Ore Geology Reviews 51 (2013) 74–78

Contents lists available at SciVerse ScienceDirect

Ore Geology Reviews

journal homepage: www.elsevier.com/locate/oregeorev

External sulphur in IOCG mineralization: Implications on definition and classification of the IOCG clan

Huayong Chen *

Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

ARTICLE INFO

Article history:
Received 16 August 2012
Received in revised form 2 December 2012
Accepted 12 December 2012
Available online 20 December 2012

Keywords:
IOCG deposit clan
External sulphur
Redefinition and reclassification

ABSTRACT

Although the sources of the ore metals remain problematic in most Iron-oxide Cu and Au (IOCG) deposits, external sulphur, either from surficial basinal brines and seawater (e.g., Central Andean and Carajás deposits) or from formation water and metamorphic fluids (e.g., the Cloncurry deposits), or introduced by magmatic assimilation of metasedimentary units (e.g., Phalaborwa), has been documented in many major Cu-rich IOCG centres. However, only the evaporite-sourced fluids yield diagnostically high $\delta^{34}S$ values (i.e., $>10‰$), while sedimentary formation water or metamorphic fluids commonly have lower values and are less clearly distinguishable from magmatic fluids, as in the Cloncurry deposits in which the involvement of external fluids is revealed by other evidence, such as noble gas isotopes. On the basis of these arguments, IOCG deposits could be redefined as a clan of Cu (–Au–Ag–U) deposits containing abundant hypogene iron oxide (magnetite and/or hematite), in which externally-derived sulphur probably plays an important role for the Cu (–Au–Ag–U) mineralization. In this definition, all "Kiruna-type" magnetite deposits, hydrothermal iron deposits (e.g., skarn Fe deposits) and magnetite-rich porphyry Cu–Au and skarn Cu–Au deposits are excluded. Two subtypes of IOCG deposits are recognized on the basis of the predominant iron oxide directly associated with the Cu– (Au–) mineralization, whether magnetite or hematite. Neither magnetite- nor hematite-rich IOCG deposits show any preference for specific host rocks, and both range in age from Neoarchean to Pleistocene, within a broad tectonic environment.

1. The IOCG deposit clan: Problematic definition and genesis

1.1. Problematic definition

The past half-century has seen major progresses in the clarification of the genesis of the majority of the long-established classes of hydrothermal ore deposits, including porphyry copper (–molybdenum and/or gold), epithermal base and precious metal, skarn/carbonate replacement, Mississippi Valley-type, and both volcanic- and sediment-hosted massive sulphide systems. At the same time, other forms of mineralization, such as Carlin-type gold–silver and unconformity-controlled uranium deposits, have been extensively documented, even if they attract continued debate as to their genesis. Against this background, the "iron oxide-copper–gold" (IOCG) clan, first formally promulgated by Hitzman et al. (1992), stands out as a focus of fundamental controversy, extending even to doubts as to its coherence and specificity. It could be argued that an abundance of such extremely common minerals as magnetite or hematite constitutes a vulnerable basis for the definition of a copper sulphide ore deposit class. Thus, why should IOCG deposits not be included under the magnetite-rich copper–gold sub-class of the porphyry clan (e.g., Ulrich and Heinrich, 2002), and what are their relationships to magnetite- and hematite-rich gold (–copper) porphyry mineralization (Vila and Sillitoe, 1991)? Similarly, the widespread development of calc-silicate alteration, largely amphibolitic but locally rich in diopside and garnet, and the calcareous host-rocks of some IOCG deposits, suggest affinities with skarn mineralization.

