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## Origin of fluids in iron oxide–copper–gold deposits: constraints from $\delta^{37}\text{Cl}$ , $^{87}\text{Sr}/^{86}\text{Sr}$ , and Cl/Br

Received: 15 May 2006 / Accepted: 22 June 2006 / Published online: 18 August 2006  
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**Abstract** The origin of the hypersaline fluids (magmatic or basinal brine?), associated with iron oxide (Cu–U–Au–REE) deposits, is controversial. We report the first chlorine and strontium isotope data combined with Cl/Br ratios of fluid inclusions from selected iron oxide–copper–gold (IOCG) deposits (Candelaria, Raúl–Condestable, Sossego), a deposit considered to represent a magmatic end member of the IOCG class of deposit (Gameleira), and a magnetite–apatite deposit (El Romeral) from South America. Our data indicate mixing of a high  $\delta^{37}\text{Cl}$  magmatic fluid with near 0‰  $\delta^{37}\text{Cl}$  basinal brines in the Candelaria, Raúl–Condestable, and Sossego IOCG deposits and leaching of a few weight percent of evaporites by magmatic-hydrothermal (?) fluids at Gameleira and El Romeral. The Sr isotopic composition of the inclusion fluids of Candelaria, Raúl–Condestable, and El Romeral confirms the presence of a non-magmatic fluid component in these deposits. The heavy chlorine isotope signatures of fluids from the IOCG deposits (Candelaria, Raúl–Condestable, Sossego), reflecting the magmatic-hydrothermal component of these fluids, contrast with the near 0‰  $\delta^{37}\text{Cl}$  values of porphyry copper fluids known from

the literature. The heavy chlorine isotope compositions of fluids of the investigated IOCG deposits may indicate a prevailing mantle Cl component in contrast to porphyry copper fluids, an argument also supported by Os isotopes, or could result from differential Cl isotope fractionation processes (e.g. phase separation) in fluids of IOCG and porphyry Cu deposits.

**Keywords** Chlorine isotopes · Strontium isotopes · Iron oxide–copper–gold deposits · Chile · Peru · Brazil

### Introduction

Iron oxide–copper–gold (IOCG) deposits are an economically important style of hydrothermal mineralization, characterised by abundant magnetite and/or hematite, variable amounts of Cu-sulfides, pyrite, gold, and REE, and variably intense and voluminous sodic  $\pm$  calcic and potassic alteration (e.g. Williams et al. 2005). They are formed by hypersaline,  $\text{CO}_2$ - and  $\text{CaCl}_2$ -rich, and S-poor fluids at shallow to mid-crustal levels within cratonic or continental margin settings and, although often occurring within magmatic rocks, they are not always clearly related to igneous activity (e.g. Pollard 2000; Williams et al. 2005).

The origin of the hypersaline fluids associated with IOCG deposits is controversial: either (1) fluids were exsolved from magmas (e.g. Pollard 2000; Sillitoe 2003; Pollard 2006), or (2) brines were derived from evaporites and heated by nearby intrusions (e.g. Barton and Johnson 1996; Haynes 2000). Geological, mineralogical, chemical, and fluid inclusion data, as well as stable isotopes of O, H, and S have been used to support both the magmatic and the evaporitic hypothesis.

In the present study, we report the first chlorine and strontium isotope data and Cl/Br ratios of fluid inclusions of three IOCG deposits (Candelaria, Raúl–Condestable, Sossego), a Cu–Au deposit considered to be a magmatic end member of the IOCG class of deposit (Gameleira; Lindenmayer et al. 2001; Pimentel et al.

Editorial handling: B. Lehmann

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2003), and a magnetite–apatite deposit (El Romeral) from South America. Since IOCG deposits constitute a variant of the iron oxide (Cu–U–Au–REE) deposit class that also includes magnetite–apatite (Kiruna-type) deposits (Hitzman et al. 1992; Hitzman 2000), comparative investigations on these types of mineralization can enhance our understanding of these ore-forming systems and hence improve exploration strategies.

