensky, 1996; Hoeve and Quirt, 1989). These saline fluids include surface-derived and connate brines, and those formed by dissolution of (meta)evaporites.

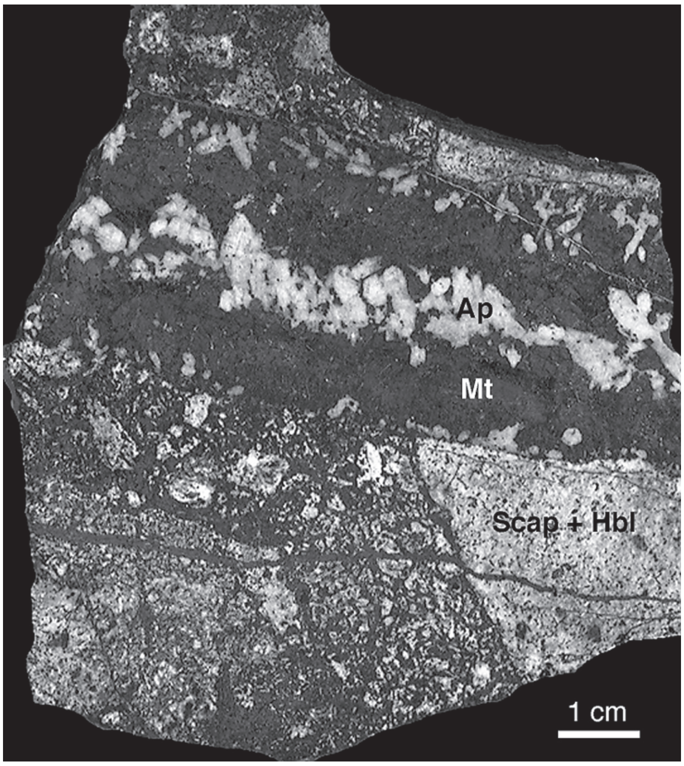


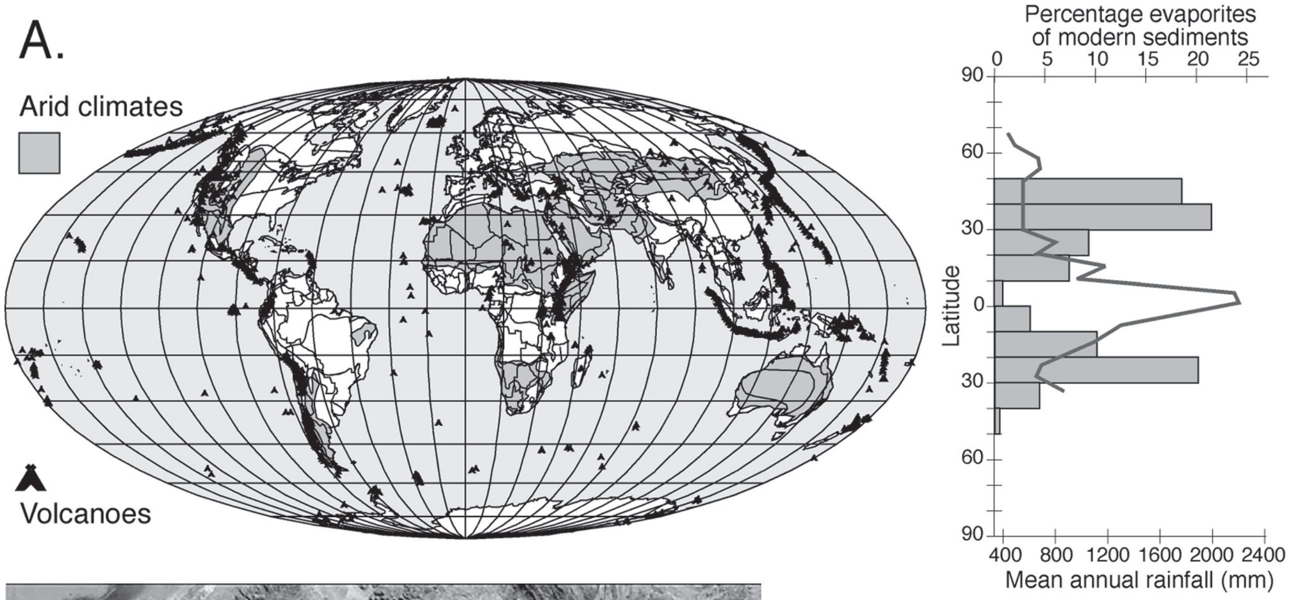
Figure 1: Hydrothermal magnetite-apatite-rich heterolithic breccias with Na scapolite + hornblende replacement of host basaltic rocks from the Jurassic-age Humboldt mafic complex, western Nevada (Johnson and Barton, 2000). This sample is representative of proximal/deep, REE-bearing, sulfide-poor assemblages found in many districts around the world. Distal to this material at Humboldt are numerous occurrences of hematite (/ magnetite) ± chalcopyrite (/ bornite) ± pyrite mineralization. The large Humboldt hydrothermal system (>900 km^3 Na ± Ca alteration; > 1 Gt Fe-oxide mineralization) represents an end-member in the overall spectrum of Fe-oxide deposits. The Humboldt system is fundamentally basaltic and has compelling geological and geochemical evidence for non-magmatic brine involvement with little if any magmatic aqueous fluid (Johnson, 2000). Such systems, which are part of a broader range from mafic to felsic, led us to postulate that non-magmatic brines can play in dominant role in some systems (Barton and Johnson, 1996; also discussion following).

Juxtaposition of non-magmatic brines and magmatism is common today (Fig. 2). Many observations indicate that in the geologic past such coincidence was common and, at certain times, much more common than it is today. This juxtaposition is worth exploring for both basic and practical reasons. What are the constraints on, and consequences of external brine involvement in igneous systems? How can their involvement be distinguished from that of magmatic brines?

Modern sedimentary brines have distinctive compositions (Fig. 3): Most are chloride-rich and typically (but not always) sulphur-poor. They tend to have alkaline pH and have variable, typically low K/Na. The latter reflects diagenetic loss of K from the original moderately high K/Na sources (streams and springs, Fig. 3). If the K is lost to a volcanic substrate, the result will be high K_2O contents (>6 wt %); as is commonly observed, for example, in the southwestern U.S. (Chapin *et al.*, 1986, Hollocher *et al.*, 1994). These altered rocks are typically highly oxidised and maroon to brick red in color. In contrast to many playa brines, marine-sourced evaporitic fluids are comparatively K-poor. This reflects the low K contents of seawater and most marine evaporites. Metasomatism in hydrothermal systems that involve evaporitic brines should reflect these distinctive compositions and volumes, in addition to the rock compositions along the flow paths.

Modern Geothermal Fluids and Metal Transport

The compositions of modern geothermal fluids vary systematically with their setting (Fig. 4A). These variations directly impact the capacity for metal transport and deposition (Fig. 4B). Geothermal systems in humid climates have modest S and Cl contents, spanning the range between fresh ground / surface waters and volcanic gases (though other sources also contribute). Volcanic gases tend to be chlorine- and, especially, sulphur-enriched. Modern marine systems overlap with seawater, although their larger compositional range implies more complex sources. Examples from arid environments span a considerable range, from mildly saline to halite-saturated (Fig 4A). These overlap with the ranges of saline surface



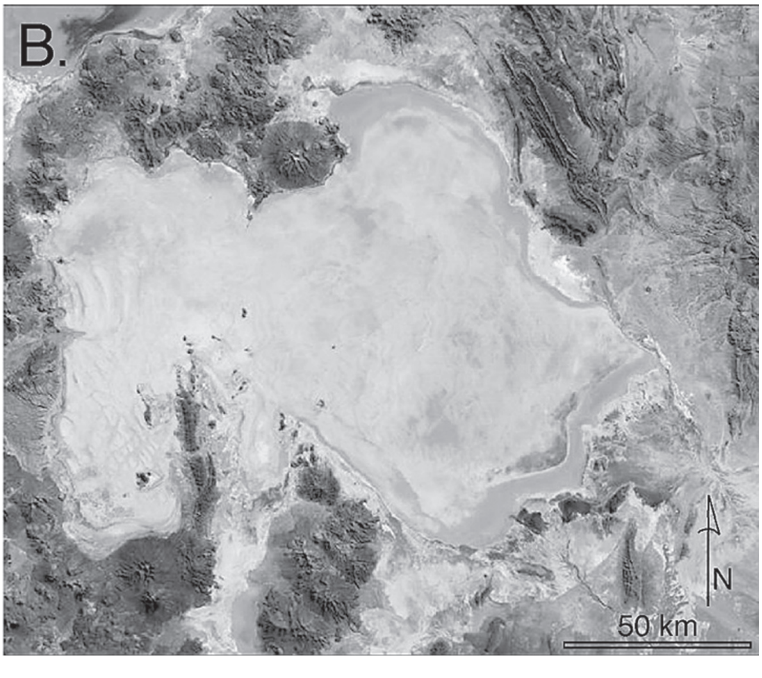


Figure 2: Overlap between modern magmatism, saline surface fluids and evaporites.
A) Map showing modern climate and volcanism plus distribution of evaporitic sediments as a function of latitude. Neogene to modern Fe-oxide-rich systems occur where magmatism overlaps with arid climates (cf. Barton and Johnson, 1996).
B) TM image of the Salar de Uyuni, Bolivia. Note the many modern volcanoes in the western half of the image. This area contains a number of young igneous- and sediment- hosted Cu and Fe-oxide occurrences (U.S. Geological Survey, 1992).

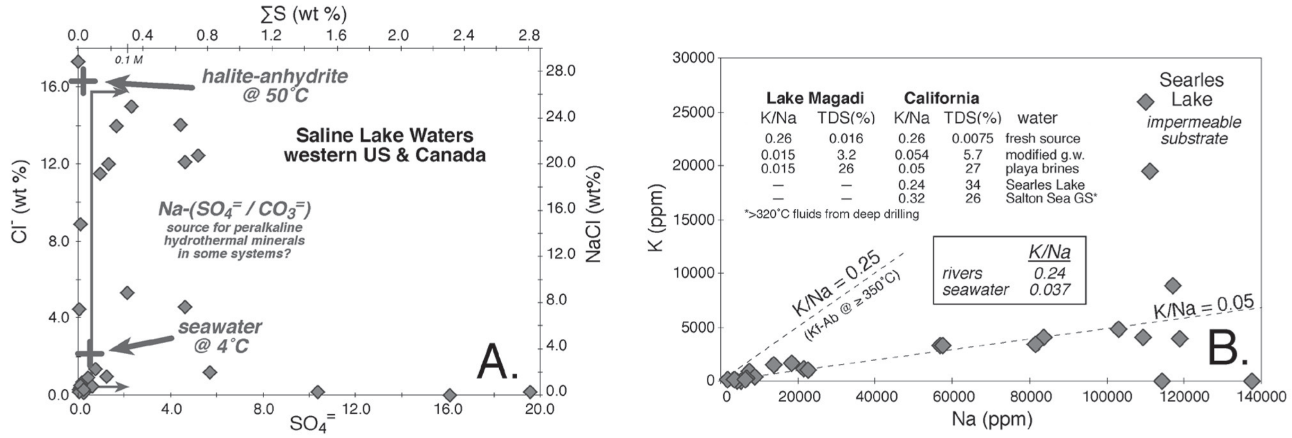


Figure 3: Compositions of some modern brines: On the left, total chloride versus sulfur for seawater and some saline lakes (Eugster and Hardie, 1978). High chloride promotes metal transport, alkali-rich alteration, whereas low sulfur inhibits precipitation of chalcophile elements (cf. Fig. 4 below). On the right, Na vs. K for the same lake waters and some others. Note that the low K/Na in most areas due to diagenetic removal of K from continental runoff (making oxidized, K_2O-rich substrates). Geothermal fluids in rocks with K-bearing hosts have elevated K as a result of high-temperature fluid-rock interaction (e.g., Salton Sea).

waters (Fig. 3), however, they can also result from low-temperature dissolution of evaporites and/or from other diagenetic processes. Fluid inclusion compositions (not included in Fig. 4) show broadly similar patterns when grouped by setting.