Indeed, it was only the 1975 discovery of the Olympic Dam hematitic breccia complex in South Australia (Woodall, 1993), a world-class source of Cu and Au as well as the largest single uranium producer (Hitzman and Valenta, 2005), that prompted the establishment of the IOCG clan as a distinct entity. The direct association (Haynes et al., 1995) of major copper sulphide mineralization with an anorogenic alkali feldspar granite stock, rather than with the inherently copper-rich intermediate (granodiorites, quartz diorites, etc.), orogenic granitoid suite which globally hosts the superficially similar porphyry copper deposits, was seen as an evidence for a fundamental ore genetic distinction. Over the past several decades, intensive exploration for deposits broadly comparable to Olympic Dam has met with only modest success, with the greenfield discovery of only a handful of large copper-rich examples in both Precambrian and Phanerozoic terranes of both orogenic and anorogenic origin (Porter, 2010). It is apparent that the vast majority of deposits which have been previously assigned to the IOCG clan (Hitzman et al., 1992), including Kiirunavaara, are magnetite-rich but sulphide-poor, containing, if any, only subeconomic copper and gold. Williams et al. (2005) and Groves et al. (2010) have therefore recommended that the IOCG designation be restricted to deposits with economic copper and/or

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* Tel.: +86 20 85292708; fax: +86 20 85290220.
E-mail address: huayongchen@gig.ac.cn.

0169-1368/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.oregeorev.2012.12.002

gold (so called "*sensu stricto*" IOCG), although maintaining a genetic connexion between Cu-rich and Cu-poor mineralization. The IOCG clan thus suffers from an inherent dichotomy: most such Cu-poor systems failed to generate significant sulphide mineralization, no matter how intense the commonly early-stage magnetite deposition.

1.2. Controversial ore genesis

Proximity to granitoid stocks, intense high-temperature hydrothermal alteration, and extensive hydrothermal brecciation have been interpreted by many (e.g., Pollard, 2006; Sillitoe, 2003) as supporting a direct genetic relationship between IOCG deposit development and hydrous fluid exsolution from crystallizing silicate melts, the abundance of Fe, Cu, Au and, locally, Co being ascribed to a mafic parental magma. Such magmatic-hydrothermal models prompt analogies with, particularly, molybdenite-poor porphyry copper–gold deposits, the vast majority of which are magnetite-rich (e.g.,Ulrich and Heinrich, 2002; Pollard et al., 2005). However, several characteristic, if not ubiquitous, features of Cu-rich IOCG's, such as intense albitization, Ca metasomatism (commonly amphibolitization), hematite- and calcite-rich sulphide mineralization and the scarcity of pyrite, as well as the overall sequence of alteration–mineralization events, are difficult to reconcile with thermally retrograde melt-aqueous fluid equilibria (Candela, 1989). In addition, many major IOCG provinces of both Proterozoic and Phanerozoic age exhibit a close correlation with mid-latitude sedimentary/volcanic basins which either incorporate evaporite sequences or preserve their metamorphic relics, i.e., regional scapolite-albite (–tourmaline) assemblages (Frietsch et al., 1997). Such relationships underlie the proposal of Barton and Johnson (1996, 2004) that the brines responsible for Cu (– Au) sulphide mineralization in IOCG deposits were derived wholly or in part through the dewatering of intra-arc or anorogenic rift basins. It is germane that two of the largest copper-rich IOCG deposits, viz. Olympic Dam and Phalaborwa (Groves and Vielreicher, 2001), formed in an anorogenic rift environment, a geodynamic setting which globally lacks significant porphyry copper mineralization. Stable isotope evidence for a non-magmatic origin, at least for sulphur and oxygen, was presented by Ullrich and Clark (1999) for La Candelaria, the most important Cu-rich IOCG deposit in the Central Andes, but the incursion of basinal fluids had earlier been documented at Olympic Dam by Haynes et al. (1995). Although the ore metals, i.e., Cu and Au in these deposits, may be, at least in part, magma-derived (Marschik and Fontboté, 2001; Rieger et al., 2010), such inherently complex genetic models have direct implications for the occurrence of, and hence exploration for, Cu-rich IOCG's, as is exemplified by the studies of Benavides et al. (2007) in the Mantoverde district of northern Chile, Chen et al. (2010, 2011) in the Mina Justa deposit of southern Peru and Monteiro et al. (2008) in the Carajás district of Brazil.