Chlorine is the main metal ligand in the hypersaline fluids of IOCG deposits and behaves more conservatively during fluid–rock interaction than oxygen and hydrogen due to the precipitation of usually lower amounts of chlorine, with respect to oxygen and hydrogen, in mineral phases resulting from the fluid–rock interaction. Therefore, chlorine isotope compositions may be a powerful tool to constrain the origin of brines of IOCG deposits.

In principle, chlorine isotopes are able to discriminate between heavy, depleted mantle-derived [ $\delta^{37}\text{Cl}=3\text{--}7\%$  (Magenheim et al. 1995) where  $\delta^{37}\text{Cl}$  is expressed with respect to seawater], and light, crust-derived ( $\delta^{37}\text{Cl}\sim 0\%$ ; Eggenkamp et al. 1995; Eastoe et al. 2001) chlorine. On the other hand, chlorine isotope compositions of fluids associated with arc magmas are poorly constrained (e.g. Stewart and Spivack 2004). Condensed volcanic gases from various volcanoes display a range of  $\delta^{37}\text{Cl}$  from  $-1$  to  $+4\%$  (Pitcairn 2002), whereas magmatic fluids associated with porphyry copper deposits at convergent margins, i.e. the setting of many IOCG deposits, have  $\delta^{37}\text{Cl}$  values between  $-0.5$  and  $+0.5\%$  (Eastoe and Guilbert 1992). Godon et al. (2000) have measured  $\delta^{37}\text{Cl}$  values of  $-0.8$  to  $+0.1\%$  for hot waters,  $+0.8$  to  $+2.0\%$  for condensates, and of  $0\%$  for an andesite in the Lesser Antilles island arc.

## Geology, geochemistry and sampling of the ore deposits

We have investigated Cretaceous deposits (Candelaria, Raúl–Condestable, El Romeral) that occur in the Peruvian and Chilean Andes in extensional to transpressional continental arc settings (e.g. Marschik and Fontboté 2001; Sillitoe 2003), and Late Archean to Early Proterozoic deposits (Gameleira and Sossego) that occur in the Carajás Mineral Province, Brazil, within rocks of either a continental rift (e.g. Olszewski et al. 1989) or a subduction-related arc environment (Dardenne et al. 1988).

### Candelaria

The Candelaria IOCG deposit (470 Mt at 0.95% Cu, 0.22 g/t Au, and 3.1 g/t Ag at a cutoff grade of 0.4% Cu; Marschik et al. 2000), situated in the Chilean Coastal Cordillera south of the city of Copiapó, is hosted by Early Cretaceous volcanic and volcanoclastic rocks, about 1 km east of the sub-alkaline to alkaline, I-type plutons of the Chilean Coastal Batholith. The latter have  $^{87}\text{Sr}/^{86}\text{Sr}_i$  (0.7031–0.7032),  $\epsilon_{\text{Nd}}$  (1.8–2.8), lead isotope ( $^{206}\text{Pb}/^{204}\text{Pb}=18.43\text{--}18.77$ ,  $^{207}\text{Pb}/^{204}\text{Pb}=15.55\text{--}15.60$ ,

$^{208}\text{Pb}/^{204}\text{Pb}=38.13\text{--}38.40$ ), and  $\delta^{18}\text{O}$  (+6.9 to +8.6 ‰) values, which indicate mixed mantle and crustal sources (Marschik et al. 2003). The  $^{187}\text{Os}/^{188}\text{Os}_i$  values of magmatic magnetite from the plutons range from 0.21 to 0.41, also suggesting mixed mantle and crustal components in these batholiths (Mathur et al. 2002). Re–Os molybdenite ages of  $114.2\pm 0.6$  and  $115.2\pm 0.6$  Ma represent the time of the main Cu–Au mineralization (Mathur et al. 2002).