Chloride and sulphur contents help govern metal transport and deposition. Other things being equal, increasing chloride increases solubility and transport of many elements, notably the alkalis, alkaline earths, and most metals. For complexes that have two or more Cl^-, the increase in solubility with chlorinity is exponential – thus highly saline fluids can transport metals far more effectively than dilute fluids. Conversely, sulphur is necessary for precipitation of many metals, especially the chalcophile elements including Cu, Zn, and Pb. Without sufficient sulphur, these metals will tend to remain in solution. Fig. 4B shows that in fluids with high Cl to S ratios, metal contents exceed sulphur contents (as indicated by the Fe > ∑S line), thus precipitation of chalcophile elements is limited by the sulphur contents. In contrast, precipitation of siderophile and lithophile elements, such as Fe, REE, P, and the alkalis, will not be affected directly by the sulphur limitation because they form oxides, phosphates, carbonates, and silicates rather than sulphides. Gold and other precious metals provide intriguing variants on these systematics because they form both sulphide and chloride complexes, depending on conditions, and they can precipitate in native form and in various compounds (cf. McKibben *et al.*, 1990).

Summarising, a high-Cl, low-S fluid will preferentially develop iron-oxide-rich, sulphide-poor mineral assemblages – *whatever the fluid source*. Non-magmatic brines of various types belong to this category, but so might some magma-sourced brines. The implications of different fluid sources are developed below, after a short review of the geological and geochemical features of some Fe-oxide-rich hydrothermal systems.

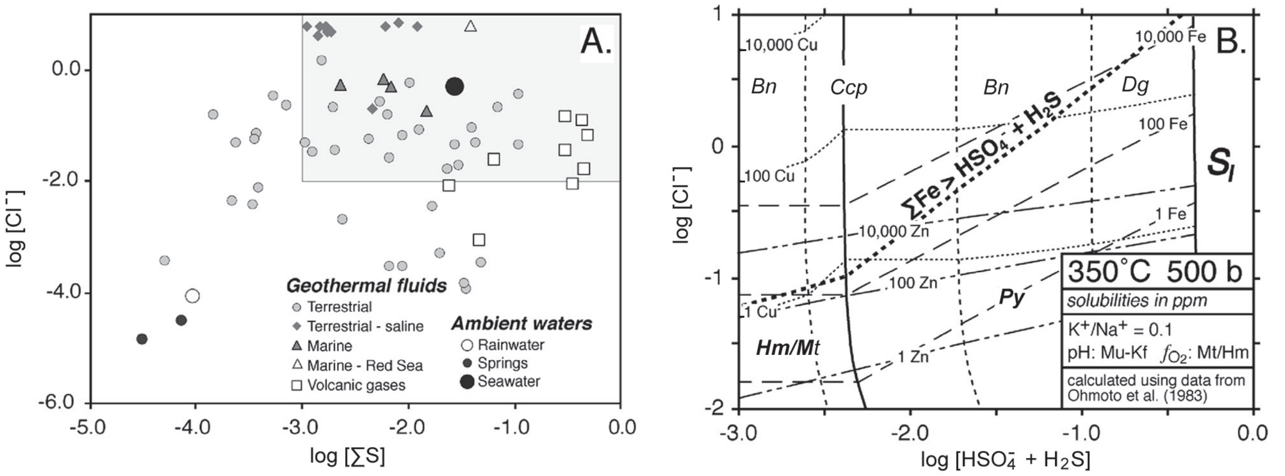


Figure 4: Log [Cl^-] vs. log [∑S] plots (molality) illustrating some natural waters and metal solubilities. A) Compositions of modern fluids grouped by environment, mostly from geothermal systems. Compiled from various sources. B) Calculated Cu-Fe-S-O sulfide and oxide mineral stabilities and Fe, Cu, and Zn solubilities (in ppm; Zn buffered by sphalerite) as a function of fluid chloride and sulfur contents at 350˚C (modified from Barton and Johnson, 1996). Same area as the inset in (A).

Characteristics of Igneous-related Fe-oxide-rich Hydrothermal Systems

Table 1 summarises many characteristics of igneous-related iron-oxide-rich hydrothermal systems. These divisions are founded on geological observations, but here are cast in terms of alternative sources of hydrothermal fluids for the purposes of this paper. Such broad comparisons are useful, particularly to identify those features that are distinctive of particular groups and which can help better understand their origins.

The first group (Table 1) comprises those that clearly have a magmatic origin. These systems are varied but comprise many Cu-Au porphyry deposits with both gold- and copper-dominated varieties. Also incorporated are rarer types such as strongly alkaline systems including carbonatites. As a whole, this group is distinguished by close association with igneous centres, abundant sulphides and modest magnetite contents, high-temperature mineralisation, and (in most cases) moderate volumes of alkali-rich (mostly potassic) alteration. Metal enrichments accompany the potassic and overprinting / distal acid styles of alteration. Related igneous rocks are broadly intermediate in composition, mildly to strongly alkaline, and with distinctly porphyritic phases that are typically related to mineralisation. This group overlaps with diorite-type and alkaline porphyry Cu-Au systems (e.g., Hollister, 1978; Lang *et al.*, 1995; Jensen and Barton, 2000).

The second and third groups contain many of the typical examples of the Fe-oxide(-Cu-Au) group. They have abundant iron-oxides (magnetite and /or hematite) and sparse sulphides, they lack a clear link to particular intrusive events, and they have voluminous alkali-rich alteration (Na- and/or K-rich). Alkali-rich alteration may be metal-enriched, but the large volumes are metal-depleted, commonly with well over half the ferrous and base metals removed (Frietsch *et al.*, 1997; Johnson 2000; Williams, 1994; Battles, 1990). Associated igneous centres vary widely in composition (from mafic to felsic, from subalkaline to alkaline) and may lack strongly porphyritic phases. Many of these systems are barren, having only geochemically anomalous contents of metals. This group has characteristics that many investigators have used to compare Olympic Dam, Kiruna and other examples (e.g., Hauck, 1990; Hitzman *et al.*, 1992; Barton and Johnson, 1996). Their origins are controversial. In Table 1, we advocate non-magmatic fluid sources, but it is the geologic character, *not* the fluid source that is the basis for classification.

The fourth group has mixed characteristics. These might result from superposition of systems or hybrid processes during formation. In some areas, such as the Yerington district, Nevada multiple kinds of fluids are clearly involved and there are several distinctive styles of mineralisation (Dilles and Einaudi, 1992; Dilles *et al.*, 2000). In other districts, such as Punta del Cobre (Candeleria), Chile, the characteristics within single systems have the flavor of both types with magnetite-rich alteration but with superimposed high-T copper mineralisation (Marschik *et al.*, this volume; Marschik and Fontebote, 1996). Analogous to the epithermal environment, many systems from the two middle columns of Table 1 conceivably could be hybrids formed from multiple fluids, each fluid imparting a necessary contribution to the end result.

Conceptual and Quantitative Models of Alternative Sources

The consequences of alternative fluid sources can be considered in terms of their expected effects on mass transfer in associated hydrothermal systems – that is, the distribution, timing and amounts of alteration and ore minerals.

Conceptual Models

Fig. 5 illustrates simple conceptual models for different combinations of magmatic and non-magmatic fluid sources. These follow the general geological characteristics outlined above, but with the added inference of fluid sources and their links to alteration types and metal sources. The nature of the hydrothermal alteration depends markedly on the path, especially the fluid sources and host rocks.

Magmatic fluid-dominated systems (porphyry-type and others) are shown on the right hand side of Fig. 5. Magmatic fluids generated during cooling and crystallisation of a magma flow outward and generally upward. Cooling produces deep K-silicate alteration with overprinting and shallower acid alteration. Metals are typically deposited at moderate to high temperatures. Early and proximal assemblages have chalcopyrite(-bornite)-magnetite. In later associations, sulphide assemblages are typically more sulphidised, with pyrite the most common iron mineral (in most systems) and copper mineralogy typically going to chalcopyrite with combinations of bornite (+pyrite), digenite, enargite and covellite. Anhydrite is common. These patterns agree well with known solubility relationships (Hemley *et al.*, 1992) along with the presence of Fe-Cu-S sulphide ± sulphate saturated magmas (e.g., Borrok *et al.*, 1999; Keith *et al.*, 1997; Streck and Dilles, 1998). Sodic alteration will form if external brines enter the system (one type of hybrid system, as illustrated in Fig. 5) or if solutions are either peralkaline (e.g., as in carbonatites) or unusually fluorine-rich (e.g., as in some granite-related systems). Distinctly alkaline magmatic systems are commonly enriched in Cu and Au however, like their subalkaline counterparts, they have systematic patterns in alteration, metal zoning, and links to magmatic chemistry and evolution (Jensen and Barton, 2000). In some districts, external fluids might contribute metals to a magmatic-fluid dominated systems (e.g., Yerington, NV porphyry Cu deposits, see Dilles and Einaudi, 1992).