2. The external sulphur: a possible prerequisite for the "*sensu stricto*" IOCG mineralization

Although the sources of the ore metals remain problematic in most IOCG deposits, external sulphur, from either surficial basinal brines and seawater (e.g., Central Andean, Olympic Dam and Carajas IOCG deposits: Benavides et al., 2007; Chen et al., 2011; Haynes et al., 1995; Monteiro et al., 2008) or formation water and metamorphic fluids (e.g., the Cloncurry deposits: Kendrick et al., 2007), or introduced by magmatic assimilation of metasedimentary units (e.g., Phalaborwa: Drüppel et al., 2006; Mitchell and Krouse, 1975), has been documented in most, if not all, major Cu-rich IOCG centres.

The addition of sulphur, and hence the attainment of sulphide mineral solubility products in originally sulphur-poor systems, are considered to be responsible for the economic Cu (– Au) mineralization in IOCG systems. This takes place through mixing of external fluids and sulphur-poor magmatic fluids (e.g., Olympic Dam, Ernest Henry and La Candelaria), or by fluid reduction through the replacement of ironstones or other host rocks by late oxidized sulphur-rich external fluids (e.g., Mina Justa and Mantoverde). Alternatively, sulphur saturation in magmas with limited sulphur capacity, such as those of the Phalaborwa carbonatite complex, may have resulted directly from the assimilation of sulphur-rich country rocks, or involvement of reduced and sulphur-rich magmatic fluids modified by Na (−K) metasomatism (fenitization) of host rocks. The different degrees of oxidation in such ore-forming systems may result in magnetite or hematite-dominant IOCG systems. In contrast, Cu-barren magnetite — dominated veins in sulphur-saturated porphyry Cu – Au and skarn Cu – Au deposits are generated at high-temperature (e.g., 450 – > 750 °C at Bajo de la Alumbrera: Ulrich and Heinrich, 2002) and relatively higher fO_2 (up to the magnetite-pyrite oxygen buffer) than later Cu – Au mineralization stages. In such an extreme environment, Cu sulphides do not attain saturation and Fe is commonly represented by iron oxides (Hezarkhani et al., 1999).

However, only the evaporite-sourced fluids yield high $\delta^{34}S$ values (i.e., > 10‰: Thodes, 1991), while sedimentary formation water or metamorphic fluids commonly have lower values and are less clearly distinguishable from magmatic fluids, as in the Cloncurry deposits in which the involvement of external fluids is revealed by other evidence, such as noble gas isotopes (Kendrick et al., 2007).

3. A possible revised definition and classification of IOCG deposits

On the basis of these arguments, IOCG deposits could be possibly redefined as a clan of Cu (– Au – Ag – U) deposits containing abundant hypogene iron oxide (magnetite and/or hematite), in which externally-derived sulphur is probably a prerequisite for the Cu (– Au – Ag – U) mineralization. In this definition, all "Kiruna-type" magnetite deposits, hydrothermal iron deposits and magnetite-rich porphyry Cu – Au and skarn Cu – Au deposits are excluded. A classification and the defining characteristics of this newly-defined IOCG clan are presented in Table 1, the salient criteria being ore and alteration mineralogy and the nature of the dominant ore-forming fluids.

3.1. Common features

In addition to the abundant iron oxide and external sulphur involvement, most IOCG deposits exhibit several common features, viz. (1) with the exception of Phalaborwa, orebodies are commonly controlled by faults (shear zones and normal faults); (2) many with location on a basin margin; (3) hydrothermal breccias; (4) regional Na (± Ca) alteration; (5) Cu (– Au) mineralization associated with K (± Cl ± Ca) alteration; (6) alteration zonation unrelated to local intrusions; and (7) low-Ti magnetite.

Two subtypes of IOCG deposits are recognized on the basis of the predominant iron oxide directly associated with the Cu – (Au –) mineralization, whether magnetite or hematite.