The results of isotope and microthermometric studies are compatible with the involvement of both magmatic and non-magmatic fluids at Candelaria (Rabbia et al. 1996; Marschik et al. 1997, 2000, 2003; Ullrich et al. 2001; Marschik and Fontboté 2001). Most of the sulfur ( $\delta^{34}\text{S}_{\text{CDT}}$  of sulfides mainly between  $-3.2$  and  $3.1\%$ ) and metals (e.g. initial  $^{187}\text{Os}/^{188}\text{Os}$  of the ore of  $0.36\pm 0.1$ ) were derived from magmatic sources (Marschik and Fontboté 2001; Mathur et al. 2002) during the main ore stage, whereas the late ore stage fluids were characterised by more oxidised and heavier S-fluids ( $\delta^{34}\text{S}_{\text{CDT}}$  of sulfides up to  $+7.2\%$ ) of probable evaporitic origin (Ullrich et al. 2001). Fluid inclusions in quartz associated with chalcopyrite from the main ore stage are hypersaline and  $\text{CO}_2$ -rich and have homogenization temperatures ranging from 328 to  $\geq 396^\circ\text{C}$ . A model in which cooling magmatic–hydrothermal fluids mix with non-magmatic (evaporitic?) fluids can explain the ore formation at Candelaria (e.g. Ullrich et al. 2001; Marschik and Fontboté 2001; Mathur et al. 2002).

We have analysed fluid inclusions in quartz from two samples. Sample PC98014, from level N464 in the former South Pit, is a quartz + sericitised feldspar vein with traces of magnetite and paragenetically later biotite and chalcopyrite, hosted in volcanic or volcanoclastic rocks with pervasive biotite–quartz–magnetite alteration. Sample PC99147, from a drill hole in the former Candelaria North Pit, is a quartz vein containing minor K–feldspar, traces of magnetite and paragenetically later chalcopyrite–pyrite, plus minor chlorite and epidote, hosted by pervasively altered (biotite–magnetite) volcanic–volcanoclastic rocks.

### Raúl–Condestable

The Raúl–Condestable IOCG deposit, with estimated cumulative production and reserves exceeding 32 Mt at 1.7% Cu, 0.3 g/t Au, and 6 g/t Ag, is located 90 km south of Lima (Peru), approximately 5 km from the Pacific coast. The ore consists of chalcopyrite, pyrite, pyrrhotite, and magnetite, and is found as dissemination, pore infill, replacement, and veins in amphibolitised rocks belonging to a Lower Cretaceous volcano–sedimentary sequence. The copper deposit, dated at  $115.2\pm 0.3$  Ma (U–Pb on hydrothermal titanite; de Haller et al. 2006), is located in the core of a dacite–andesite volcanic edifice ( $116.7\pm 0.3$  Ma, U–Pb on zircon). Its age is similar, within error, to that of two tonalite intrusions dated at  $114.8\pm 0.4$  and  $115.1\pm 0.4$  Ma (U–Pb on zircon, de Haller 2006), respectively, which

occur at the core of the mineralised zone (de Haller 2006).

The sulfur isotopic compositions of the sulfides range from  $-5$  to  $+26.3\%$   $\delta^{34}\text{S}_{\text{CDT}}$ , with the majority of the values close to  $+5\%$  (Ripley and Ohmoto 1977; de Haller et al. 2002; de Haller 2006). These data are consistent with sulfur derivation from a magmatic source and from seawater or evaporite (Ripley and Ohmoto 1977; de Haller et al. 2002; de Haller 2006).

Four types of fluid inclusions are found in quartz from stockwork and veins (de Haller 2006): (1) four-phase (liquid–vapour–halite–iron chloride), (2) three-phase (liquid–vapour–halite), (3) two-phase (liquid–vapour) liquid-dominated, and (4) two-phase (liquid–vapour) vapour-dominated. Vapour homogenization temperatures [ $T_{\text{h(v)}}$ ] are similar for the three liquid-dominated inclusion types and range from  $137.2$  to  $231.7^\circ\text{C}$  ( $n=34$ ) with a mean at  $172^\circ\text{C}$ . For most hypersaline inclusions (probably up to  $>50$  to  $60$  wt%  $\text{NaCl}_{\text{eq}}$ ), the final homogenization would occur through daughter salt dissolution (not measured due to leaking of the fluid inclusions). Salinities of the two-phase, liquid-dominated inclusions range from  $11.7$  to  $19.0$  wt%  $\text{NaCl}_{\text{eq}}$  ( $n=4$ ), with eutectic melting between  $-34.6$  and  $-58^\circ\text{C}$ , indicating complex polysaline fluids. These inclusions are interpreted as magmatic fluids trapped in amorphous silica that has been precipitated at high temperature ( $>350^\circ\text{C}$ ) during a lithostatic to hydrostatic pressure change and has subsequently crystallised to fine-grained quartz. The measured  $T_{\text{h(v)}}$  probably records the minimum trapping temperature in quartz and not the true fluid temperature. Similar to the S isotopes, fluid inclusions record a mixing between magmatic and seawater-derived fluids.

