

SOURCES OF ORE FLUID COMPONENTS IN IOCG DEPOSITS

^{1,2} Patrick J. Williams, ³ Mark A. Kendrick and ⁴ Roberto Perez Xavier

¹ Economic Geology Research Unit, School of Earth and Environmental Sciences, James Cook University, Townsville, Qld., Australia

² Clump Mountain Geoscience Pty Ltd, PO Box 560, Mission Beach, Qld., Australia

³ School of Earth Sciences, University of Melbourne, Vic., Australia

⁴ Departamento de Geologia e Recursos Naturais, Instituto de Geociências, Universidade Estadual de Campinas, (SP), Brazil

Abstract - Many diverse hydrothermal copper deposits containing iron oxides are classified as IOCG deposits. Genetic models need to consider a number of different ore fluid components that may not all have the same source in an individual ore system, and also that economic IOCG deposits may include examples in which key components (especially copper) had different sources. The principal components of interest are: (1) water \pm other volatiles, (2) chlorine, (3) sulphur, (4) iron, copper, gold (the diagnostic ore components), and (5) other potentially economic components (e.g. uranium) that may be differently-sourced to the copper and gold.

Geochemical studies are providing growing insights into source contributions to IOCG deposits, but their interpretation is commonly limited by inadequate baseline data for lithospheric to regional scale reservoirs and/or by incomplete understanding of natural fractionations that may affect the chemical systems. Where contributions from contemporary igneous rocks are evident, it is generally not clear whether these came directly from a volatile phase evolved from the magmas, or by leaching from previously consolidated rocks. Key aspects of current knowledge include: (1) IOCG deposits formed in a variety of different hydrological systems including (a) high level systems in which cool surficial fluids were able to interact with deeply-sourced fluids, and (b) deeper systems, some but not all of those for which suitable data are available, display evidence for a direct input of magmatic fluid; (2) Despite uncertainty about the compositions of source reservoirs and fractionations with silicate minerals, there is good evidence that many IOCG ore fluids had salinities derived from more than one source and that these were not the same in each case (e.g. \pm magmatic, \pm dissolved evaporite/meta-evaporite, \pm evaporated surface water); (3) Only circumstantial evidence links the principal economic metals in IOCG deposits to any particular source such as (a) the correspondence of higher copper concentrations in those fluid inclusions from mineralised systems in the Cloncurry district that have Br/Cl ratios characteristic of a regional magmatic source, and (b) the correlation of copper endowment and contemporaneous mantle-derived REE in deposits in the Gawler craton. Many gaps still remain to be filled in the knowledge base for IOCG deposits and the potential sources of their components. Nevertheless there is already good evidence that there are fundamentally different genetic types of IOCG deposit.

Introduction

Iron oxide-copper-gold (IOCG) deposits occur in a range of very different geological environments and the original geotectonic settings of many important Precambrian examples are poorly understood. Their broad and empirical definition is that they are hydrothermal copper deposits containing abundant low-Ti iron oxides, but exclude deposits that have clear causative relationships with igneous centres such as porphyry-related copper-gold and skarn deposits (cf. Williams *et al.*, 2005). As such, IOCG deposits share geochemical features but could reflect a number of fundamentally different processes that occurred in a variety of geotectonic settings. Many diverse ore systems conform with the IOCG definition of Williams *et al.* (2005). Other iron oxide-rich deposits that lack copper should not be referred to as IOCGs (Williams *et al.*, 2005). However, some IOCG districts contain polymetallic deposits, including economic ones, that do not conform strictly to the IOCG definition in that they lack either iron oxides or copper as a principal metal of economic interest. Such deposits may be directly related to IOCG metallogeny and can display transitional IOCG characteristics, meaning they need to be considered as integral parts of IOCG systems.

IOCG and closely-affiliated deposits appear to be restricted to certain metallogenic belts where porphyry-related copper (-molybdenum-gold) deposits are generally absent or spatially distinct. There has been much discussion of IOCG deposits as part of an even broader family of deposits such as “Kiruna-type” iron oxide \pm apatite mineralisation and various igneous affiliated iron oxide \pm apatite \pm copper \pm gold \pm rare metal deposits (e.g. Hitzman *et al.*, 1992; Porter, 2000; Groves and Vielreicher, 2001; Williams *et al.*, 2005).

The sources of the various ore fluid components and causes of ore deposition in economic deposits need to be established to characterise metallogenic processes, identify any fundamentally-distinct subgroups, and help pinpoint the most prospective districts and systems for exploration. Considerable attention has been paid to these matters in recent years and this paper reviews the pertinent literature on IOCG fluid chemistry with emphasis on developments since the publication of the Economic Geology 100th Anniversary Volume (i.e., since the review by Williams *et al.*, 2005).