3.2. Magnetite subclan

Magnetite is the major iron oxide associated with the main Cu – Au mineralization stage(s) in these deposits. Hematite formed at a late paragenetic stage and, if it formed earlier, is replaced by magnetite ("mushketovite"; e.g., La Candelaria). The mineralization comprises economic Cu and Au (> 0.2 g/t), with minor Co, Bi and U-REE (e.g., Tennant Creek), locally rich in P, Ni, F and Mg (e.g., Phalaborwa). The main ore assemblage includes magnetite, chalcopyrite, pyrite and/or pyrrhotite, but locally includes the magnetite–chalcopyrite–bornite–chalcocite association (e.g., Salobo and Phalaborwa). Regional Na ± Ca (albite–scapolite ± actinolite) alteration is common, but, except at Phalaborwa, Cu – Au mineralization is closely associated with potassic (biotite and/or K-feldspar) alteration, and locally with Ca- (actinolite or clinopyroxene) alteration

Table 1
Proposed Classification of IO and IOCG Deposits.

Deposit types	Iron oxide (IO)[a]	IOCG	
Subtype	Magnetite	Magnetite subclan	Hematite subclan
Ore-forming fluids	Magmatic[b]	Magmatic[c] and hybrid magmatic — non-magmatic	Hybrid magmatic — non-magmatic and non-magmatic
Examples	Lightning Creek, Acropolis (Australia); Acarí, Morritos, part of CIB[d] (Central Andes); Benson, Cornwall (USA); Esfordi (Iran); and "ironstone" in IOCG	Sossego, Salobo (Carajás); Ernest Henry, Eloise (Cloncurry); West Peko (Tennant Creek); La Candelaria-Punta del Cobre, Raúl-Condestable (Central Andes); Tjårrojåkka, Aitik[f] (Norbotten); Khetri (NW India); Boss-Bixby (SW Missouri); Wernecke, Nico (Canada); Guelb Moghrein (Akjoujt); Ossa Morena (Spain); Phalaborwa (South Africa)	Olympic Dam, Prominent Hill, Redbank (South Australia); Mantoverde, Mina Justa, Mantos Blancos (Central Andes); Alvo 118 (Carajás); Mont-de-l'Aigle, Sue-Dianne (Canada); Salton Sea (USA); Malundae (Lufilian arc); Boleo (Mexico)
Economic elements	Fe (±P)	Cu–Au (±Co±Bi±U±REE±Ni)(P-Mg: Phalaborwa)	Cu±Ag±Au±Co±Zn (U-REE: Olympic Dam)
Ore assemblages	mt-act-apt-qtz±ab±cpx±bt±K-feldspar±py±cpy	Commonly: mt-cpy-py±po±hem Locally: mt-cpy-bn-cc (Salobo, Phalaborwa)	hem-cpy-bn-cc and hem-cpy-py
Hydrothermal alteration	Regional: Na-Ca±Cl±B Mineralization-related: Fe–K–Ca	Regional: Na±Ca Mineralization-related: K±Fe±Ca±Cl±Na	Regional: weak Na±Cl±Ca Mineralization-related: K-Cl±Na±Ca
Ore morphology	Veins, stockwork; local breccias	Veins and breccias; local lenses (Salobo)	Breccias, lenses (manto) and veins
Ore precipitation mechanism	Cooling	Fluid mixing and cooling	Fluid mixing and fluid reduction
Non-magmatic fluids	No	Basinal brine/seawater (Candelaria); $\delta^{34}S_{fluids} > 10‰$; Metamorphic fluids/formation water (Ernest Henry; Guelb Moghrein): $\delta^{34}S_{fluids} < 10‰$	Basinal brine/seawater: $\delta^{34}S_{fluids}$ commonly >10‰
Characteristics of ore-forming fluids	High T (>450 °C) and salinity (>25 wt.% NaCl eq.); CO_2-rich or CO_2-bearing[e]	High-T (Ernest Henry: >350 °C) or wide range of T (Salobo: 100–500 °C); moderate-high salinity (15–50 wt.% NaCl eq.); Na-Ca dominant and Na>Ca; CO_2-rich or CO_2-bearing	Moderate-low T (<300 °C), and moderate-high salinity (>15 wt.% NaCl eq.); Ca–Na dominant and Ca>Na; CO_2-bearing or CO_2-poor
Mineralization level	Deep (>3 km) to shallow	Deep (>6 km, Ernest Henry) to shallow (<3 km, Candelaria)	Shallow (generally <3 km)
Ore-controlling structure	Shear zone, local rift	Shear zone	Normal fault-detachement-dilational zone/Shear zone
Subtype	Magnetite	Magnetite subclan IOCG	Hematite subclan IOCG
Host rocks	Sedimentary and volcanic rocks and intrusions	Sedimentary and volcanic rocks and intrusions	Sedimentary and volcanic rocks and intrusions
Distance to syn-mineralization magmatism	Close (<3 km)	Close (<3 km) — Sossego, Eloise, La Candelaria; Far (>3 km) — Ernest Henry, Wernecke	Close (<3 km) — Olympic Dam; Mantos Blancos Far (>3 km) — Mina Justa, Mantoverde[g]
Mineralization age	Mesoproterozoic to Tertiary	Archean to Tertiary	Mesoproterozoic to Pleistocene
Tectonomagmatic setting	(A) (Acropolis) (B) (Central Andean deposits) (C) (Lightning Creek)	(A) Precambrian intracratonic basins, anorogenic; A-type magmatism (Carajás, Norbotten, SW Missouri, Phalaborwa) (B) Inversion of basins in extensional arc on subduction-related continental margin; calc-alkaline arc magmatism (Central Andes) (C) Inversion of post-collisional orogenic basins; calc-alkaline magmatism postdating metamorphic peak (Cloncurry) (D) extension following retrograde metamorphism (Guelb Moghrein, Wernecke)	(A) (Olympic Dam, Prominent Hill) (B) (Central Andean deposits) (C) (Mont-de-l'Aigle)