We have analysed fluid inclusions in quartz from two massive quartz veins (samples AH-10 and AH-114), one located in the Raúl mine (veta Argentina) and the other (unnamed) close to the Condestable mine.

## El Romeral

El Romeral is one of several magnetite–apatite deposits (e.g. Cerro Negro Norte, Los Algarrobos, Los Colorados) that form the Chilean iron belt. The deposits occur in the Coastal Cordillera between latitudes  $25^\circ$  and  $31^\circ$  S, in a similar setting to Candelaria, and are hosted by Late Palaeozoic metasediments cut by Early Cretaceous andesite porphyry and diorite. The magnetite–apatite mineralization of El Romeral, which has been dated at  $110$  Ma (Munizaga et al. 1985), consists of magnetite intergrown with actinolite and apatite and displays gradational contacts with the enclosing rocks, which also contain magnetite, actinolite, diopside, clinozoisite, scapolite, and tourmaline amongst other mineral phases. The diorite predates magnetite formation, which was accompanied by pervasive actinolitisation at temperatures in the  $475$ – $550^\circ\text{C}$  range. Bookstrom (1977) suggests a hydrothermal–metasomatic model for El Romeral in which the mineralisation was caused by magmatic–hydrothermal fluids derived from the Romeral diorite.

Mathur et al. (2002) measured  $^{187}\text{Os}/^{188}\text{Os}_i$  values (1.2 to 8) in magnetite from three magnetite–apatite deposits of the Chilean iron belt, including El Romeral, which indicate a strong crustal signature. These  $^{187}\text{Os}/^{188}\text{Os}_i$  values contrast with those of the Manto Verde and Candelaria IOCG deposits, which are more primitive (0.20 and 0.36, respectively). Mathur et al. (2002) suggest that magnetite–apatite deposits were formed predominantly from basin-derived, non-magmatic brines, in contrast to the IOCG systems, which contain a significant magmatic–hydrothermal fluid component.

We have analysed fluid inclusions in apatite of an apatite vein cutting magnetite–amphibole (sample CIB99818) in the El Romeral open pit.

## Sossego

The Sossego IOCG deposit (355 Mt with 1.1% Cu, 0.28 g/t Au at a 0.4% cutoff) is located in the Carajás Mineral Province, Pará State, Brazil (Lancaster et al. 2000; Marschik et al. 2003). The latter consists of a Late Archean volcano–sedimentary sequence (Itacaiúnas Supergroup) deposited on high-grade tonalitic and trondhjemitic gneisses of the southern part of the Central Brazilian Shield and intruded by 2.56–2.76 Ga alkaline and calc-alkaline granites and by 1.8–1.9 Ga anorogenic granites (e.g. Machado et al. 1991; Barros et al. 2001). The Sossego deposit consists of two major ore bodies, Sossego Hill and Sequeirinho, which are hosted by intensely sodium(–calcium) metasomatised Archean volcanic and intrusive rocks. The Cu–Au ore occurs mainly as veinlets, veins, and breccias comprising chalcopyrite, magnetite, minor to scarce pyrite, and trace molybdenite. The mineralization is locally associated with elevated concentrations of REE, P, F, Mo, Y, U, Th, Co and Ni. Disturbed  $^{40}\text{Ar}/^{39}\text{Ar}$  spectra of ore-related amphibole point to a minimum alteration age of 2.2–2.3 Ga (Marschik et al. 2003). Sulfur isotope ratios in chalcopyrite ( $\delta^{34}\text{S}_{\text{CDT}}=2.0$  to  $3.8$  ‰) are compatible with sulfur derived from an igneous source. Hypersaline fluid inclusions with salinities of around 30 wt%  $\text{NaCl}_{\text{eq}}$  have been observed in quartz and calcite. The widespread sodic(–calcic) alteration overprinting potassic alteration and oxygen isotope ratios in hydrothermal quartz ( $\delta^{18}\text{O}_{\text{SMOW}}=3.0$  to  $10.2\%$ ), combined with preliminary fluid inclusion homogenization temperatures between  $146$  and  $454^\circ\text{C}$ , suggest a non-magmatic fluid component in the studied portions of the fossil hydrothermal system. Marschik et al. (2003) propose that mixing of a magmatic–hydrothermal fluid with a surficial non-magmatic fluid may be responsible for ore formation at Sossego.