Fluid Source

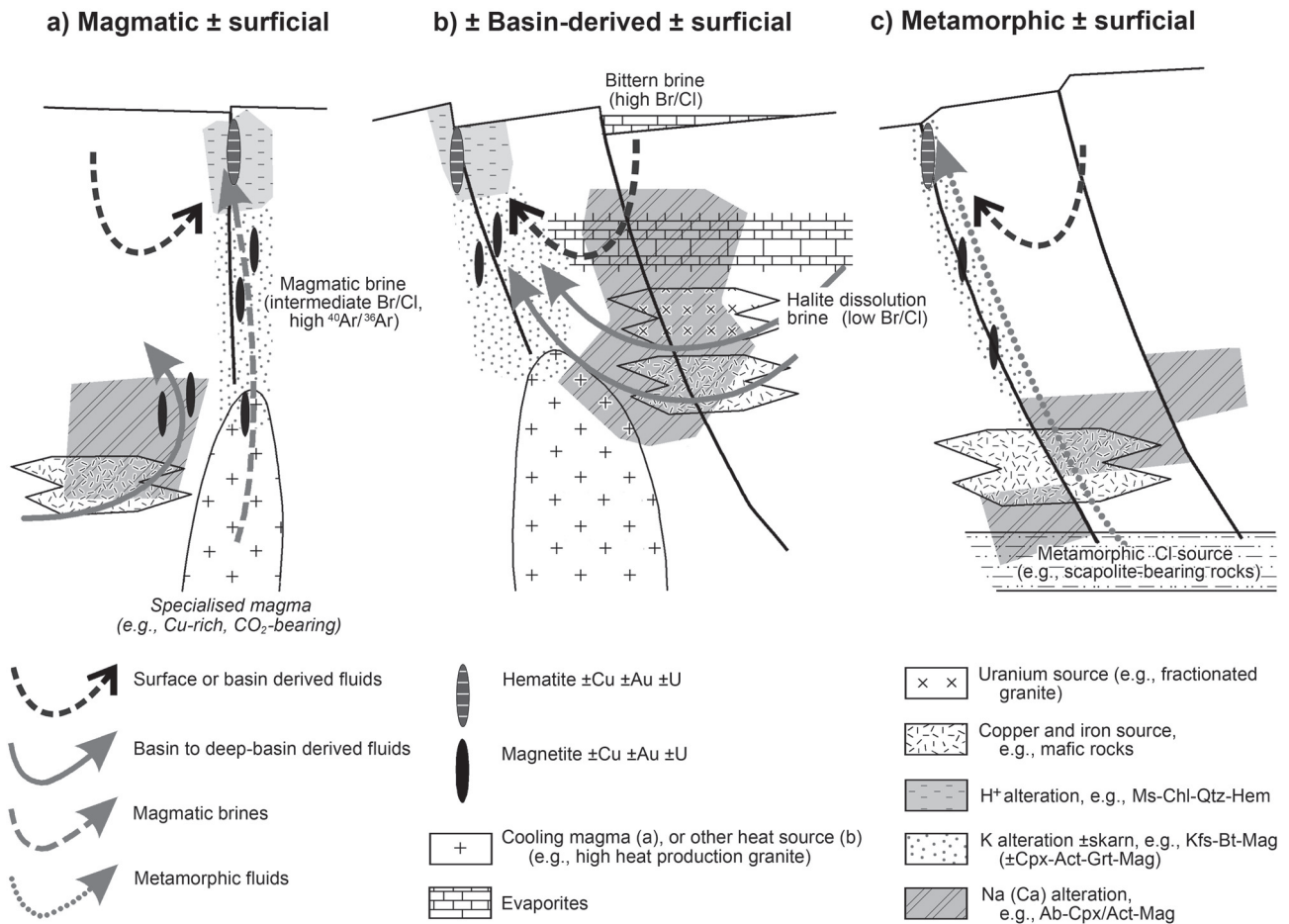


Figure 1: A range of schematic models for IOCG genesis illustrating possible roles for different types of hot brines. Adapted from Barton and Johnson (2004) and incorporating host rock metal source concepts (e.g., Williams, 1994; Hitzman and Valenta, 2005). It should be noted that these approximate to “end member” models and are not mutually exclusive. That is, IOCG deposits may be formed in hybrid systems with coeval or superimposed contributions from different types of deep-seated brine. Part (a) also illustrates how deposits with fundamentally different fluid sources might form simultaneously in a single system. In the specific case illustrated, economic copper-gold deposits are conceptually restricted to the part of the system with a magmatic fluid component and absent from iron oxide bodies formed in parts of the system dominated by external fluids. Abbreviations: Ab = albite; Act = actinolite; Bt = biotite; Chl = chlorite; Cpx = clinopyroxene; Grt = garnet; Hem = hematite; Kfs = K feldspar; Mag = magnetite; Ms = muscovite; Qtz = quartz.

Characteristics of IOCG Deposits and Metallogenic Issues

IOCG Characteristics

The economically most important IOCG deposits occur in the Carajás Mineral Province, Brazil (Archaean, Amazon Craton); in Proterozoic rocks of the Gawler Craton and Cloncurry districts, Australia, and in the Jurassic to Cretaceous coastal batholithic belt in Chile and Peru (Williams *et al.*, 2005). The largest deposits include Salobo, Cristalino, Sossego and Igarapé Bahia/Alemão (Carajás), Olympic Dam, Prominent Hill (Gawler Craton), Ernest Henry, Mount Elliott (Cloncurry district), and Candelaria-Punta del Cobre and Manto Verde (Chile). These have resources of greater than 100 Mt ranging up to more than 1000 Mt, with metal grades exceeding those of most porphyry-related copper±gold deposits. The majority of IOCG deposits formed in settings where broadly coeval magmatism was associated with crustal-scale pervasive alkali metasomatism. IOCG deposits are variably and differentially enriched in a suite of minor elements including F, P, Co, Ni, As, Mo, Ag, Ba, LREE

and U. They occur in many different types of host rocks that in some cases are broadly similar in age to the ore (e.g., Olympic Dam and Candelaria-Punta del Cobre) but in others, significantly predate mineralisation (e.g., Salobo and Ernest Henry).

IOCG mineralisation is interpreted to have occurred over a wide depth range from around 10 kilometres (e.g., several deposits in the Cloncurry district and Salobo) to the immediate subsurface (e.g., Olympic Dam). Structural controls are pronounced, with deposits characteristically localised by faults, shear zones, rock contacts and/or breccia bodies. Host rocks in the vicinity of ore bodies are typically strongly altered. Variable P-T conditions and chemistry of alteration and mineralisation are reflected in a spectrum of deposits ranging from those in which the dominant iron oxide is magnetite and alteration is characterised by higher temperature K-Fe-Ca silicate assemblages (K feldspar-biotite, fayalite-almandine, clinopyroxene/actinolite, etc.) to hematite-dominated systems associated with hydrous phases, particularly sericite and chlorite. Where present, Na- and Na-Ca alteration tends to be developed more distally, on a larger scale, and commonly observed to predate K-Fe alteration

and mineralisation (e.g., Mark *et al.*, 2006; Monteiro *et al.*, 2008). Carbonates are commonly abundant, and where present in magnetite-dominated systems, tend to share a late stage paragenesis with the copper-bearing sulphides. Variable fO_2 - fS_2 (-T) conditions produced deposits ranging from pyrite-poor examples, with complex copper mineral associations including chalcopyrite, bornite and chalcocite (e.g., Salobo, Cristalino, Sossego, Igarapé Bahia/Alemão, Olympic Dam and Prominent Hill), to others in which pyrite and chalcopyrite are the main sulphides (e.g., Ernest Henry and Candelaria).