[a] Melt-origin "Kiruna-type" magnetite–apatite deposits not included.
[b] Magmatic fluids without external sulphur.
[c] Magmatic fluids with external sulphur, e.g., Phalaborwa.
[d] CIB-Chilean Iron Belt.
[e] Defined in this table: CO_2-rich — fluid inclusions containing $CO_2 \geq 20\%$; CO_2-bearing: a few fluid inclusions (<20%) contain CO_2; CO_2-poor: no CO_2 identified in fluid inclusions.
[f] Late IOCG-like magnetite–bornite–chalcopyrite stage.
[g] Intra-mineralization dykes locally developed.

(e.g., La Candelaria and Eloise). The shear zone-controlled orebodies are composed of veins and breccias, but are locally lensoid (e.g., Salobo). At Phalaborwa, the ore-controlling structures are not clear and mineralization occurs in a vertical carbonatite pipe, in which disseminated grains and massive blebs of sulphides are hosted by fine- to coarse-grained carbonate matrix. Evidence of the incursion of non-magmatic fluids is unambiguous in most magnetite subclan IOCG's, and metal precipitation is inferred in most examples to have resulted from fluid mixing and concomitant cooling. The main Cu mineralization at Phalaborwa and Swartbooisdrif is intimately associated with and hosted by carbonatite and lacks evidence of non-magmatic fluids, but the sulphur isotopic values (up to +5‰: Mitchell and Krouse, 1975) and εNd and εSr (Harmer, 2000; Yuhara et al., 2005) of the carbonatite indicate either that metasedimentary, probably evaporitic, units were assimilated by the carbonatitic magma, and/or magmatic fluids modified through fenitization invaded the carbonatitic magma (Harmer, 2000). Such reduced, sulphur-rich fluids may have triggered sulphide saturation and sulphide melt immiscibility in the carbonatite magmas at temperatures exceeding 650 °C (Helz and Wyllie, 1979). The external fluids involved in other hydrothermal, magnetite-dominant IOCG systems were probably derived from either basinal brine/seawater with high $\delta^{34}S$ values (commonly > +10‰: La Candelaria and Raúl- Condestable), or metamorphic fluids/formation water from the middle crust or from sedimentary units with lower $\delta^{34}S$ values (commonly < +10‰: Ernest Henry and Guelb Moghrein). The ore-forming fluids were high-temperature (e.g., Ernest Henry: 350–440 °C) or record a wide range