The magmatic environment is well suited to metal concentration because fluid release tends to be focused, magmas can be saturated in sulphides (thus near Cu sulphide saturation at high temperature), and because temperature decreases rapidly (with concomitant decrease in sulphide solubility) near the tops of magma chambers where fluids

Table 1: Characteristics of igneous-related Fe-oxide-rich hydrothermal systems*

Interpreted fluid source	Magmatic	Non-magmatic[1]		Hybrid or superimposed systems
		Coeval brines	Older brines / evaporites	
Examples[2]	Grasberg, Maricunga, Palabora, Bayan Obo(?)	Humboldt, Cortez, Kiruna (?), Olympic Dam (?)	Salton Sea, Korshunovsk, some Cloncurry deposits (?)	Yerington, Candelaria (?), some Cloncurry deposits (?)
Magmatic	• close link to particular intrusive events; porphyries typical • good correlation with magma type ± setting • typically intermediate to felsic calc-alkaline to alkaline (± carbonatites)	• lack of correspondence with particular intrusive events, porphyries scarce • varied magma types and tectonic settings • mafic to felsic, subalkaline to alkaline	• lack of correspondence with particular intrusive events; porphyries scarce • varied magma types and tectonic settings • basalts to rhyolites, subalkaline to alkaline	• varied settings; porphyry-type mineralization generally present in region; may be present in district, yet Fe-Cu-Au lacks close link to porphyritic units
Geologic setting	• tectonic settings: typically arcs both extensional and compressional; linked to magma types • no correlation with associated sedimentary environments	• varied tectonic settings: typically extensional in the upper crust (can be in compressional orogens) • correlation with coeval arid zones; evaporites common but not required	• varied tectonic settings: may or may not be extensional • evaporites or meta-evaporites present; no correlation with coeval arid zones	• generally arc-related; commonly with extensional component • evaporitic conditions or materials in region
Structural controls	• intrusion-centered fractures dominant over external structural or stratigraphic controls (latter important distally)	• association with igneous centers, but broader structural (regional, volcanic) and / or stratigraphic controls	• association with igneous centers, but broader structural (regional, volcanic) and / or stratigraphic controls	• no close association with intrusion-centered stockworks; stratigraphic or regional structural controls typical
Metals	• Cu and Au enriched and typically well correlated; U and Co generally low; sulfides common • metals with high-T Qz veins and K-alteration ± acid assemblages • widespread Mt (<5 to 15%); Hm present, but uncommon • REE not strongly enriched (except carbonatites); phosphates minor • commonly zone to Au-Ag and base metal	• variable Au and Cu; Co common; U variable; sulfides scarce • metals typically late, with mod-T paragenesis (K, Na or acid alteration) • Mt abundant (typically >15%) deep; also shallow in more mafic systems • Hm widespread both late (commonly >15%) and shallow, ± syngenetic • high REE; phosphates common (esp. apatite) • uncommonly zone to 5 element or base metal	• variable Au and Cu; Co common; U variable; sulfides scarce • metals typically late, with mod-T paragenesis (K, Na or acid alteration) • Mt abundant (typically >15%) deep; also shallow in more mafic systems • Hm widespread both late (commonly >15%) and shallow, ± syngenetic • high REE; phosphates common (esp. apatite) • uncommonly zone to 5 element or base metal	• typically Cu and Au ± Ag enriched, may or may not have Co and U • metals typically late, but can be with either mod-T *or* high-T paragenesis • Mt (> ± Hm) abundant (typically >15%), typically pre-sulfide (may substantially pre-date) • REE variable, typically high where hydrothermal phosphates are common • rarely (?) zones to base-metal-Ag
Grades	• key parts typically are well mineralized; some Cu- and Au-poor, pyrite- or magnetite-rich variants	• most occurrences are “barren” (only geochemically anomalous); can be high-grade with favorable traps	• most occurrences are “barren” (only geochemically anomalous); can be high-grade with favorable traps	• recognized occurrences are typically well mineralized, but may not be economic

Alteration	• K-alteration high-T only (Bi ± Kf, localized (generally <1-5 km^3); commonly coincident with metals • high-T quartz veins abundant except in silica-undersaturated systems • complex superimposed to distal (shallow) acid alteration, commonly pyrite-rich • Na-Ca alteration not an intrinsic part in most except in some strongly alkaline systems (or hybrid systems) • high-T sulfates common (anhydrite) • skarns typically andradite-rich	• two types of K-alteration can occur: voluminous (>1-5 km^3) Kf + Hm commonly stratabound; intermediate to felsic systems host localized Kf-Bi ± Act in upwelling zones (rare in mafic) • quartz is subordinate to FeOx at high-T, but prominent with acid alteration (except in mafic) • voluminous Na±Ca alteration (commonly >10 km^3); Alb-Act-Chl-Crb accompanies Mt ± Hm ± sulfides in many systems (esp. mafic ones) • chlorite- or sericite-dominated acid alteration (+ abundant Hm); ± sulfide-poor advanced argillic alteration • high-T sulfates absent • skarns can be garnet-poor	• local K-alteration: mod- to high-T Kf-Bi ± Act in upwelling zones of intermediate to felsic systems (rare in mafic); voluminous Kf + Hm is rare • quartz is subordinate to FeOx at high-T, but prominent with acid alteration (except in mafic) • voluminous Na±Ca alteration (commonly >10 km^3); Alb-Act-Chl-Crb accompanies Mt ± Hm ± sulfides in many systems (esp. mafic ones) • chlorite- or sericite-dominated acid alteration (+ abundant Hm); ± sulfide-poor advanced argillic alteration • high-T sulfates absent • skarns can be garnet-poor	• K alteration common (Kf-Bi-Act), but not always present near deposit; can be of both high- and low-T types • high-T quartz and anhydrite can be common, but may be absent • voluminous Na±Ca alteration (commonly >10 km^3) • acid alteration chlorite- or sericite-rich, may or may not have associated metals; generally sulfide-poor • skarns can have andraditic garnet but tend not to be garnet-dominated
Fluids	• mod- to high-salinity, can be hypersaline, late fluids can be dilute; daughter minerals: Cpy common, other primary Fe minerals rare	• mod- to high salinity, can be hypersaline; late fluids saline; daughter minerals: Fe minerals widespread, sulfides absent	• mod- to high salinity, can be hypersaline; late fluids saline; daughter minerals: Fe minerals widespread, sulfides absent	• mod- to high salinity, can be hypersaline; late fluids saline; daughter minerals: Cu and/or Fe phases
Hydrology	• lithostatic to hydrostatic • fracture control by intrusion > distal structural and lithologic control	• hydrostatic to locally overpressured • structural control (regional or volcanic) ~ lithologic control	• hydrostatic to locally overpressured • structural control (regional or volcanic) ~ lithologic control	• variable: probably hydrostatic to lithostatic • structural and stratigraphic control
Isotopes	• isotopic evidence indicates igneous source (typically magmatic, from other evidence) ± late external fluids	• isotopic evidence variable; some clearly non-magmatic, but igneous (or igneous-like) signatures can be present	• isotopic evidence variable; some clearly non-magmatic, but igneous (or igneous-like) signatures can be present	• isotopic evidence variable; some clearly non-magmatic, but igneous (or igneous-like) signatures are common
Metal source(s)	• magmas (magmatic sulfide?)	• igneous or older rocks, dispersed sulfide or in other minerals	• igneous or older rocks, dispersed sulfide or in other minerals	• magmas or host rocks, perhaps both
Traps	• cooling ± wall-rock reaction and phase separation	• cooling ± wall rock reaction for Fe, REE; mixing, boiling or S-rich host to make ore-grade Cu etc.	• cooling ± wall rock reaction for Fe, REE; mixing, boiling or S-rich host to make ore-grade Cu etc.	• cooling ± mixing and wall rock reaction most likely but boiling or S-rich host could be important

* Distinctive features of each group are *italicized.*

[1] Some examples (detachment systems) may lack a necessary magmatic connection but still share most of the features seen in the surface-sourced variants.

[2] Districts in which our group has worked are underlined.

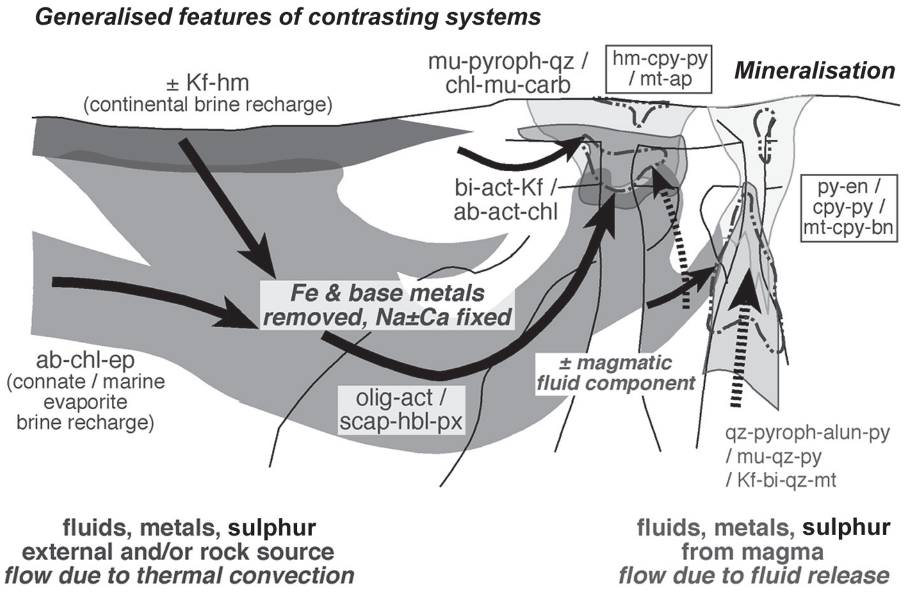


Figure 5: Simple conceptual models of hydrothermal alteration and mineralisation for alternative fluid sources and host rocks (cf. Table 1). See text for discussion.

are expelled. If magmatic sulphides are present, Cu and Au will be substantially enriched in the fluid relative to Fe given that all these phases are present and thus saturated in the fluid. This contrasts with the external brine sources.

Circulation of external brines by thermal convection (Fig. 5, left) creates both distal and proximal alkali-rich alteration. Voluminous metal-depleted, sodic(-calcic) ± shallow K-feldspar-hematite alteration form in inflow zones – their distribution and character will be a function of the external brine source and the plumbing system. Near the magmatic heat source these fluids are focused in structurally or lithologically favorable zones. There, on rising and cooling, they produce intense sodic (typical in mafic host) and/or potassic alteration (typical in felsic host) plus overprinting and shallower hydrolytic alteration assemblages (sericite or chlorite to pyrophyllite). Mixing with shallow surface-derived fluids could also be important for precipitation and possibly for metal introduction (Fig. 5; see Haynes *et al.*, 1995). Metals are leached distally; they precipitate proximally only insofar as possible. In other words, metals form oxides or sulphides (to the limit of available sulphur), otherwise they are lost (e.g., most Zn, Pb and variable amounts of Cu). Ore mineral assemblages are sulphur-poor: magnetite to hematite with subordinate chalcopyrite(-bornite-chalcocite) ± pyrite. Lithophile elements such as P, REE, and U can be concentrated and reworked in this environment. Where magmatic fluids enter these systems (Fig. 5, centre-right), the extra sulphur and/or metals would favor earlier and more efficient precipitation of chalcophile metals (e.g., as possible at Candelaria, see Marschik *et al.*, this volume).