Metallogenic Issues

Metallogenic theories for IOCG genesis (cf. Fig. 1) need to consider a number of different ore fluid components. They must bear in mind that these may not all have the same source in an individual ore system, and also that economic IOCG deposits may include examples in which key components (e.g., copper) had different sources from case to case. Furthermore, individual IOCG systems may have changed through time such that the dominant sources of fluid components may have varied as they evolved through pre- syn- and post-mineralisation stages. From a process perspective, the principal components of interest are: (1) water \pm other volatiles (i.e., the solvent in which the ore elements were transported to the site of deposition); (2) chlorine (the principal ligand for co-transport of iron, copper and gold); (3) sulphur (the principal precipitant for copper), (4) iron, copper and gold (the diagnostic ore components which may not have a single source or may be sourced in different proportions from mixed sources), and (5) other components of economic interest (e.g., uranium) that may be differently-sourced to the copper and gold.

Debate on IOCG genesis initially focussed on whether these ore systems may be fundamentally magmatic or amagmatic (cf. Fig. 1). That is, whether they involved a dominantly magmatic source of ore fluid and metals (e.g., Pollard, 2000; 2006; Fig. 1a), or had host rock sources of metal and chlorine, and basinal and/or surficial source of fluids (Barton and Johnson, 1996; Haynes, 2000; Fig. 1b). The exploration implications of this distinction are profound, given that the former implies that IOCG deposits will be found only in association with suitably specialised intrusions that were emplaced at, or below the depths of mineralisation and able to evolve copper-bearing fluids, whereas the latter implies that the local crust must have contained ample older sources of metals and that either older or contemporary evaporites must have been present as sources of chlorine.

A further important genetic issue is the mechanism(s) of ore deposition, which might have a number of different types of interrelationship to the fluid source (e.g., cooling of hot metal-bearing fluid evolved from a magma or from rocks undergoing metamorphism, versus fluid mixing in a case where critical ore-forming components such as metals and sulphur were introduced in different fluids and where physical and/or chemical gradients in the mixing environment led to mineral precipitation).

Notwithstanding the great diversity of IOCG petrological features, a useful comparison can be made between porphyry copper-gold deposits and certain IOCG deposits that have similar hydrothermal mineral associations (Fig. 2). This emphasises the fact that whereas there is a general acceptance that the porphyry deposits are products of cooling brine released from partly consolidated magmas, even those IOCG deposits with

hydrothermal associations similar to those of porphyry-related deposits (i.e., K-silicate, skarn) display features consistent with a distinct, and more complex mode of origin.

Potassic alteration (\pm K feldspar \pm biotite \pm magnetite) characterises the ore-bearing parts of porphyry-related ore deposits and is a predictable consequence of the interaction of hot magmatic brine with cooler plagioclase-bearing rock (Giggenbach, 1984). The typical quartz stockworks of porphyry copper deposits are the result of exsolution of aqueous fluids from large (generally >100 km³) upper crustal magma chambers at depths of >5 km below the surface. These fluids ascend as saline (~ 5 to 10% NaCl_{equiv.}) to hypersaline (up to 70% NaCl_{equiv.}) brines and vapour in buoyant bubble-rich magma plumes, into the cupola zone and shallow apophyses of the magma chamber and/or to higher level subvolcanic stocks and dykes at 1 to 5 km depth (Ulrich *et al.*, 2001; Richards, 2005 and sources cited therein). Decreasing pressure accompanying the ascent, results in the brines and vapour being released, causing repeated hydrofracturing at the brittle-ductile transition in the cooling magma and surrounding rocks, corresponding to the zone of ore deposition (e.g., Ulrich *et al.*, 2001, Richards, 2005; Seedorf *et al.*, 2005). Temperatures in this zone vary from magmatic ($>600^\circ\text{C}$) in the core of the host intrusive, to $<400^\circ\text{C}$ in the cooler, immediately adjacent country rocks. Brines moving outwards and upwards across this temperature gradient cause extensive deposition of quartz, accompanied by abundant magnetite (cf. Fig. 2a) in the higher temperature core of diorite-related porphyry copper-gold deposits, passing progressively outwards into copper-gold and pyrite shells in the cooler rocks of the outer intrusive and country rocks. Fractures are held open under lithostatic to hydrostatic pressure as they are filled and sealed (e.g., Ulrich *et al.*, 2001). During the early stages, cooler formation and/or meteoric waters circulate in the periphery of the system maintaining the temperature gradient, but are not likely to interact with the magmatic brines due to the pressure gradient. However, with time, as the temperature and pressure declines to hydrostatic levels, meteoric and formational waters may interact with the magmatic brines, accompanied by phyllic and argillic/advanced argillic alteration (e.g., Ulrich *et al.*, 2001; Seedorf *et al.*, 2005).

In contrast, many, if not all, IOCG deposits contain little hydrothermal quartz, implying either that the ore-forming fluid was unusually depleted in silica or that temperature and/or pressure drops were less pronounced in the process of ore deposition compared to those experienced by ore fluids in porphyry deposits, or in some cases perhaps that mineralisation occurred in the low pressure retrograde silica solubility regime (e.g., Fournier, 1985). The co-enrichment of Fe, Cu, Au and Ag in both types of deposits is an indication that hot brine was the agent of metal introduction and deposition, and this is supported by many studies that have documented high salinity (e.g., >50 wt.% salts) fluid inclusions that homogenise at high temperatures ($>500^\circ\text{C}$) in both types of system (see also below). However, whereas the brines responsible for porphyry Cu-Au mineralisation are likely to be relatively pristine exsolution products from mantle and lower crust derived magmas, those in IOCG deposits are likely to have undergone protracted and possibly complex interactions with a wide range of crustal materials in large-scale alteration systems.