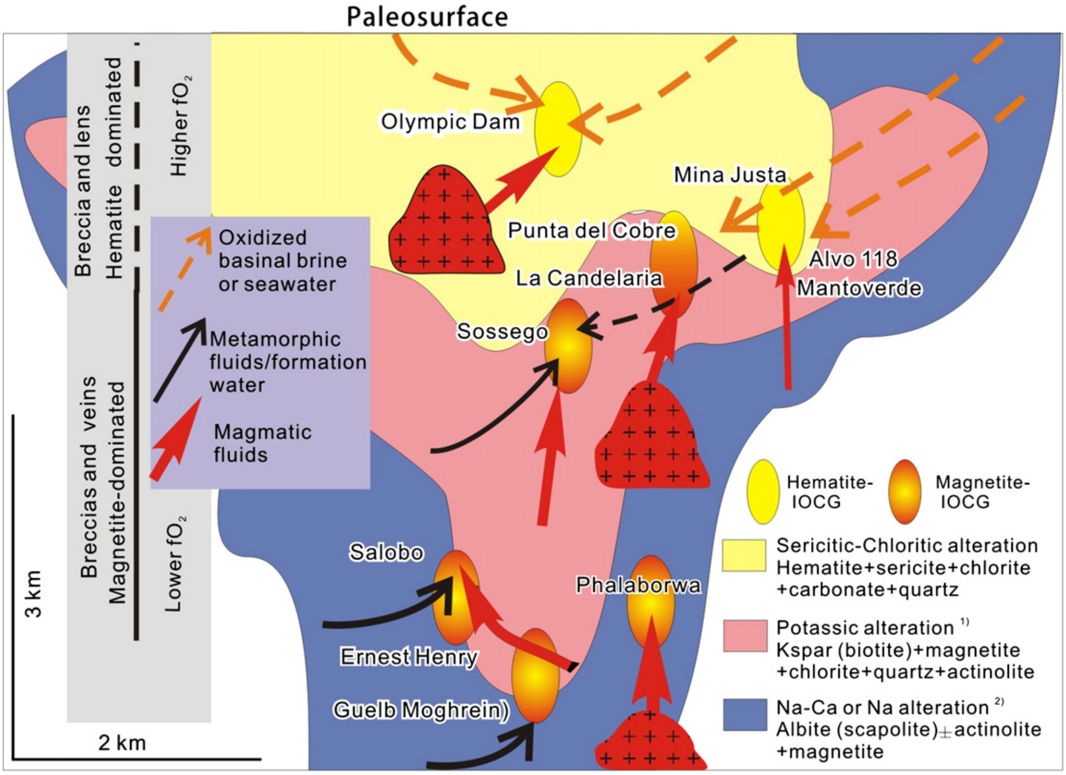

Fig. 1. Carton illustrating the settings of IOCG deposits. Alteration zoning in IOCG deposits is summarized from Williams et al. (2005). Regional Na – Ca or Na alteration commonly precedes mineralization, while potassic alteration and hydrolytic (sericite–chlorite) alteration are usually mineralization-related. 1) Ca-metasomatism dominates the La Candelaria-Punta del Cobre district. 2) Na – Ca alteration widespread in the Cloncurry district, whereas Na-alteration dominates the Central Andean IOCG centres. NB. Under conditions of high thermal gradient/heat-flow, the Y-axis will be compressed. The thicknesses of arrows indicate the relative contributions of different fluid sources. Basinal brines or seawater are probably more oxidized than magmatic and metamorphic fluids.