Thermal convection of external fluids is the rule in shallow magmatic settings and, if the fluids are saline, metal mobility will be high. Unlike the situation with magmatic fluids, metals such as copper will not likely have as high concentrations and their precipitation will be strongly influenced by the availability of sulphur or other chemically favourable circumstances in the shallower portions of ore-forming systems. In most circumstances, lacking a favourable trap, metals will be lost or dispersed in low concentrations through large volumes of rock (see below).

Quantitative Approaches

Quantitative approaches based on energy and mass balance and on numerical modelling illustrate and better define the differences between the alternative fluid sources.

Mass and Energy Balance Models

Fig. 6 and Table 2 show the framework and principal results for calculations of mass and energy balance for contrasting fluid sources. Both scenarios begin with an intrusion of 1000 km^3. In the case of magmatic fluids, 20% of the intrusion contributes plausible amounts of chloride, metals, silica and alkalis to an aqueous magmatic fluid (e.g., cf. Dilles, 1987). If this fluid is focused into 1 km^3 where all constituents are precipitated, the result would have reasonable numbers for a porphyry copper system (Table 2) – 2.5 Gt with 0.5 % Cu, 5 volume % quartz veins, and a moderate amount of hydrothermal magnetite (comparable to the amount of quartz). From these mass balance consideration alone, fluids would contain about 0.1% Cu which is close to experimentally determined solubilities of Cu-bearing sulphides at magmatic conditions (Hemley *et al.*, 1992). Gold grades, if derived from the same magmatic sulphides and quantitatively precipitated, would be ~0.5 ppm (i.e., Cu:Au ~ 10 000:1 by weight). For all but peralkaline or fluorine-rich magmas little if any sodic(-

calcic) alteration can form from these fluids, consistent with the scarcity of this style of alteration in many magnetite-rich porphyry systems. Pyrite and anhydrite are abundant, but not ubiquitous in this environment. In this simple analysis, they reflect the oxidised sulphur content of the original magmas. More reduced variants will not produce as much sulphate and the higher sulphidation states. The key features then are relatively low magnetite to quartz ratios (near unity or less), early forming Cu-Fe sulphides, and a close spatial relationship to fluid-producing magma bodies (e.g., porphyries).

The analogous calculations for circulation of external brines are shown in the right-hand column of Table 2. For the same size intrusion (1000 km^3) the results demonstrate that it is plausible to move large quantities of metals while making geologically observed amounts and styles of alteration. In contrast to the above scenario where the mass of magma limits the amount of fluid, in this scenario, the limit on fluid involvement is heat balance. Here, 10% of magmatic heat is used to circulate fluids, a conservative choice compared to amounts that can be circulated in shallow intrusive settings (e.g., Cathles, 1981). Even in deeper settings, where fluids might be sourced from basins or by destruction of older (meta)evaporitic materials, heat balance would not be limiting, permeability structure would be the key as it is in shallow settings.

Predicted metal mobility using published solubilities, rock compositions, and reaction paths would lead to transport of 1 to 4 Mt of Cu and 500 to 1000 Mt of Fe. The smaller Cu values would reflect a source solely within intense sodic(-calcic) alteration (cf. Fig. 5), whereas the larger values would reflect additional sourcing from sodic / propylitic and low-temperature potassic alteration. The latter is consistent with metal loss commonly seen in these systems (Johnson, 2000; Cooke *et al.*, 1998; Hollocher *et al.*, 1994). If the metals precipitate together in a single location (sulphur limitation being severe for Cu and other chalcophile elements), the result would be approximately 2000 Mt of 50% magnetite with 0.05 to 0.2 % Cu. Substantial silica would be added (if rocks along the path are quartz-bearing) but overall Fe-oxide to quartz ratios would be high because of the more effective transport of iron (in both this scenario and the one for magmatic sourced fluids, hydrolysis reactions can produce much more quartz from destruction of original silicate minerals in the rocks hosting the deposit.) In contrast to magmatic sourced systems, large volumes of sodic-calcic alteration form on the inflow path and, in some circumstances, will accompany or substitute for potassium-silicate assemblages on the outflow (cooling) paths and accompany formation of oxide and sulphide minerals.

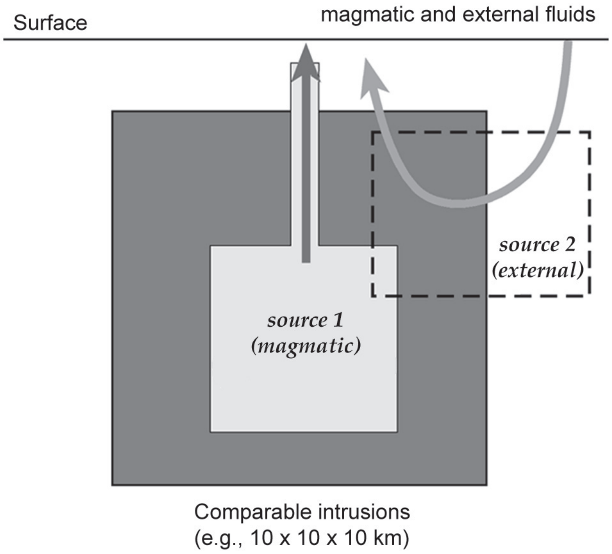


Figure 6: Framework for quantitative comparison of hydrothermal systems magmatically and externally sourced fluids. Mass and energy balance is based on an intrusion system of 1000 km^3 (e.g., 10 x 10 x 10). Key results and model parameters are given in Table 2. See text for discussion.

These results demonstrate that large amounts of metals can be moved (consistent with the evidence noted below), however, for this scenario to lead to an economic deposit, the key will be trapping the copper (gold etc.) in a fraction of the iron oxide volume or beyond it. Such traps may occur only in a small subset of igneous-related systems, similar to the relatively small fraction of well mineralised sedimentary Cu systems. Where metals are distributed throughout the volume, contents would be geochemically anomalous but low. This is illustrated in Table 3 where the numbers illustrate what would form if the relevant elements were uniformly enriched along with iron in deposit that contains 50% Fe. These values are remarkably similar to those seen in iron “skarns” (carbonate and igneous-hosted) around the world, with the exception of the apatite content which is unusually high.

Overall, both scenarios can move large amounts of metal. One, the magmatic source, has a natural means of concentrating chalcophile metals, whereas the other depends on serendipity to create economic concentrations rather than simply geochemically anomalies. The latter thus predicts the widespread occurrence of “barren” systems, and the small number with economic metal concentrations. The latter deposits could be due to mixing, boiling or reaction with favorable wall rocks, or they could be hybrid systems with a magmatic component.

Numerical Models

The results of the mass and energy balance calculations above are compatible with the results of finite difference mass and energy transport models. These models derive from earlier models for transport of heat and materials in intrusive environments and were originally developed to better understand igneous-related metamorphism in the western United States (Barton *et al.*, 1988; Hanson and Barton, 1989; Hanson *et al.*, 1993; Hanson, 1995). These calculations use geologically realistic values for permeabilities, thermal parameters, and other transport properties combined with a simple thermodynamic-based treatment of silica solubility and alkali-exchange equilibria.

Table 2: Some predicted geologic features consistent with mass and energy balance models.

	Magmatic source	External Source
"Deposit" (mass & contents)	• 2,500 Mt (~1 km^3) @ 0.5 wt % Cu (12.5 Mt)[1] 4 wt % magnetite 5 wt % quartz added[2] • vol Mt / vol Qz ~ 0.5 • up to 18 wt% K-feldspar (or equivalent in biotite / sericite)	• 2,000 Mt (~0.6 km^3) @ 0.06[0.18]. wt % Cu (1.25[3.75] Mt)[1] 50 wt % magnetite 6 wt % quartz added[2] • vol Mt / vol Qz ~5 • up to complete conversion of aluminous minerals to K-feldspar, biotite, or sericite
Other alteration	• ~0 km^3 Na(Ca) alteration (unless external brines or peralkaline magmatic fluids are present) • alteration with inflow can be limited • [large volumes (>1 km^3) of shallow acid alteration (sericite ± chlorite; advanced argillic) and distal propylitic]	• ~20 km^3 Na(Ca) alteration (@ 20 vol% new albite) • 1-3 times additional volume can be altered to propylitic ± low-T potassic on inflow • [large volumes (>1 km^3) of acid alteration with Fe-oxides and distal on outflow]
System parameters	• intrusion size: 1000 km^3; 20% of magma chamber contributes magmatic fluids • magma has 2.5 % H_2O, 1000 ppm Cl • fluid moves 1 wt % SiO_2 • fluid moves Fe/(Na+K+Fe) ~0.2 • 25 ppm Cu available from magma	• intrusion size: 1000 km^3; 10% of magmatic heat circulates external fluids • external fluids have 25% $NaCl_{eq}$ • fluid moves 0.2 wt % SiO_2 • fluid moves Fe/(Na+K+Fe) ~0.1 • 25 ppm Cu available from altered rock (sodic or sodic+propylitic+low–T potassic)

[1] Cu grades and contents based on quantitative precipitation of all ore constituents over the entire volume. Higher grades are obtained if traps are localized; conversely much of the metal can be lost (as is the case with Zn). The larger numbers (in brackets) for the external brine system reflect the amounts obtained when using external propylitic and low-T potassic alteration as additional sources.

[2] Quartz contents estimated from silica transported by fluid flow. Large amounts of quartz can also form in both kinds of settings by hydrolysis reactions.

The modeling shows that recharge of surface-derived brines can create laterally extensive K_2O-rich alteration overlying deeper and more extensive sodic alteration (Fig. 7A). The geometry of this low-T K-rich alteration resembles that seen in many districts primarily those with felsic rocks in continental settings (e.g., Fig. 7B). If the source fluids are K-poor (e.g., from basinal brines or a marine evaporitic source) then the shallow K-rich alteration is missing, but the deep sodic(-calcic) alteration still forms (Fig. 5). On upwelling, non-magmatic brines can create intense K- or Na-rich alteration, or both, depending on the composition of the host rock and overall amount of fluid flow. In Fig. 7A, fluid flow near the top of the intrusions has both upwelling deep fluids and shallow recharge from the right – an example where complex parageneses would be expected and mixing could be an important process for ore formation (cf. Haynes *et al.*, 1995). For the case of magmatic brines and fresh external waters, K-silicate alteration develops above and within the upper parts of the intrusions (not illustrated in Fig. 7, but the counterpart to Fig. 7D). It is not quite as intense as for the external brine source (there being less fluid overall); sodic alteration is minor and due to local recirculation of magmatic brines. Silica redistribution is substantial in both

Table 3: Element contents for uniform concentration from an intermediate igneous source *

	Fe	P	Ce	Cu	S	Co	Ni	Au
Content @ 50% Fe	50 %	1.29 %	250 ppm	570 ppm	0.45 %	250 ppm	190 ppm	0.047 ppm
	Magnetite	Apatite	RE_2O_3 in apatite	Chalcopyrite	Pyrite	Co in pyrite	Ni in pyrite	Au in pyrite
Content as minerals	68.5 %	7.0 %	0.91 %	0.16 %	0.96 %	2.7 %	2.0 %	4.9 ppm
	76.5% ore minerals (including apatite) 23.5% others							

* These numbers reflect uniform enrichment of all of these elements by the amount necessary to achieve 50% Fe concentration from the contents in an andesitic composition rock (i.e., by about 10 times). The contents are then distributed among likely minerals (analogous to calculating a norm for an igneous rock).

cases (Figs. 7C, 7D) with greater quartz added in the magmatic case primarily due to the superposition of magmatic-sourced silica with the silica redistributed by external fluids. Unlike the situation with the alkalis, both brines and fresh water redistribute similar amounts of silica. This is evidenced by the spatial distribution and intensity of the leached zones (stippled) in Figs. 7C and 7D. The numerical results, although preliminary, provide an independent check that is consistent with the mass and energy transport models presented earlier.