We have analysed fluid inclusions in quartz and calcite from six drill-core samples of the Sossego Hill (XB99216, XB99506) and Sequeirinho (XB99308, XB99449, XB99536, XB99540) ore bodies. Samples XB99308 and XB99536 are quartz from barren quartz veins hosted by a locally foliated amphibole-rich rock with trace disseminated chalcopyrite and by a foliated pervasively biotitised rock,

respectively. Sample XB99540 is quartz from a quartz veinlet with paragenetically later chalcopyrite, hosted by a pervasively altered rock. Sample XB99449 is quartz from a quartz–chalcopyrite–pyrite veinlet in an amphibole-rich host rock with disseminated chalcopyrite. Samples XB99216 and XB99507 are calcites from the ore stage calcite–chalcopyrite veins, in which the chalcopyrite crosscuts both host rock and calcite veins and also occurs interstitial to the calcite.

## Gameleira

The Gameleira deposit is interpreted to be a magmatic end member of the IOCG class of deposit (Lindenmayer et al. 2001; Pimentel et al. 2003). The ore, hosted by the late Archean volcanic rocks of the Itacaiúnas Supergroup in the Carajás mineral province, consists mainly of biotite and sulfide-rich veins and quartz–grunerite–biotite–gold veins. Molybdenite from Gameleira yields an age of  $2614 \pm 14$  Ma, which is considered as a more plausible mineralisation age (Marschik et al. 2005) than the Proterozoic Sm–Nd and Ar–Ar alteration ages (Pimentel et al. 2003). The range of  $\delta^{34}\text{S}_{\text{CDT}}$  values of sulfides ( $+2.0\%$  to  $+4.81\%$ ) is consistent with a magmatic sulfur source (Lindenmayer et al. 2001; Marschik et al. 2002). Vein quartz associated with chalcopyrite and biotite from Gameleira (sample XB 2K001B) yields a  $\delta^{18}\text{O}_{\text{SMOW}}$  of  $+8.8\%$  (Marschik et al. 2002), and carbon and oxygen isotopes in carbonate have  $\delta^{18}\text{O}_{\text{SMOW}}$  from  $+9.1$  to  $+10.0\%$  and  $\delta^{13}\text{C}_{\text{PDB}}$  from  $-8.41$  to  $-9.45\%$  (Lindenmayer et al. 2001). Fluid inclusions in vein quartz, fluorite, and calcite are similar (Ronchi et al. 2000; Lindenmayer et al. 2001) and consist of aqueous two-phase inclusions and hypersaline inclusions co-existing with vapour-rich and aqueous-carbonic fluid inclusions. Two-phase fluid inclusions have salinities between 8 and 21%  $\text{NaCl}_{\text{eq}}$  and homogenization temperatures between 80 and 160°C, whereas halite-saturated fluid inclusions homogenise mainly between 200 and 400°C. Based on the isotope geochemical characteristics, Lindenmayer et al. (2001) and Pimentel et al. (2003) conclude that the ore at Gameleira formed at moderately deep levels from magmatic fluids.