of temperatures (e.g., Salobo: 100–500 °C, La Candelaria: 275–450 °C), which may imply fluid mixing. Na is the dominant cation in the fluids, but Ca was invariably present and locally abundant (e.g., Eloise and Aitik). CO_2 is commonly a major fluid constituent, particularly in the Cloncurry deposits and at Phalaborwa. Hot, CO_2-rich and hypersaline brines have been identified in many magnetite-rich IOCG deposits (Pollard, 2006). However, the areal separation of mineralization and syn-mineralization intrusions is commonly considerable (e.g., ~15 km at Ernest Henry), in strong contrast to magnetite-rich porphyry Cu – Au and skarn deposits. Magnetite subclan IOCG deposits were emplaced over a wide depth interval, from more than 6 km at Ernest Henry and Guelb Moghrein, to relatively shallow levels (e.g., Candelaria and Sossego). In contrast, the hematite-series IOCG deposits were all emplaced at shallow level (i.e., <3 km) and close to surface (Fig. 1).

3.3. Hematite subclan

Hematite- and sulphide- cemented hydrothermal breccias are common in this subtype, and the Cu sulphides are dominated by Fe-poor chalcopyrite–bornite–chalcocite (and/or digenite) assemblages, although only chalcopyrite occurs in some deposits (e.g., Mantoverde). In contrast to magnetite-rich IOCG deposits, Au is only locally enriched in the hematite subtype (e.g., Olympic Dam), whereas Ag and Zn are more abundant. Vertical and lateral sulphide zonations, from chalcopyrite–pyrite to bornite–chalcocite, are documented in many hematite IOCG's (e.g., Olympic Dam, Mantos Blancos and Mina Justa). Hydrothermal alteration associated with Cu mineralization is dominated by sericitic or K-feldspar-chlorite alteration, rather than the biotite ± amphibole assemblages characteristic of magnetite-rich IOCG deposits, and regional Na – Ca alteration is only weakly developed around most hematitic IOCG systems. The ore-forming fluids in hematite IOCG's also differ from those of the magnetite subtype. They are usually cooler (<300 °C), and have higher contents of Ca (Ca > Na) and less CO_2. External fluids, mainly basinal brines and modified seawater with high $\delta^{34}S$ values, commonly > + 10‰, unambiguously played a major role in the hematitic IOCG ore-forming systems. Fluid mixing was directly responsible for Cu mineralization at Olympic Dam, Mantos Blancos and Mantoverde, all dominated by breccias, whereas at Mina Justa, manto orebodies formed through the replacement of ironstone or other host- rocks by heated basinal brines or seawater, with fluid reduction as the dominant mechanism for Cu mineralization.

Neither magnetite- nor hematite-rich IOCG deposits show any preference for specific host rocks, and both range in age from Neoarchean to Pleistocene. The tectonomagmatic settings include: Precambrian intracratonic rifts with A-type (Olympic Dam, Sossego), or even carbonatitic (Phalaborwa) magmatism; inverted basins within extensional arcs along convergent continental margins with calc-alkaline arc magmatism (Central Andean IOCG's); and inverted post-collisional orogenic basins with calc-alkaline magmatism (Cloncurry, the Lufilian arc). Extension following retrograde metamorphism may accompany IOCG mineralization at Guelb Moghrein and Wernecke.

4. Conclusion

Since Williams et al. (2005), the "*sensu stricto*" IOCG deposits, i.e., those Cu (– Au)-rich IOCG systems, has been widely accepted as the represented group for this previously broadly defined and classified deposit clan. Iron oxide deposits, either Kiruna-type or Chilean iron belt-type magnetite deposits, were excluded from the current IOCG clan, even though some genetic connexion may still exist between Cu-rich and Cu-poor groups. Most of Cu-poor iron oxide systems failed to develop Cu (– Au) mineralization due to the lack of external sulphur which is either from direct basinal brines or assimilation of sedimentary rocks into the magma. The "*sensu stricto*" IOCG deposits can be classified based on their major containing iron oxide, i.e., magnetite and hematite, some distinguishable features can be assigned to these two sub-groups.

Acknowledgement

Author thanks Professor Alan Clark and Kurt Kyser for their supervision during his Ph.D. study and generous support for this project.

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