In the porphyry deposits, the production of highly concentrated ore brine is commonly deduced to have involved the separation of a low density (“vapour”) phase from a primary low to moderate salinity magmatic fluid at pressures below ca 1.4 kbar (Pitzer and Pabalan, 1986; Hedenquist and Lowenstern, 1994). However, to date there is no evidence for a similar process in the origin of very

high salinity fluid inclusions observed in IOCG deposits. Furthermore, in some IOCG provinces (e.g. the Cloncurry district in Australia and Carajás Mineral Province in Brazil), it is clear that fluids had a significant carbonic component, as revealed by large amounts of typically late-stage carbonates in the ores, and by the presence of CO₂-rich fluid inclusions that commonly have high densities.

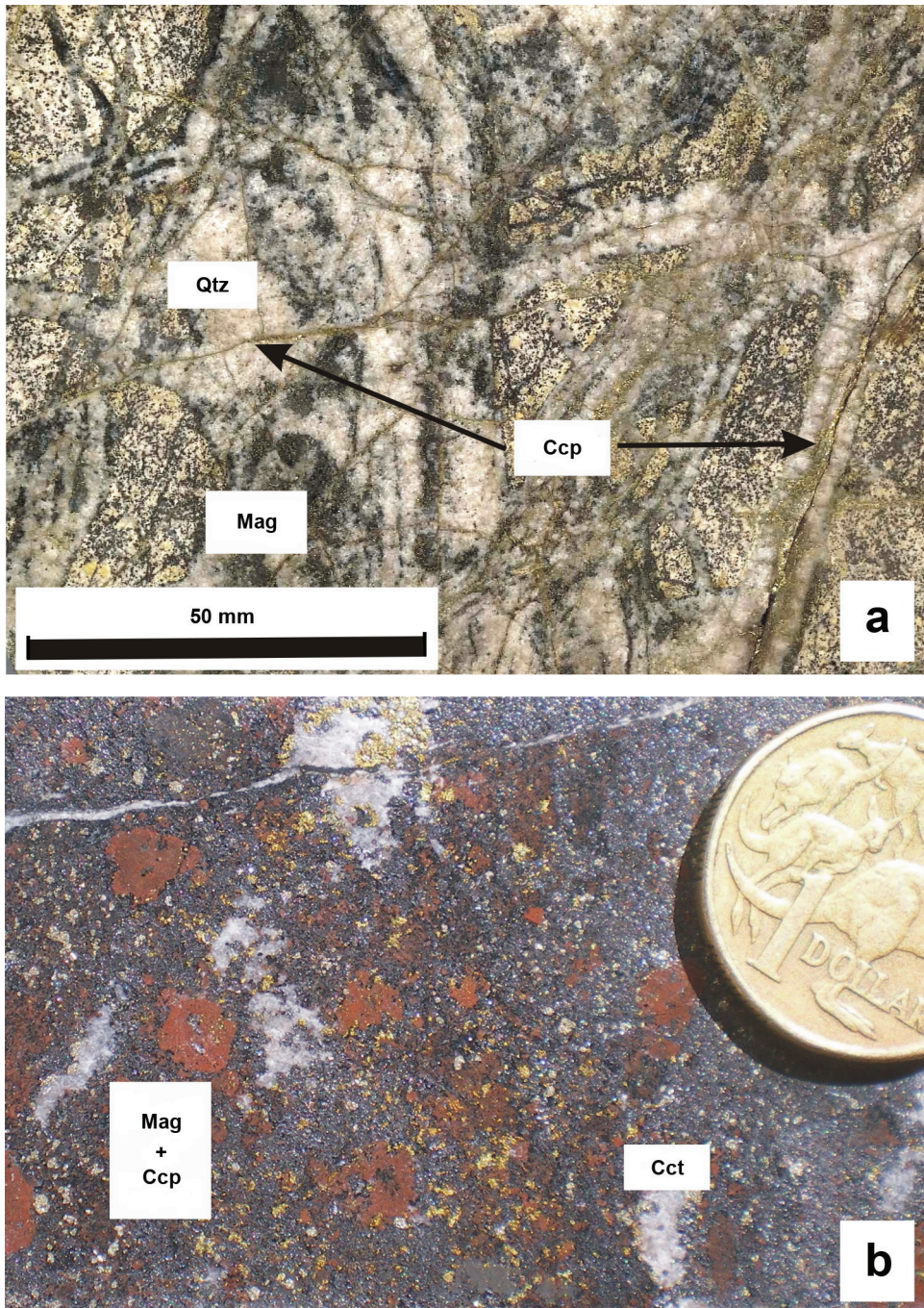


Figure 2: Contrasting ore types from (a) the Grasberg (West Papua, Indonesia; e.g. Pollard and Taylor, 2002) porphyry-type copper-gold deposit, and (b) the Ernest Henry IOCG deposit (Mark *et al.*, 2006). In some respects, these rocks are rather similar but in others they are distinct in ways that reflect differences in the respective ore forming environments and processes. In both cases the host rock has an intermediate igneous composition and underwent pervasive potassic alteration (at this scale represented by K feldspar) prior to fracturing/brecciation and the deposition of the ore minerals. Both contain abundant hydrothermal magnetite (Mag), have copper and gold with subordinate silver as the economically-significant metals, and at this scale (that is in ore grade material) contain chalcopyrite (Ccp) as the principal sulphide (i.e., both have high ratios of magnetite:pyrite and chalcopyrite:pyrite). Obvious differences include (i) the very abundant pre-chalcopyrite quartz infill in the Grasberg ore as compared to the paucity of quartz in Ernest Henry ore, (ii) a closer textural association of chalcopyrite and magnetite in the Ernest Henry ore breccia matrix as compared to the distinctly earlier paragenesis of magnetite at Grasberg (NB. occurrence of chalcopyrite as hairline and centreline infill cutting quartz-magnetite stockwork veins), and (iii) the presence of abundant carbonate (calcite - Cct) in late dilational features in the Ernest Henry ore, some of it intergrown with sulphides as compared to the absence of carbonates in the Grasberg ore. More subtle chemical differences manifested in accessory minerals or by element substitutions in the major hydrothermal minerals are enrichments in elements in the Ernest Henry ore such as F, Ba (present here as barian K feldspar), As, Co, REE and U that generally do not characterise magmatic-hydrothermal porphyry or closely affiliated mineralisation (e.g. skarns).