We have analysed fluid inclusions in quartz of two samples (XB2K001A and XB2K001B) from drill hole Poj F69 (see Marschik et al. 2005). Sample XB2K001A is a hydrothermal vein consisting of green biotite, quartz, molybdenite, and chalcopyrite. Sample XB2K001B is a vein of quartz, chalcopyrite, tourmaline, with subordinate green biotite and minor fluorite.

## Analytical methods

Vein slabs of ca.  $1\text{ cm}^3$  were gently crushed in an agate mortar to disaggregate mineral grains, which were then selected under a binocular microscope until an amount of

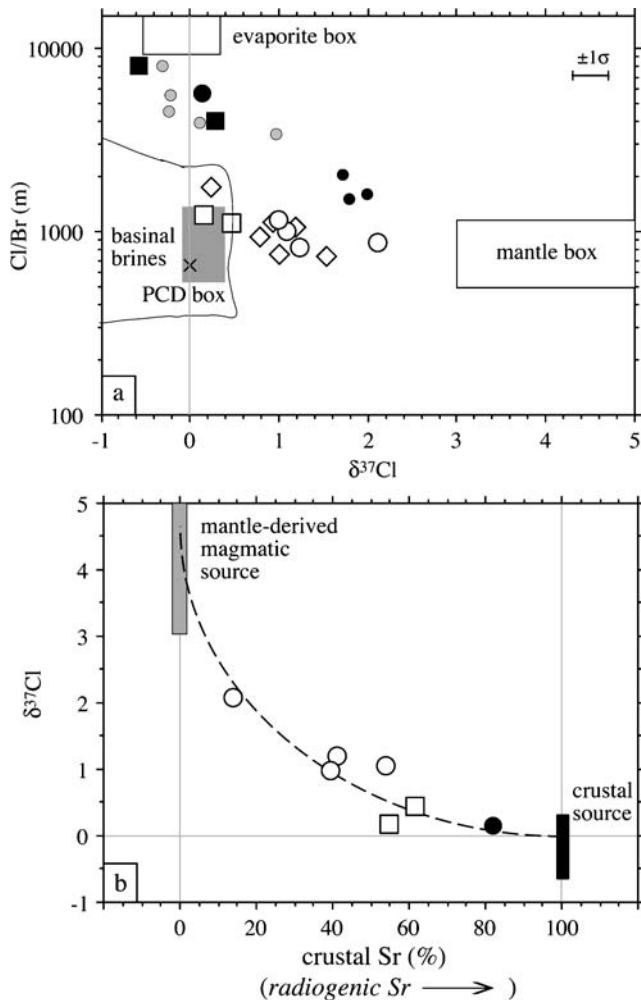
0.5–1 g of pure mineral separate (quartz, calcite or apatite) was obtained. Quartz mineral separates were cleaned by boiling in aqua regia and then boiling several times in deionised water. Calcite and apatite mineral separates were boiled several times in deionised water. Mineral separates were subsequently electro-stripped in deionised water over 7 days to remove ions possibly adsorbed onto mineral surfaces and finally ground in an agate mortar. Five milliliters of deionised water were added and the slurry was filtered through 0.45- $\mu\text{m}$  polyethylene filters. The solutions were analysed for stable chlorine and strontium isotope compositions by thermal ionization mass spectrometry (TIMS) and for  $\text{Cl}^-$  and  $\text{Br}^-$  concentrations by ion chromatography, following the methods of Banks et al. (2000) and Cliff and Meffan-Main (2003) at the Centre for Geochemical Mass Spectrometry of the University of Leeds, UK. Cation concentrations were measured on an Agilent 7500c ICP-MS, also at the School of Earth and Environment of the University of Leeds.