Evidence Cited for Different Sources of Components

Table 1 and the discussion above outline many of the kinds of features that have been used to infer sources of fluids and other components. Igneous sources (though not necessarily magmatic) for many elements are undoubted, as demonstrated, for example, with the rare earth elements (Johnson and McCullough, 1995; Gleason *et al.*, 2000). Many papers emphasise magmatic fluid sources for Fe-oxide deposits based on a variety of geologic and geochemical evidence (see Pollard, this volume; Pollard *et al.*, 1998; Hauck, 1990; Perring *et al.* 2000). Evidence cited includes proximity to intrusions, inferred correlations with intrusion compositions, stable and radiogenic isotopic data consistent with a magmatic source, and mineral assemblage and fluid inclusion data that are interpreted to require magmatic fluids. For many magnetite-bearing deposits of the porphyry and alkaline families (Table 1, first column), these inferences are buttressed by compelling field relationships for a magmatic link, evidence that is hard to find in the iron-oxide dominated systems.

In contrast to discussion of magmatic sources, only a handful of papers evaluate non-magmatic brines as important (not necessarily the sole) contributors to mineralisation (e.g., Eugster and Chou, 1979; Rose *et al.*, 1985; Haynes *et al.*, 1995; Barton and Johnson, 1996) or the significance of the common association with voluminous sodic alteration (Dilles and Proffett, 1995; Battles and Barton, 1995). These papers have emphasised many of the features

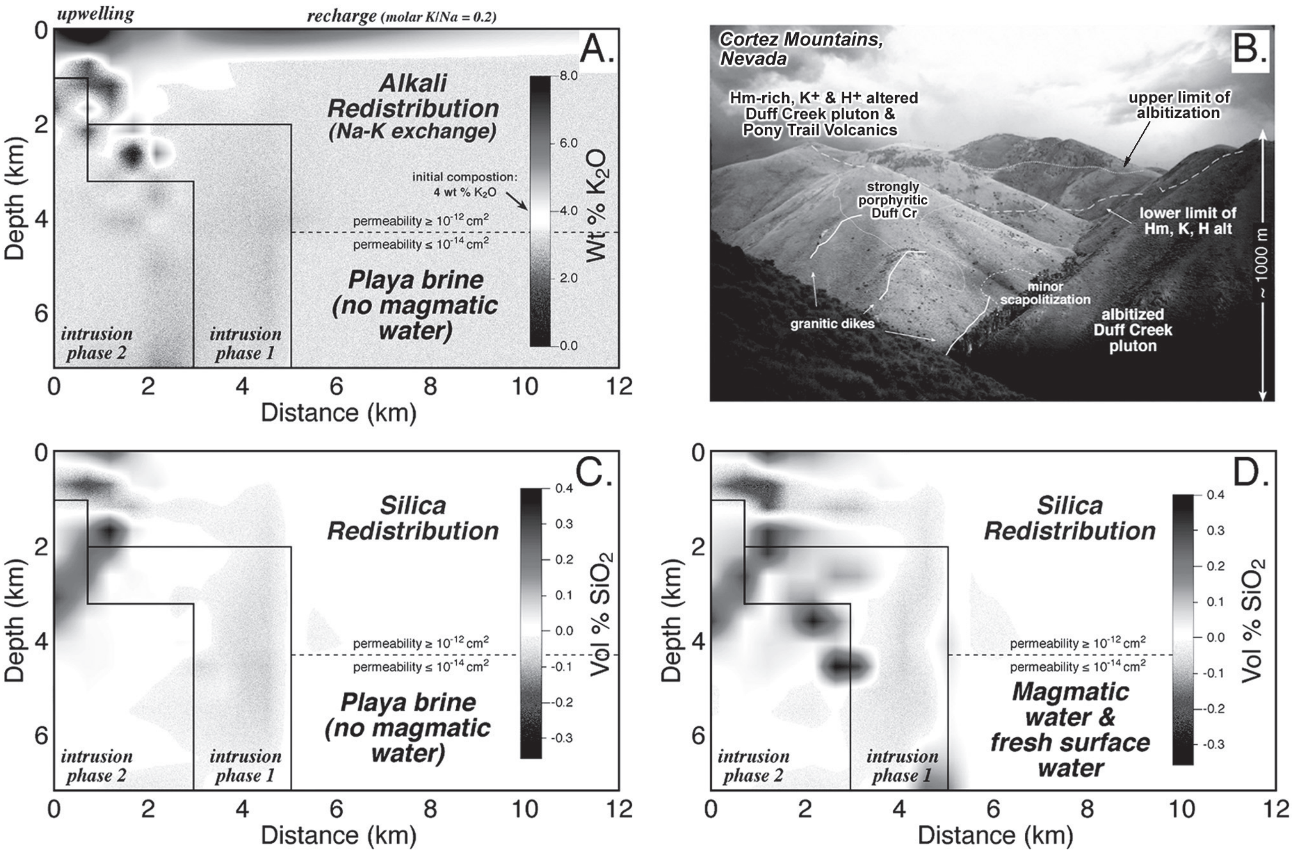


Figure 7: K-Na exchange and silica mass transfer results for numerical models of energy and mass transport in brine systems of various types (Hanson, 1995; Barton et al., 1998). The models have the same permeability structure and the same two-stage intrusion emplaced on the left. The left boundary is symmetric. A) Alkali redistribution in felsic rocks. Note (1) the laterally extensive K_2O-rich rocks where brines recharge (this will be oxidized, low-T potassic alteration), (2) the abundant Na_2O alteration (stippled) at depth, and (3) the intense concentrated K_2O addition where the brines rise toward to the surface (second type, with Fe oxides and (presumably) other ore minerals). B) An example of alteration like that modeled in (A). Photo showing shallow hematite and K-silicate-altered felsic volcanic + hypabyssal rocks (with minor Fe-oxide-Cu-Au mineralization) overlying sodically altered granitoids. Jurassic igneous complex, Cortez Mountains, Nevada. C) Silica redistribution in system with external brine. Note concentration in upwelling zone over center of intrusion and dispersed zone of leaching (stipple). D) Similar diagram showing silica redistribution for a combination of magmatic fluids and fresh water. The larger silica addition in (D) compared to (C) is due mainly to magmatic fluids.

highlighted in the middle two columns of Table 1: the diversity of associated magmas, the volumes and styles of alkaline alteration, the correlation with sources of external brines (contemporaneous or older), and geochemical and petrological evidence for remobilisation of metals and other constituents by external fluids.

The coincidence of intense alkaline alteration and iron-oxide mineralisation goes back at least a century (e.g., Lindgren 1913, p. 713) and has been widely noted in recent years (Song *et al.*, 1981; Barton *et al.*, 1988; Hitzman *et al.*, 1992; DeJong and Williams, 1995; Frietsch *et al.*, 1997). It is the source of this alkaline alteration that has been controversial and what, if any, link it has to mineralisation. In some areas, such as the southwestern North America, the relative youth of the systems allows a fairly complete understanding of the geologic setting. In combination with evidence from the hydrothermal systems themselves, this clearly points to a non-magmatic origin (Dilles and Einaudi, 1992; Battles and Barton, 1995). In other areas, alternative interpretations prevail. In some environments (e.g., carbonatites) magmatic fluids are clearly dominant, but in others it is less clear. What is obvious is that there are a number of examples where non-magmatic fluids are very important and where large quantities of metals have moved.

Challenges in Interpretation

In spite of the power of geochemical and theoretical tools – modeling, isotope geochemistry, fluid inclusion studies, etc. – they rarely lead to unique interpretations in these systems. In concert with geological constraints, they can eliminate some interpretations while supporting others. However, consistency with a model is no guarantee of its validity. Modeling, as described above, shows that there are multiple ways to generate a common metallogenic signature, but that there may be distinguishable geologic differences at both the deposit and systems scales. Few observations are truly diagnostic. Isotopic studies (not reviewed here) commonly yield evidence for igneous (not necessarily magmatic) components – which could be consistent with either kind of fluid source – but even they are subject to uncertainty. For example, sulphur and oxygen isotopic values in the Salton Sea geothermal system (McKibben and Hardie, 1997) fall in the “magmatic” range, yet the geology clearly requires that these components are of non-magmatic derivation. Conversely, it is possible to generate “non-igneous” values from magmatic sources.

Fluid inclusions reveal much and there should be systematic differences among groups (Table 1). Salinities are not diagnostic as there are multiple ways of achieving hypersaline compositions. Most inclusions are studied in the vicinity of deposits, and they form largely in minerals on cooling paths where minerals precipitate rather than dissolve. This biases results against inclusion evidence for warming fluids. More extensive application of multi-element micro-analytical techniques will help by allowing more complete comparisons against possible sources. Other geochemical observations, for example of halogen ratios (Böhlke and Irwin, 1992; Yardley, this volume), can provide a powerful clue to sources of brines. As with the other tools these are complicated by variability within and between possible sources – for example, the wide variability found in sedimentary brines and complexities possible for nominally magmatic fluids (e.g., Campbell *et al.*, 1995).

Key Examples of Non-magmatic Fluid Involvement – Mafic and Young Systems

Basalt-driven hydrothermal systems and young examples illustrate that non-magmatic fluids *can* generate Fe-oxide-rich, sulphide-poor REE-Cu-Co-Au-Ag bearing mineralisation. Basaltic examples are informative because external fluids (of several types) are clearly documented and magmatic fluids are subordinate or absent. Young systems are informative because their settings are clearer than with old deposits, particularly in active systems. The Salton Sea geothermal system in southern California provides a compelling modern analog, demonstrating that iron-oxide rich, Cu-REE-Co-Au-bearing mineralisation can form by igneous-driven convection of evaporite-sourced brines.