In IOCG deposits such as Ernest Henry and Igarapé Bahia/Alemão, these inclusions appear to have been trapped at pressures of several kbar, consistent with depths of mineralisation for at least some components of the system being much greater than those of most porphyry-related deposits. Porphyry deposit-forming fluids appear to have been generally rich in oxidised sulphur species inherited from parent magma compositions, as revealed for instance by the occurrence of anhydrite gangue, and as a daughter mineral in fluid inclusions. Indeed, the temperature-dependent disproportionation of SO_2 producing H_2S is widely believed to be an important influence on space-time magnetite-sulphide distributions in porphyry-related ore systems (e.g., Seedorf *et al.*, 2005). However, in IOCG deposits, the common occurrence of barite (a highly insoluble sulphate mineral which does not characterise porphyry-related deposits) and/or Ba-rich hydrothermal feldspars, argues in these cases for the involvement of a fluid with a low oxidised sulphur content that was able to transport barium. Where oxidised sulphur was evidently available at the depositional site (i.e., where barite is present), this may be an indication that more than one fluid was involved raising the possibility that various ore components may have been introduced in different fluids (as was proposed by Haynes *et al.*, 1995 in the case of Olympic Dam). In IOCG deposits, the common and variable enrichments of a wide range of other elements with different solution chemistries adds further weight to this possibility. Analyses of fluid inclusions suggest another possibly important distinction, namely that brines involved in IOCG hydrothermal systems may on the whole have had about an order of magnitude lower copper concentrations (100 to 1000 ppm; Williams *et al.*, 2001; Bastrakov *et al.*, 2007; Baker *et al.*, 2008) compared to magmatic brines in porphyry copper systems (1000 to 10 000 ppm, e.g. Ulrich *et al.*, 2001; Rusk *et al.*, 2004).

Geochemical Evidence for the Origins of Ore-Forming Components

Conventional Light Stable Isotopes (H, C, O, S)

There have now been many studies of IOCG deposits, particularly those in Australia and Brazil, that have characterised the associated hydrothermal fluids using fluid inclusion petrography and microthermometry along with “conventional” light element (i.e., H, C, O, S) stable isotope geochemistry (see reviews in Partington and Williams, 2000; Williams and Pollard, 2003; and more recent works including Benavides *et al.*, 2007; Davidson *et al.*, 2007; Dreher *et al.*, 2008; Monteiro *et al.*, 2008; Xavier *et al.*, 2010, this volume). These studies have uniformly confirmed the role of brines, commonly associated with a carbonic phase, and in many examples provide evidence that more than one type of brine was present. At Lightning Creek in the Cloncurry district, fluid inclusions preserve good evidence for exsolution of iron- and copper-rich brine from a magmatic body associated with a magnetite-rich, transitional, magmatic-hydrothermal vein-sill complex, though in this case no direct connection can be made to any known IOCG deposit (Perring *et al.*, 2000).

In some cases, particularly where hematite is abundant (e.g., Olympic Dam), and/or where late stage parageneses have been investigated, there is clear evidence for the involvement of $\delta^{18}\text{O}$ -depleted surface-derived fluid (e.g., Oreskes and Einaudi, 1992; Benavides *et al.*, 2007;

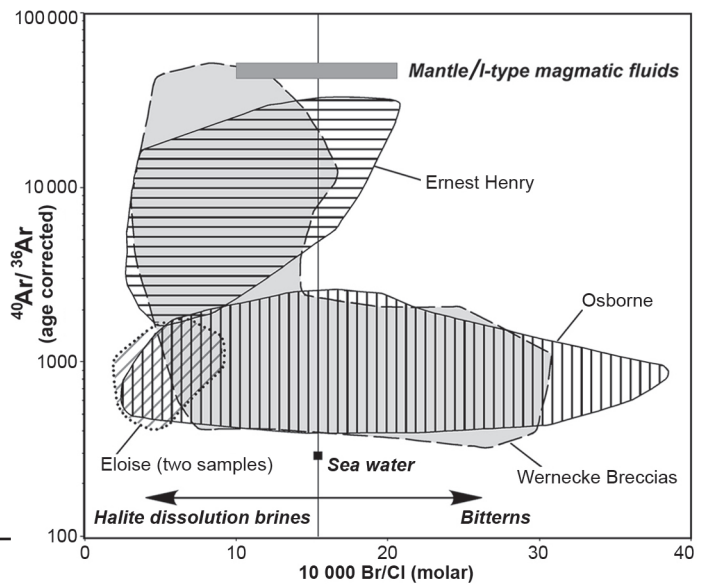
Davidson *et al.*, 2007; Dreher *et al.*, 2008). At Mantoverde in Chile, high $\delta^{34}\text{S}$, coupled with low $\delta^{18}\text{O}$, has been taken as evidence for the involvement of seawater derived fluids (Benavides *et al.*, 2007). However, in general there is evidence for earlier and/or higher temperature fluids in IOCG systems whose origin (i.e., magmatic versus metamorphic versus basinal) cannot be uniquely determined by these methods due to the overlapping isotopic compositions of such fluids, and the likelihood that the measured compositions had been modified during interactions with rocks (e.g., Marshall and Oliver, 2006; Edfeldt, 2007; Smith *et al.*, 2007; Monteiro *et al.*, 2008; Xavier *et al.*, 2010, this volume). Fluid compositions deduced from hydrous silicates in the high temperature magnetite-dominated Ernest Henry and Mount Elliott IOCG deposits in the Cloncurry district Australia, as well as the associated regional alteration, display comparatively large variations of δD compared to $\delta^{18}\text{O}$ that might be a signature of water sourced from variably degassed magmas (Wang and Williams, 2001; Mark *et al.*, 2004; 2005). A few combined δD - $\delta^{18}\text{O}$ analyses of minerals from IOCG prospects in the Olympic Dam region gave a different pattern that was interpreted to be more indicative of compositions controlled by interaction with rocks (Bastrakov *et al.*, 2007). The Ernest Henry deposit also preserves evidence of varying $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ through time, corresponding to increasing equilibration with carbonate reservoirs in the regional host rocks (Mark *et al.*, 2005; Marshall *et al.*, 2006).