Although slightly less precise than the dual inlet stable isotope ratio mass spectrometry (SIRMS) analyses (Rosenbaum et al. 2000), chlorine isotope measurements by TIMS require as little as a few micrograms of chlorine, compared to the approximately 1-mg Cl required by SIRMS, thus increasing the probability of analysing a representative fluid population. A consistent amount of 10  $\mu\text{g}$  of Cl was loaded onto tantalum filaments together with a graphite solution, and the isotopic composition was measured on a MM30 thermal ionization mass spectrometer at the School of Earth and Environment (University of Leeds) as the ratio of masses 303 and 301 ( $^{133}\text{Cs}_2^{37}\text{Cl}^+$  and  $^{133}\text{Cs}_2^{35}\text{Cl}^+$ , respectively; e.g. Magenheimer et al. 1994). The  $\delta^{37}\text{Cl}$  values were calculated with respect to the average 303/301 value of 74 replicates of Sargasso seawater (GPS1) during the analysis period, which were externally reproducible within 0.2‰ ( $1\sigma$ ). Control on the reproducibility of the data was performed by duplicate or triplicate analyses on different aliquots of all samples and on the Sargasso seawater (GPS1) standard. Strontium of the inclusion fluids of the Cretaceous ore deposits (Candelaria, Raúl–Condestable, El Romeral) was separated by extraction exchange chromatography on Eichrom Sr-spec resin and Sr isotope ratios were measured on a Finnigan TRITON thermal ionization mass spectrometer at the School of Earth and Environment after loading the samples onto tungsten filaments with a tantalum chloride activator. Raw strontium isotope ratios of the inclusion fluids were corrected for the time-integrated decay of  $^{87}\text{Rb}$  to  $^{87}\text{Sr}$  using Rb and Sr concentrations measured on the same fluids with the Agilent 7500c ICP-MS. Time-integrated corrections were relatively small (between 0.3 and 0.9‰ of the raw values) due to low Rb/Sr of the fluid inclusions. Analyses of the SRM987 international standard on 1–10 ng Sr loads averaged  $0.710250 \pm 0.000003$ .



## Results

Figure 1a shows the inclusion fluid compositions of samples from the investigated ore deposits in the Cl/Br vs  $\delta^{37}\text{Cl}$  space together with the compositional fields of



**Fig. 1** a Cl/Br (molar) vs  $\delta^{37}\text{Cl}$  diagram of fluids from the investigated deposits. The brine field is from Eastoe et al. (2001), the field of mantle-derived magmatic fluids is from Magenheimer et al. (1995) and Johnson et al. (2000), the halite field is from Eggenkamp et al. (1995), and the porphyry copper fluid (PCD) field is from Eastoe and Guilbert (1992) and Kendrick et al. (2001). b  $\delta^{37}\text{Cl}$  vs crustal Sr (%) diagram for the fluids of Candelaria, Raül-Condostable, and El Romeral deposits. The crustal Sr (%) contribution has been calculated using the mixing equations  $X_{\text{magmatic}} \times R_{\text{magmatic}} + X_{\text{crustal}} \times R_{\text{crustal}} = R_{\text{measured}}$  and  $X_{\text{magmatic}} + X_{\text{crustal}} = 1$ .  $X$  represents the percentage of contribution from the mantle-derived magmatic or crustal source,  $R_{\text{magmatic}}$  is the  $^{87}\text{Sr}/^{86}\text{Sr}$  values reported in Table 1 for the magmatic rocks associated with the various deposits, and  $R_{\text{crustal}}$  is  $^{87}\text{Sr}/^{86}\text{Sr} = 0.7073$  taken as the average value of an evaporitic source during the Cretaceous–Jurassic (McArthur et al. 2001)

IOCG deposits	Magnetite-apatite and "magmatic" IOCG deposits	Other fluids
◇ Sossego	■ Gameleira	× seawater
□ Candelaria	● El Romeral	○ Capitan Pluton
○ Raul		● SW-England Pluton