Basaltic Systems

Fe-oxide-rich, Cu-Co-Au-Ag bearing systems associated with mafic magmatism are widespread (e.g., Barton and Johnson, 1996). A number of regions contain large iron-deposits; most of these have accessory base and precious metals which have been recovered from some deposits. Notable examples include magnetite deposits in the Siberian platform (Sokolov and Grigorev, 1977; Vakrushev and Ryabkov, 1984), the Mesozoic basins in the eastern U.S. (mainly Pennsylvania; Rose *et al.*, 1985; Robinson, 1988), and the Humboldt mafic complex in Nevada (Reeves and Kral, 1955; Johnson, 2000), and active mineralisation in the Danakil depression, Eritrea (Bonatti *et al.*, 1972). In contrast to intermediate or felsic systems, little or no magmatic fluid is expected in most of these examples. Furthermore, they can be compared directly with other mafic-driven hydrothermal systems. In marine settings, seafloor hydrothermal systems are thoroughly documented with distinctive styles of alteration and mineralisation, notably including Cyprus- and Besshi-type massive sulphide systems (Franklin *et al.*, 1993; Scott, 1997). Extensive sodic and magnesian alteration reflects seawater involvement, but the concentrations of metals are comparable to sulphur in solution thus they precipitate mainly as sulphides. In terrestrial settings, fresh water dominated systems are well documented (e.g., modern Iceland; the British / Greenland Tertiary Province; Norton and Taylor, 1979; Manning and Bird, 1995; Forster and Taylor, 1977; Ferry, 1987). The latter have widespread hydrothermal alteration – dominated by stable isotope exchange and volatile addition, not uncommonly up to near-magmatic temperatures, but they lack extensive mass transfer, a direct reflection of the lack of chloride and other ligands that are necessary to move most elements in quantity.

Young Systems

As illustrated in Fig. 2, there is considerable overlap between Neogene magmatism and evaporitic sedimentary systems, thus one would expect there to be young examples of geothermal systems with non-magmatic brines. Modern geothermal systems in the Eritrea (Danakil Depression) and California (Salton Trough) provide modern analogs, whereas young Fe-oxide-rich deposits in Chile, Bolivia, and the United States may provide recent arc- and extension-related examples (e.g., the Neogene El Laco and other oxide-rich, Au-Cu-bearing deposits, eastern Chile; Grez *et al.*, 1991; Rhodes *et al.*, 1999; Hitzman, this volume; mid-Tertiary detachment deposits, southern Basin and Range Province, Wilkins *et al.*, 1986; Spencer and Welty, 1989).

The active Salton Sea geothermal system in southern California provides a modern example of what can happen in a hydrothermal system dominated by non-magmatic brines (for an excellent review, see McKibben and Hardie, 1997, and the many papers cited therein). The Salton Trough is a rift basin that is isolated from the sea by the delta of the Colorado River. It is filled with continental-sourced sediments including halite-bearing evaporites. Active bimodal magmatism drives circulation of brines generated from dissolution of the evaporites into paleo-river water within the basin (McKibben *et al.*, 1988). All evidence indicates that magmatic water contributions are absent or very small, although the isotopic compositions of sulphur, oxygen and hydrogen have igneous-like values ($dD \sim -70‰$, $d^{18}O \sim 3‰$, $d^{34}S_{sulphide} \sim 0‰$) a result of fluid-rock interaction, partial sulphate reduction, and a mixed surface water source (McKibben and Hardie, 1997).

The fluids (mostly 20-30% TDS) are metal-rich (>2,000 ppm combined Fe-Mn-Zn-Pb-Cu), sulphur-poor (<100 ppm $\sum S$), and contain significant amounts (near 1 ppb) of Au and PGEs (McKibben *et al.*, 1990). The brines form iron-oxide(-Cu-Au-REE-Co-Ag-U)-bearing veins and scales (Fig. 8). Widespread specular hematite-rich veins contain chalcopyrite, Co-bearing pyrite, minor quartz, and REE-rich epidote group minerals. Magnetite-rich scales that form near the flash point in the geothermal wells can contain thousands of ppm each of Au, U, Co, Cu and other elements. (Thus implying that boiling of similar brines elsewhere could generate metal concentrations.) Mineral assemblages in the altered sedimentary rocks change systematically with depth: from shallow hydrolytic (carbonate - illite - chlorite ± K-feldspar; T<325˚C) to intermediate potassic (biotite ± chlorite ± K-feldspar ± actinolite; 325 to 360˚C) to deep sodic-calcic (salite - actinolite - oligoclase - biotite - andradite; T>330-360˚C) – another parallel with ancient systems. Lead and zinc remain in solution due to limited sulphur contents, although earlier veins in the system are more reduced and contain sphalerite + pyrrhotite more like the brines in the modern Brawley field to the south of the Salton Sea. (Our thermodynamic models for similar brines can generate multiple redox and sulphidation states depending on the fluid history – from reduced pyrrhotite or arsenide assemblages to fully oxidised hematite ± sulphate assemblages.)

Mass Transfer

Many areas with Fe-oxide-rich mineralisation have well documented metal-depletion (commonly nearly complete removal) in spatially associated sodic(-calcic) and low-temperature potassic alteration (Hollocher *et al.*, 1994; Williams, 1994; Frietsch *et al.*, 1997; Cooke *et al.*, 1998; Johnson, 2000). Where volumes have been quantified, the amounts of metals removed can be huge, comparable to or exceeding the amounts concentrated in world class deposits. Nonetheless, only rarely can the metal losses be balanced against known deposits in the same district (Fig. 9). Part of this deficit is in the undocumented: deposits are comparatively small, hidden, or eroded, or, the metals can be dispersed in large volumes of modestly enriched rock. The other part of this deficit is due to metals being lost from the system. This loss varies element by element. With iron, precipitation in oxides can capture much of the fluid inventory either in the subsurface or at the surface. In a few areas that have decent control (e.g., the mafic Humboldt and felsic Cortez complexes in Nevada), a substantial fraction (>10%) of the iron can be identified in known deposits. In contrast, base metals are dispersed where traps are absent (e.g., in the case of Zn and, in many cases, with Cu).

Here too, the Salton Sea provides a useful case study. In the geothermal field the zinc inventory lost from the rock balances well with the large amount in the brine reservoir (ca. 5 Mt). Manganese and lead in solution also approximately mass balance with the deep leaching (McKibben and Hardie, 1997). In contrast, much copper (and perhaps iron) are missing. Using published data it appears that at least as much copper has been leached as lead (perhaps more), yet whereas there is approximately 1 Mt of lead in solution, there is almost no copper in solution. A similar calculation for iron, ratioed to dissolved manganese, would suggest that roughly 100 Mt of iron and 1 Mt of copper have moved, but do not presently reside in solution. These amounts are equivalent to the contents of a fair-sized deposit (e.g., Ernest Henry).

The amount of metals transferred in many of these systems is so large that, like mid-ocean ridge hydrothermal systems, it impacts the chemical budget and geological interpretations of the significant parts of the crust. For example, in the southern Basin and Range Province large volumes of calc-alkaline volcanic rocks have been converted to "alkaline" compositions by this process, to the extent that their origin and significance in regional studies was obscured until this alteration was generally recognised in the last 15 years (Chapin *et al.*, 1986; Hollocher *et al.*, 1994). In how many areas of older rocks, with complex geologic histories have such features been overlooked? Where have the billions of tonnes of metals mobilised during this alteration gone?

Some Implications

Contrasting fluid sources should be considered in the origin of Fe-oxide(-Cu-Au) systems. Review of global geologic and geochemical observations indicates that both magmatic and external brines can be present and that their characteristics lead to systematic differences in the characteristics of the deposits. Nonetheless, the relative importance, indeed the presence, of these types remains to be established in many examples. The differences, however, are fundamental in understanding the nature of the hydrothermal systems and particularly in the location and characteristics of related mineral deposits. As described in this paper, there is a consistent variation in the characteristics of the deposits that varies from systems where a magmatic fluid dominates to others where non-magmatic fluids are major contributors.

For magmatically sourced systems:

- histories will tend to be clearly related to one or a few magmatic events,
- mineralisation is correlated with igneous compostions and perhaps texturally distinct units,
- moderate volumes (a few km^3) of alkali-rich alteration (K > Na in almost all cases), most of which is proximal; distal acid alteration carries metal but generally less overall,
- metals commonly correlated with high-T, magnetite rich, quartz-rich centre of system,
- cooling is the fundamental trap, locally aided by wall rock reaction and mixing,
- favorable areas will thus:
  - (a) need proper magma types,
  - (b) be near the tops of (former) magma chambers,
  - (c) be localised with intense Si and K ± Fe (as Mt) metasomatism.

For externally sourced systems:

- histories can be prolonged and not clearly related to individual magmatic events,
- large volumes (many km^3) of alkali-rich (Na-Ca, ±K) alteration, much of which may be distal (*and metal depleted*),
- most metals commonly external to the high-T, magnetite-rich centre of system,
- nature of metal traps is varied (mixing, wall-rock reaction, boiling, cooling); good traps may not be present, thus many well developed hydrothermal systems can be barren (or have metals trapped distal to the iron-oxides),
- favorable areas will thus:
  - (a) need an external brine source (surface, connate, remobilised),
  - (b) be structurally or stratigraphically controlled near a heat source,
  - (c) be localised in upwelling zones with Na, K or H ± Fe (Mt or Hm) ± Si metasomatism.

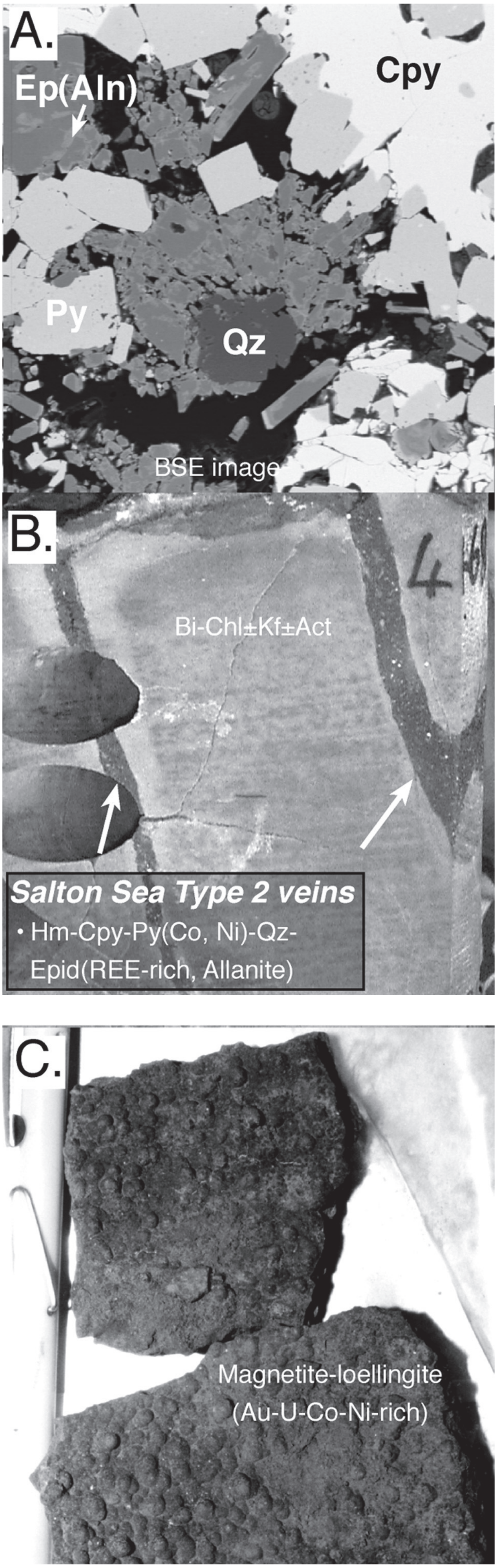


Figure 8: Fe-oxide-rich mineral assemblages in veins and scales from the Salton Sea geothermal system, California.