At Sossego in the Carajás Mineral Province (Brazil) the $\delta\text{D}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of fluids that formed Na-Ca alteration distal from the main orebodies overlap the characteristic range for primary magmatic and low temperature metamorphic waters. These same $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values could also have resulted from high temperature equilibration of deeply circulating basinal or formational/meteoric waters with the host rock units (Monteiro *et al.*, 2008). Furthermore, paragenetically later copper-gold mineralisation is characterised by the introduction of $\delta^{18}\text{O}$ -depleted fluids (-0.4 to -5.2‰, at 300°C), reinforcing the importance of significant influx of surficial fluids for ore deposition. Sulphur isotope compositions for the Carajás IOCG deposits vary from values close to that expected for a mantle source (e.g., $\delta^{34}\text{S} = 0.9$ to 3.5) to ^{34}S -enriched values (>7.5‰) in the Sossego deposit in which contribution of meteoric fluids was significant, possibly reflecting input of heavy sulphur (sulphate) from surficial reservoirs. Fluid mixing between a high-temperature, hypersaline, intermediate oxidation state, metalliferous brine and oxidised surface-derived fluids could represent the principal ore deposition mechanism in the world-class Sossego and Alvo 118 deposits (Xavier *et al.*, 2010, this volume).

Radiogenic Isotopes (Rb-Sr, Sm-Nd, Re-Os)

Further insights have come from comparatively fewer studies that have applied radiogenic isotope methods to tracing sources of ore components. A particularly intriguing result from these studies is the observation that Nd isotopic compositions of ores from the giant Olympic Dam deposit appear to require a large contribution of the contained REE from coeval mantle-derived rocks or magmas (Johnson and McCulloch, 1995), whereas rocks from sub-economic IOCG deposits in the same region lack evidence for such a contribution (Skirrow *et al.*, 2007). Sm-Nd data for a number of iron oxide-apatite

Figure 3: Compilation of Br/Cl and $^{40}\text{Ar}/^{36}\text{Ar}$ data for IOCG and spatially-associated iron oxide deposits. Sources of data: Perring *et al.* (2000); Williams *et al.* (2001); Chiaradia *et al.* (2006); Kendrick *et al.* (2006; 2007); Baker *et al.* (2008); Fisher and Kendrick (2008); Kendrick *et al.* (2008b); Gleeson and Smith (2009). For explanation of reference values for seawater and regional magmatic fluids see Kendrick *et al.* (2008a;b). Note that magmatic fluids have variable Br/Cl ratios in the districts investigated. Single inclusion PIXE analyses are generally predicted to produce greater variation and more discrete data populations than analyses by bulk extraction methods. Br/Cl ratios measured by PIXE of interpreted magmatic fluid inclusions from Lightning Creek in the Cloncurry district (Perring *et al.*, 2000) extend to lower values than have been measured by bulk extraction methods in diamonds and porphyry copper fluids used to define the mantle/I-type box in the upper diagram.



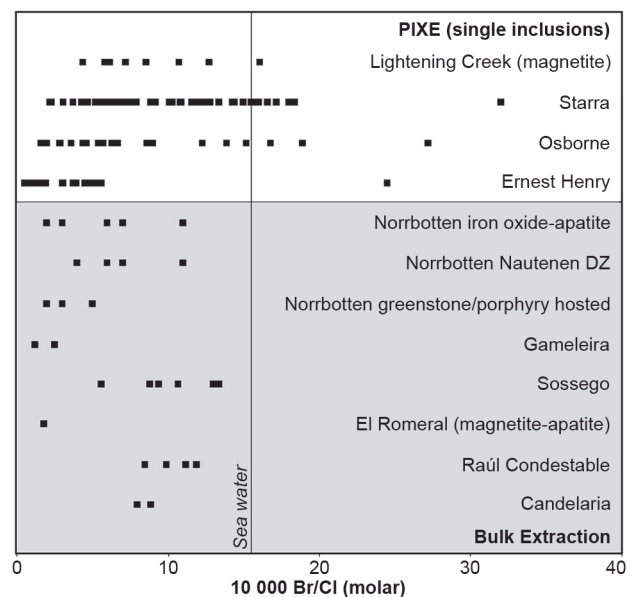
deposits with different ages, tectonic settings and magma type associations consistently indicated that the principal sources of REE in the ores were the coeval igneous rocks (Gleason *et al.*, 2000).

Re-Os data from Olympic Dam suggest that this isotope system was reset several hundred m.y. after mineralisation and cannot be used to place constraints on the original source of Os in the system (McInnes *et al.*, 2008). A Re-Os isochron based on magnetite, chalcopyrite and pyrite from Candelaria in Chile is compatible with the Re-Os molybdenite and $^{40}\text{Ar}/^{39}\text{Ar}$ ages and gives an initial $^{187}\text{Os}/^{188}\text{Os}$ ratio similar to that derived from magnetites in the nearby granitoids that indicates a mixed mantle-crust magmatic source (Mathur *et al.*, 2002). A similar initial Os isotope ratio (i.e., Os source) was calculated for the Manto Verde IOCG deposit in the same belt (Mathur *et al.*, 2002). As such, the data are compatible with derivation of ore components at Candelaria from the granitoids, whereas magnetites from some iron oxide-apatite deposits were found to have rather more radiogenic Os, compatible with a distinct but unknown crustal source (Naslund *et al.*, 2003).

There are very few published mineral Sr isotope data for major IOCG deposits and districts. The Sr in carbonates from Igarapé Bahia/Alemão (Carajás Mineral Province, Brazil) has a variable, highly radiogenic composition, indicating it is derived from more than one crustal source (Tallarico *et al.*, 2005). Barton *et al.* (2005) reported that unpublished Sr isotope data for altered rocks and host rocks in Candelaria-Punta del Cobre IOCG district (Chile) imply there are large contributions of non-igneous Sr in the former, requiring that the ore systems involved influx of fluids from outside the local batholithic granitoids.

Halogens, Noble Gases and Sr Isotopes in Fluid Inclusions

Recent attention has turned to less conventional methods of investigating ore fluid components, such as halogens and noble gases, that may be more diagnostic for source characterisation owing to their very large compositional variation that makes them exceptionally effective discriminators of fluid and salinity sources (cf. Fig.1). Williams *et al.* (2001) noted that whereas the Br/Cl ratios in fluid inclusions from the Starra IOCG deposit in the Cloncurry district (Australia) are consistent with a magmatic salinity component, their



overall variability might point to contributions from other sources (cf. Fig. 3). Fluid inclusion halogen and noble gas isotopic ratios were subsequently measured in three differently aged Cloncurry IOCG deposits, namely Eloise, Osborne and Ernest Henry (Mark *et al.*, 2005; Kendrick *et al.*, 2006; 2007; Baker *et al.*, 2008; Fisher and Kendrick, 2008). The Ernest Henry data are consistent with mixing of two brines, one with a halogen signature similar to the mantle, and a high $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of 30 000 that is typical of magmatic fluids in the Cloncurry district (Fig. 3). The other had low Br/Cl and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of ≈ 1000 , suggestive of halite (i.e., evaporite) dissolution by near surface sedimentary formation waters (or scapolite breakdown) that are thus deduced to have been circulated to the estimated 6 to 10 km depths of mineralisation. The same technique at the Osborne deposit revealed similarly variable Br/Cl and I/Cl, but in this case associated with uniformly low $^{40}\text{Ar}/^{36}\text{Ar}$ ratios that provide no support for the involvement of A- or I-type magmatic fluids (Fisher and Kendrick, 2008; Fig. 3). The latter data were interpreted to reflect mixing of fluids generated during metamorphism which is consistent with the interpreted ages of both mineralisation and peak metamorphism at this location. The combined noble gas and halogen approach was also applied to the Wernecke Mountains IOCG

prospects in northwest Canada. This was undertaken in the expectation of constraining a non-magmatic variety of IOCG deposit because there are no known igneous rocks coeval with the IOCG deposits in the Wernecke district (e.g., Hunt *et al.*, 2007). However, the noble gas data (Ar and Ne) reveal a highly radiogenic fluid end member analogous to that in the Ernest Henry deposit which was interpreted as indicating involvement of magmatic fluids (Kendrick *et al.*, 2007, 2008b). This suggests that a cryptic magmatic event could have been responsible for the abundant hydrothermal brecciation coeval with IOCG metallogenesis in the Wernecke district (see also Hitzman *et al.*, 1992).

Chiaradia *et al.* (2006) measured Br/Cl values in fluid inclusions from the Sossego (Carajás, Brazil) and Candelaria and Raúl-Condestable (Andes Coastal Belt) IOCG deposits along with strontium isotope ratios for the latter two. These data consistently imply a combination of evaporite and mantle-derived magmatic contributions to both the fluid salinity and strontium content. A sample from the El Romeral magnetite-apatite deposit in the Andes Coastal Belt was found to contain very radiogenic Sr, consistent with the comparatively strong crustal contribution observed in the Os data from such deposits in the same region (Mathur *et al.*, 2002). Chiaradia *et al.* (2006) also reported $\delta^{37}\text{Cl}$ values in fluid inclusions from IOCG deposits that were apparently higher than those from porphyry copper deposits, which these authors believed might imply a greater contribution of mantle-derived chlorine in the IOCG deposits. However, this interpretation assumes a mantle Cl isotope composition that has been disputed in subsequent work (e.g., Sharp *et al.*, 2007; cf. Gleeson and Smith, 2009). Furthermore, the possibility that chlorine isotopic compositions might have been modified by fractionation could not be excluded.

Gleeson and Smith (2009) undertook a similar study ($\delta^{37}\text{Cl}$ and Br/Cl) of samples from Palaeoproterozoic IOCG and iron oxide-apatite deposits in Norrbotten, northern Sweden. Fluids from one group of copper-gold deposits hosted by greenstones and metaporphyrries were found to have a narrow range of Br/Cl ratios (2×10^{-4} to 5×10^{-4} molar) and $\delta^{37}\text{Cl}$ that were interpreted to favour a magmatic-hydrothermal source of salinity. However, the measured Br/Cl ratios are also consistent with the involvement of evaporites (Fig. 3). Deposits hosted in a regional shear zone had higher Br/Cl ratios coupled with $\delta^{37}\text{Cl}$ values that suggest the initial Cl source was seawater or evaporites, although it may have been recycled through magmas. In general, the variable Br/Cl and $\delta^{37}\text{Cl}$ values reflect diverse origins of salinity in these related deposit types, similar to that observed in the Cloncurry and Chilean districts. Finally, several of the samples investigated by Gleeson and Smith (2009) had unexpectedly low $\delta^{37}\text{Cl}$ values that might result from an undocumented type of Cl-isotope fractionation involving Cl-bearing silicates in regional alteration systems. If such fractionations do occur in nature, then this may preclude the effective discrimination of mantle and crustal Cl from fluid inclusion $\delta^{37}\text{Cl}$ data (cf. Chiaradia *et al.*, 2006).