A) Back-scattered electron image of hematite-chalcopyrite-pyrite (up to 3 wt % Co)-epidote(allanite, up to 18 wt % RE_2O_3)-quartz vein (image and data courtesy F. Mazdab).

B) Same hematite-rich veins in biotite-chlorite±K-feldspar±actinolite altered metasedimentary rocks.

C) Scales from geothermal wells: magnetite-rich with significant Au-U-Co-As-Cu. Shallower scales have low-sulfidation Cu-Ag-minerals and REE-bearing Fe-silicates. See text for discussion.

In conclusion, hydrothermal environments in the upper crust are diverse. Some produce mineral deposits, others may not. The spectrum is worth investigating, if, as in the case of hydrothermal Fe-oxide-rich deposits, similar features can be generated by multiple processes. Young systems, where the geologic framework can be fully established, may provide a key to resolving the relative importance of the different modes of origin and to identifying those processes and features that distinguish well mineralised systems from their barren siblings.

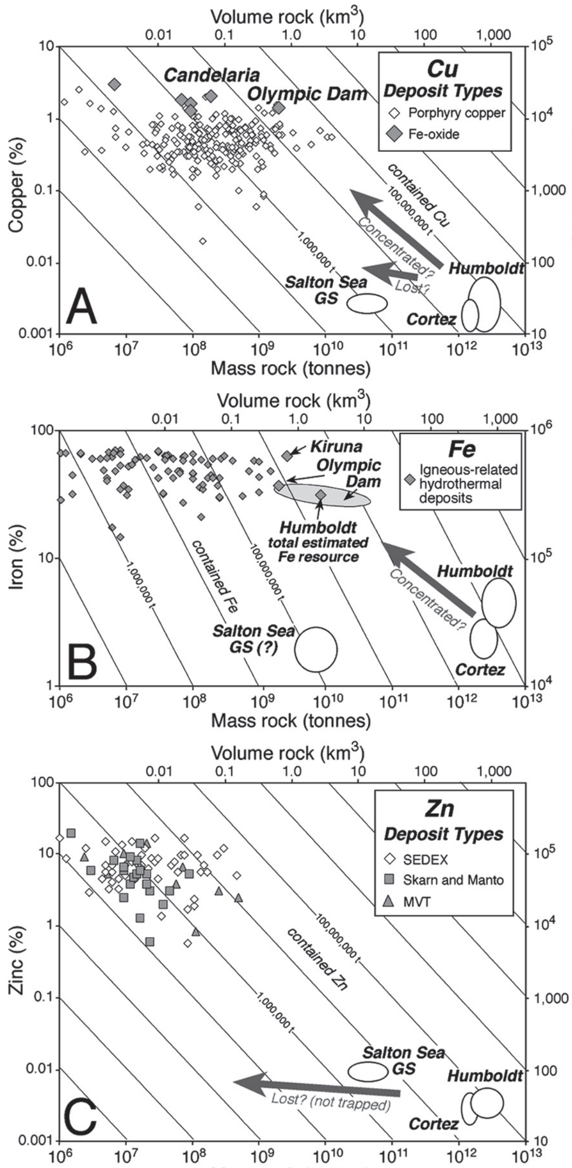


Figure 9: Grade-tonnage diagrams for Cu, Fe and Zn showing metals redistributed in three western U.S. systems and a comparison with metal inventories in some major deposit types. The open ellipses indicate documented amounts of metals moved. The Humboldt mafic complex and Cortez Mountains granite-rhyolite complex are Jurassic in age, are exposed at multiple structural levels by tilting, and have reasonably well constrained volumes of alteration (Johnson, 2000). The Salton Sea masses are inferred from the content of the modern brine reservoir, depletions in the host rocks, and mass balance with other elements (McKibben and Hardie, 1997). The arrows contrast behaviour of these elements: in all systems some iron and some copper are reprecipitated (the fractions are uncertain) whereas zinc is lost to solution, largely due to lack of sulfur. See text for discussion.

Acknowledgments

We thank Eric Jensen for helpful comments on the manuscript. Our work has been supported by grants from the U.S. National Science Foundation (most recently EAR 98-15032), by companies participating in the University of Arizona Mexico Consortium, and by the U.S. Geological Survey. Stimulating conversations with many individuals over many years have contributed to the sharpening observations and ideas in this paper. Brooks Hanson has contributed fundamentally over the years through collaboration on numerical modeling and thinking about broad issues of the roles of fluids in the igneous environment.

References

Barton, M.D., Battles, D.A., Debout, G.E., Capo, R.C., Christensen, J.N., Davis, S.R., Hanson, R.B., Michelsen, C.J. and Trim, H.E., 1988 - Mesozoic contact metamorphism in the Western United States.*Rubey Volume* 7, pp. 110-178.

Barton, M.D. and Johnson, D.A., 1996 - Evaporitic-source model for igneous-related Fe oxide-(REE-Cu-Au-U) mineralization.*Geology, v.* 24, pp. 259-262.

Barton, M.D., Johnson, D.A. and Hanson, B.R., 1998 - Evaluation of possible roles of non-magmatic brines in igneous-related hydrothermal systems, especially Fe(-Cu-Au-REE) deposits, *in* Anonymous, ed.*Geological Society of America Abstracts with Programs*, v. 30, p. 127.

Battles, D.A., 1990 - The hydrothermal evolution of the Shamrock Batholith, western Nevada, and the origin of sodium-rich alteration in the Western United States: Unpub.Dissertation thesis: *University of California*.

Battles, D.A. and Barton, M.D., 1995 - Arc-related sodic hydrothermal alteration in the western U.S.*Geology*, v. 23, pp. 913-916.

Bohlke, J.K. and Irwin, J.J., 1992 - Laser microprobe analyses of Cl, Br, I, and K in fluid inclusions; implications for sources of salinity in some ancient hydrothermal fluids.*Geochimica et Cosmochimica Acta*, v. 56, pp. 203-225.

Bonatti, E., Fisher, D.E., Joensuu, O., Rydell, H.S. and Beyth, M., 1972 - Iron-manganese-barium deposit from the northern Afar Rift.*Economic Geology*, v. 67, pp. 717-730.

Borrok, D., Kesler, S.E. and Vogel, T.A., 1999 - Sulfide minerals in intrusive and volcanic rocks of the Bingham-Park City belt, Utah.*Economic Geology*, v. 94, pp. 1213-1230.

Campbell, A.R., Banks, D.A., Phillips, R.S. and Yardley, B.W.D., 1995 - Geochemistry of Th-U-REE mineralizing magmatic fluids, Capitan Mountains, New Mexico.*Economic Geology*, v. 90, pp. 1271-1287.

Cathles, L.M., 1981 - Fluid flow and genesis of hydrothermal ore deposits.*Economic Geology Seventy-fifth anniversary volume*, pp. 424-457.

Chapin, C.E. and Lindley, J.I., 1986 - Potassium metasomatism of igneous and sedimentary rocks in detachment terranes and other sedimentary basins; economic implications.*Arizona Geological Society Digest*, v. 16, pp. 118-126.

Cooke, D.R., Bull, S.W., Donovan, S. and Rogers, J.R., 1998 - K-metasomatism and base metal depletion in volcanic rocks from the McArthur Basin, Northern Territory; implications for base metal mineralization.*Economic Geology*, v. 93, pp. 1237-1263.

Criss, R.E. and Taylor, H.P., 1986 - Meteoric-hydrothermal systems.*Reviews in Mineralogy*, v. 16, pp. 373-424.

De Jong, G. and Williams, P.J., 1995 - Giant metasomatic system formed during exhumation of mid-crustal Proterozoic rocks in the vicinity of the Cloncurry Fault, Northwest Queensland.*Australian Journal of Earth Sciences*, v. 42, pp. 281-290.

Dilles, J.H., 1987 - Petrology of the Yerington Batholith, Nevada; evidence for evolution of porphyry copper ore fluids.*Economic Geology*, v. 82, pp. 1750-1789.

Dilles, J.H. and Einaudi, M.T., 1992 - Wall-rock alteration and hydrothermal flow paths about the Ann-Mason porphyry copper deposit, Nevada; a 6-km vertical reconstruction.*Economic Geology*, v. 87, pp. 1963-2001.

Dilles, J.H., Einaudi, M.T., Proffett, J. and Barton, M.D., 2000 - Overview of the Yerington porphyry copper district: Magmatic to non-magmatic sources of hydrothermal fluids, their flow paths, alteration affects on rocks, and Cu-Mo-Fe-Au ores, *in* Thompson, T.B., (ed.), Society of Economic Geologists Guidebook, in press.

Dilles, J.H. and Proffett, J.M., 1995 - Metallogenesis of the Yerington batholith, Nevada.*Arizona Geological Society Digest*, v. 20, pp. 306-315.

Eugster, H.P. and Chou, I.M., 1979 - A model for the deposition of Cornwall-type magnetite deposits. *Economic Geology*, v. 74, pp. 763-774.

Eugster, H.P. and Hardie, L.A., 1978 - Saline lakes, *in* Lerman, A., ed., Lakes; chemistry, geology, physics: *Springer-Verlag, New York*, pp. 237-293.

Ferry, J.M., Mutti, L.J. and Zuccala, G.J., 1987 - Contact metamorphism/hydrothermal alteration of Tertiary basalts from the Isle of Skye, Northwest Scotland.*Contributions to Mineralogy and Petrology*, v. 95, pp. 166-181.

Field, C.W. and Fifarek, R.H., 1985 - Light stable-isotopes systematics in the epithermal environment. *Reviews in Economic Geology*, v. 2, pp. 99-128.

Forrester, R.W. and Taylor, H.P., 1977 - 18O/16O, D/H and 13C/12C studies of the Tertiary igneous complex of Skye, Scotland.*American Journal of Science*, v. 277, pp. 136-177.

Franklin, J.M., 1993 - Volcanic-associated massive sulphide deposits, *in* Kirkham, R.V., Sinclair, W.D., Thorpe, R.I., and Duke, J.M., eds., Mineral deposit modeling., Geological Association of Canada: Toronto Special Paper 40, ON, Canada: *Geological Association of Canada*, pp. 315-334.