Xavier *et al.* (2009), reported Br/Cl and Na/Cl ratios, obtained in fluid inclusions using ion chromatographic analyses (bulk extraction), and suggested that the chlorine involved in the formation of IOCG deposits in the Carajás Mineral Province was sourced from two main end member fluids: (1) a residual evaporated seawater (bittern fluid)

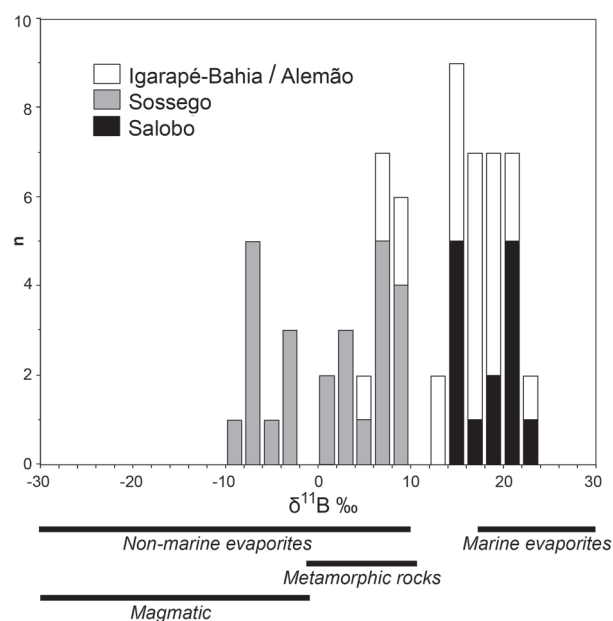


Figure 4: Boron isotope compositions of tourmaline from three IOCG deposits in the Carajás Mineral Province (Brazil), compared with those of natural boron reservoirs (Xavier *et al.*, 2008).

and (2) magma-derived brines. In this interpretation, fluids from the Igarapé Bahia/Alemão and Alvo 118 IOCG deposits are almost entirely evaporated seawater, whereas those at Sossego define different degrees of mixing between bittern and magmatic brines.

While these recent studies have significantly improved the understanding of the sources of fluids and salinity in IOCG deposits, considerable uncertainty remains about the origins of metals. In one case, namely the Cloncurry district, PIXE analysis of individual fluid inclusions has revealed a correspondence of higher copper-contents with Br/Cl ratios typical of magmatic fluids in that district. Lower copper-contents were measured in inclusions with lower Br/Cl ratios suggestive of salinity derived from evaporites or their metamorphosed equivalents (Baker *et al.*, 2008).

Boron Stable Isotopes

Another approach applied in the Carajás Mineral Province (Xavier *et al.*, 2008) involved the measurement of $\delta^{11}\text{B}$ in the common accessory mineral, tourmaline (Fig. 4). Tourmalines from the Igarapé Bahia and Salobo IOCG deposits have high $\delta^{11}\text{B}$, implying that the ore-forming fluids in these cases acquired a large proportion of their boron by interaction with marine evaporites (Fig. 4). However, tourmalines from the Sossego deposit have lower $\delta^{11}\text{B}$ values that are not diagnostic of any specific source, but could reflect a mixture of magmatic and marine evaporite boron.

Conclusions

Geochemistry has been providing growing insights into the sources of mineralising components in IOCG deposits. However, the interpretation of such data is limited by several factors, including the critical inability of any tracer to directly imply the origin of other components (i.e., diagnostic ore elements in IOCG deposits). Whereas this is a universal issue in the application of geochemical tracers in metallogenic studies, the problem is amplified for IOCG deposits because the other geochemical tracers reveal a general pattern of mixed source contributions and

suggest that these vary from case to case. Interpretation is also commonly limited by inadequate baseline data at lithospheric to regional scale and/or by an incomplete understanding of natural fractionations that may affect the chemical systems. Where contributions from contemporary igneous rocks are evident, it

is generally not clear whether these came directly from a volatile phase evolved from the magmas or by leaching from previously consolidated rocks.

Currently, the key factual observations relating to IOCG deposits include:

- (1) A variety of different hydrological systems have resulted in the formation of IOCG deposits including: (a) high level systems in which cool surficial fluids interacted with deeply-sourced fluids, and (b) deeper systems, some but not all of which, display evidence for a direct input of magmatic fluid. The very few studies undertaken so far that used tracers that are relatively immune to exchange reactions with rocks imply that surficial fluids may contribute to IOCG genesis even in the deepest (metamorphic) settings.
- (2) Despite some uncertainty regarding the compositions of source reservoirs and fractionations with silicate minerals, there is good evidence, particularly where halogens have been used in combination with other tracers, that IOCG ore fluids had salinities derived from different sources, but that evaporites (or meta-evaporitic scapolite) were highly significant in most cases (e.g., \pm magmatic \pm dissolved evaporite/meta-evaporite \pm evaporated surface water). In one district (Carajás Mineral Province, Brazil) boron isotopes provide independent evidence that there is a contribution from marine evaporites in at least some of the ore systems.
- (3) To date, only circumstantial evidence links the principal economic metals in IOCG deposits to any particular source such as: (a) the correspondence of higher copper concentrations in fluid inclusions with magmatic Br/Cl ratios in the Cloncurry district, where contemporary intrusions also display evidence for evolution of copper-rich brines; and (b) the correlation of copper endowment and contemporary mantle-derived REE in systems of the Gawler craton.

Many gaps still remain to be filled in the knowledge base for IOCG deposits and the potential lithospheric sources of their diverse components. Nevertheless there is already good evidence that there are deposits included in this class that had fundamentally different modes of genesis.

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