Frietsch, R., Tuisku, P., Martinsson, O. and Perdahl, J.A., 1997 - Early Proterozoic Cu-(Au) and Fe ore deposits associated with regional Na-Cl metasomatism in northern Fennoscandia.*Ore Geology Reviews*, v. 12, pp. 1-34.

Gleason, J., Marikos, M.A., Barton, M.D. and Johnson, D.A., 2000 - Neodymium isotopic study of rare earth element sources and moblity in hydrothermal Fe oxide (Fe-P-REE) systems. *Geochimica et Cosmochimica Acta*, v. 64, pp. 1059-1068.

Grez, E., Aguilar, A., Henriquez, F. and Nyström, J.O., 1991 - Magnetita Pedernales; a new magmatic iron deposit in northern Chile.*Economic Geology*, v. 86, pp. 1346-1349.

Hanson, R.B., 1995 - The hydrodynamics of contact metamorphism.*Geological Society of America Bulletin*, v. 107, pp. 595-611.

Hanson, R.B. and Barton, M.D., 1989 - Thermal development of low-pressure metamorphic belts; results from two-dimensional numerical models. *Journal of Geophysical Research, B, Solid Earth and Planets*, v. 94, pp. 10,363-10,377.

Hanson, R.B., Sorensen, S.S., Barton, M.D. and Fiske, R.S., 1993 - Long-term evolution of fluid-rock interactions in magmatic arcs: Evidence from the Ritter Range pendant, Sierra Nevada, California, and numerical modeling.*Journal of Petrology*, v. 34, pp. 23-62.

Hauck, S.A., 1990 - Petrogenesis and tectonic setting of middle Proterozoic iron oxide-rich ore deposits; an ore deposit model for olympic dam-type mineralization, Pratt, Walden P., Sims, P.K.The Midcontinent of the United States; permissive terrane for an olympic dam-type deposit?, U.S.Geological Survey Bulletin 1932: *U.S.Geological Survey*, pp. 4-39.

Haynes, D.W., 1995 - Olympic Dam Ore Genesis: a fluid-mixing model.*Economic Geology*, v. 90, pp. 281-307.

Hedenquist, J.W. and Lowenstern, J.B., 1994 - The role of magmas in the formation of hydrothermal ore deposits. *Nature (London)*, v. 370, pp. 519-527.

Hemley, J.J., Cygan, G.L., Fein, J.B., Robinson, G.R. and D'Angelo, W.M., 1992 - Hydrothermal ore-forming processes in the light of rock-buffered systems: 1. Iron-copper-zinc-lead-sulfide solubility relations.*Economic Geology*, v. 87, pp. 1-22.

Hitzman, M.W., Oreskes, N. and Einaudi, M.T., 1992 - Geological characteristics and tectonic setting of Proterozoic iron oxide (Cu-U-Au-REE) deposits. *Precambrian Research*, v. 58, pp. 241-287.

Hoeve, J. and Quirt, D., 1989 - A common diagenetic-hydrothermal origin for unconformity-type uranium and stratiform copper deposits?, *in* Boyle, W., Brown, C., Jefferson, W., Jowett, C., and Kirkham, R.V., eds., Sediment-hosted stratiform copper deposits., Geological Association of Canada Special Paper 36: Toronto, ON, Canada: *Geological Association of Canada*, pp. 151-172.

Hollister, V.F., 1978 - Geology of the Porphyry Copper Deposits of the Western Hemisphere: *AIME, SME, New York, NY.*

Hollocher, K., Spencer, J. and Ruiz, J., 1994 - Composition changes in an ash-flow cooling unit during K metasomatism, west-central Arizona.*Economic Geology*, v. 89, pp. 877-888.

Jensen, E.P. and Barton, M.D., 2000 - Gold deposits related to alkaline magmatism.*Reviews in Economic Geology*, v. 13, pp. 279-314.

Johnson, D.A., 2000 - Comparative studies of iron-oxide mineralization: Great Basin: Unpub.Dissertation thesis: *University of Arizona*.

Johnson, D. A. and Barton, M. D., 2000, Time-Space Development of an external-brine-dominated, igneous-driven hydrothermal system: Humboldt mafic complex, western Nevada: *in* Dilles, J. H., Barton, M.D., Johnson, D.A., Proffett, J.M. and Einaudi, M.T., (eds.), 2000, Contrasting Styles of Intrusion Associated Hydrothermal Systems: *Society of Economic Geologists, Guide Book Series*, v. 32, pp. 145-162.

Johnson, J.P. and McCulloch, M.T., 1995 - Sources of mineralizing fluids for the Olympic Dam Deposit (South Australia); Sm-Nd isotopic constraints. *Chemical Geology*, v. 121, pp. 177-199.

Keith, J.D., Whitney, J.A., Hattori, K., Ballantyne, G.H., Christiansen, E.H., Barr, D.L., Cannan, T.M. and Hook, C.J., 1997 - The role of magnetic sulfides and mafic alkaline magmas in the Bingham and Tintic mining districts, Utah.*Journal of Petrology*, v. 38, pp. 1679-1690.

Komninou, A. and Sverjensky, D.A., 1996 - Geochemical modeling of the formation of an unconformity-type uranium deposit; *Economic Geology*, v. 91, 590-606.

Lang, J.R., Stanley, C.R. and Thompson, J.F.H., 1995 - Porphyry copper-gold deposits related to alkalic igneous rocks in the Triassic-Jurassic arc terranes of British Columbia.*Arizona Geological Society Digest*, v. 20, pp. 219-236.

Lindgren, W., 1913 - Mineral Deposits: *McGraw-Hill Book Company, Inc. New York.*

Manning, C.E. and Bird, D.K., 1995 - Porosity, permeability, and basalt metamorphism.*Geological Society of America Special Paper* 296, pp. 123-140.

Marschik, R. and Fontbote, L., 1996 - Copper(-iron) mineralization and superposition of alteration events in the Punta del Cobre Belt, northern Chile.*Society of Economic Geologists Special Publication* 5, pp. 171-190.

McKibben, M.A. and Hardie, L.A., 1997 - Ore-forming brines in active continental rifts, *in* Barnes, H.L., ed., Geochemistry of hydrothermal ore deposits: *John Wiley & Sons, New York, NY, United States*, pp. 877-935.

McKibben, M.A., Williams, A.E. and Hall, G.E.M., 1990 - Solubility and transport of plantinum-group elements and Au in saline hydrothermal fluids; constraints from geothermal brine data. *Economic Geology*, v. 85, pp. 1926-1934.

McKibben, M.A., Williams, A.E. and Okubo, S., 1988 - Metamorphosed Plio-Pleistocene evaporites and the origins of hypersaline brines in the Salton Sea geothermal system, California; fluid inclusion evidence.*Geochimica et Cosmochimica Acta*, v. 52, pp. 1047-1056.

Norton, D. and Taylor, H.P., 1979 - Quantitative simulation of the hydrothermal systems of crystallizing magmas on the basis of transport theory and oxygen isotope data; an analysis of the Skaergaard Intrusion.*Journal of Petrology*, v. 20, pp. 421-486.

Perring, C.S., Pollard, P.J., Dong, C., Nunn, A.J. and Blake, K.L., 2000 - The Lightning Creek sill complex, Cloncurry district, Northwest Queensland: A source of fluids for Fe oxide Cu-Au mineralization and sodic-calcic alteration. *Economic Geology*, v. 95, pp. 1067-1090.

Pollard, P.J., Mark, G. and Mitchell, L.C., 1998 - Geochemistry of Post-1540 Ma granites in the Cloncurry District, Northwest Queensland. *Economic Geology*, v. 93, pp. 1330-1344.

Reeves, R.G. and Kral, V.E., 1955 - Iron ore deposits of Nevada - Part A, Geology and iron ore deposits of the Buena Vista Hills, Churchill and Pershing Counties, Nevada.*Nevada Bureau of Mines Bulletin*, v. 53, p. 32.

Rhodes, A.L. and Oreskes, N., 1999 - Geology and rare earth element geochemistry of magnetite deposits at El Laco, Chile.*Society of Economic Geologists Special Publication* 7, pp. 299-332.

Robinson, G.R.J., 1988 - Base- and precious-metal mineralization associated with igneous and thermally altered rocks in the Newark, Gettysburg, and Culpeper early Mesozoic basins of New Jersey, Pennsylvania, and Virgina, *in* Manspeizer, W., (ed.), Triassic-Jurassic Rifting, Continental Breakup and the Origin of the Atlantic Ocean and Passive Margins, Part A.Developments in Geotectonics: *Elsevier*, pp. 621-648.

Rose, A.W., Herrick, D.C. and Deines, P., 1985 - An oxygen and sulfur isotope study of skarn-type magnetite deposits of the Cornwall type, southeastern Pennsylvania.*Economic Geology*, v. 80, pp. 418-443.

Scott, S.D., 1997 - Submarine hydrothermal systems and deposits, *in* Barnes, H.L., ed., Geochemistry of hydrothermal ore deposits.*John Wiley & Sons, New York, NY,* pp. 797-875.

Sillitoe, R.H., Hannington, M.D. and Thompson, J.F.H., 1996 - High sulfidation deposits in the volcanogenic massive sulfide environment. *Economic Geology*, v. 91, pp. 204-212.

Sokolov, G.A. and Grigorev, V.M., 1977 - Deposits of iron, *in* Smirnov, V., (ed.), Ore deposits of the USSR; *Pitman Publishing Corp., Belmont, California, USA*, v. 1, pp. 7-109.

Song, X.X., Chen, Y.C., Sheng, J.F. and Ai, Y.D., 1981 - On iron deposits formed from volcanogenic-hypabyssal ore magma.*Acta Geologica Sinica*, v. 55, pp. 41-53.

Spencer, J.E. and Welty, J.W., 1989 - Mid-Tertiary ore deposits in Arizona.*Arizona Geological Society Digest*, v. 17, pp. 585-607.

Streck, M.J. and Dilles, J.H., 1998 - Sulfur evolution of oxidized arc magmas as recorded in apatite from a porphyry copper batholith.*Geology*, v. 26, pp. 523-526.

U.S.Geological Survey & Servicio Geologico de Bolivia., 1992 - Geology and mineral resources of the Altiplano and Corillera Occidental, Bolivia, U.S.Geological Survey Bulletin 1975, *U.S.Geological Survey, Reston, VA*, 365p.

Vakhrushev, V.A. and Ryabkov, V.G., 1984 - The geologic position and distinctive mineralogical and geochemical features of the ore deposits in the Angara-Tunguska iron-ore province.*Soviet Geology and Geophysics* 25, 60-65.

Wilkins, J.J., Beane, R.E. and Heidrick, T.L., 1986 - Mineralization related to detachment faults; a model.*Arizona Geological Society Digest*, v. 16, pp. 108-117.

Williams, P.J., 1994 - Iron mobility during synmetamorphic alteration in the Selwyn Range area, NW Queensland; implications for the origin of ironstone-hosted Au-Cu deposits.*Mineralium Deposita*, v. 29, pp. 250-260.