potential reservoirs (mantle, basinal brines, evaporites) and of fluids of porphyry copper deposits. The fluid inclusion data cluster into two groups: one comprising the IOCG deposits (Raül-Condostable, Candelaria, Sossego) characterised by  $\delta^{37}\text{Cl}$  values between 0 and 2.1‰ and Cl/Br between 800 and 1,500, and the other comprising the other variants of the iron oxide (Cu–U–Au–REE) class (Gameleira and El Romeral), characterised by  $\delta^{37}\text{Cl}$  values between  $-0.6$  and  $+0.3$ ‰ and Cl/Br ratios  $\geq 4,000$ . The first group defines an inversely correlated ( $R = -0.67$ ) array between magmatic mantle-derived fluids and basinal brines. The second group falls at the high Cl/Br end of an inversely correlated trend ( $R = -0.89$ ), including also magmatic fluid inclusions of the Capitan Pluton (Mexico) and SW-England Pluton (Banks et al. 2000), between magmatic mantle-derived fluids and evaporites. The Gameleira deposit is also distinctive from the IOCG and the magnetite–apatite deposits for the high F/Cl ratio of its fluid (Table 1).

The initial strontium isotope compositions of El Romeral, Raül-Condostable and Candelaria fluids are significantly more radiogenic ( $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.7065, 0.7051–0.7062, 0.7053–0.7056$ , respectively; Table 1) than those of the associated magmatic rocks ( $^{87}\text{Sr}/^{86}\text{Sr}_i \sim 0.703–0.704, 0.7042, 0.7031$ , respectively; Table 1). This implies the presence of a radiogenic, non-magmatic component of Sr. Strontium contributions from a Jurassic to Cretaceous marine or evaporite source of Sr to the fluids of El Romeral, Raül-Condostable and Candelaria, calculated with respect to the corresponding magmatic strontium (crustal Sr in Fig. 1b), are significantly correlated with  $\delta^{37}\text{Cl}$  values (Fig. 1b).

## Sources of chlorine and strontium in inclusion fluids

The low amount of chlorine required for Cl isotopic analyses by TIMS has allowed us to analyse selected small sample portions where the fluid composition is dominated by the hypersaline brine. Despite this, we cannot exclude sampling of mixed fluid populations even in the relatively small volumes of sample used. Therefore, the isotopic and geochemical data of the inclusion fluids here presented reflect a time-integrated average composition of the fluid(s) involved in the formation processes of the investigated deposits, compared to S, O and C isotope data, which are obtained on minerals bound to a specific stage of the ore event.

The inclusion fluid data of Gameleira and El Romeral plot close to the evaporite box in Fig. 1a, at the high Cl/Br end of the trend defined also by fluids of the Capitan and SW-England Plutons. The latter were interpreted by Banks et al. (2000) to define a mixing trend between mantle and evaporitic chlorine sources, in which chlorine from the Capitan Pluton was derived dominantly from evaporites, whereas the SW-England Pluton contained a more pristine mantle-derived chlorine component. The near 0‰  $\delta^{37}\text{Cl}$  and high Cl/Br values of the El Romeral and Gameleira fluids are compatible with a chlorine component derived

**Table 1** Cl/Br and F/Cl molar ratios, Cl, Br, F, Rb, and Sr concentrations,  $\delta^{37}\text{Cl}$  and Sr isotope compositions of fluids of the investigated samples

Sample	Mineral/ rock	Deposit	Cl/Br (mol)	F/Cl (mol)	Cl (ppb)	Br (ppb)	F (ppb)	$\delta^{37}\text{Cl}$	$^{87}\text{Sr}/^{86}\text{Sr}$	Rb (ppb)	Sr (ppb)	$^{87}\text{Sr}/^{86}\text{Sr}_i^a$
CIB99818	Apatite	El Romeral	5,707	bdl	7,344	3	bdl	+0.16	0.70716	2.6	18	0.70648
B2K001A	Quartz	Gameleira	4,071	0.9708	9,031	5	4,698	+0.28	–	–	–	–
B2K001B	Quartz	Gameleira	8,196	0.8214	10,910	3	4,802	–0.58	–	–	–	–
PC98-014	Quartz	Candelaria	1,121	0.0004	36,738	74	8	+0.46	0.70599	6	83	0.70564
PC99-147	Quartz	Candelaria	1,244	0.0001	85,942	156	5	+0.20	0.70584	14	134	0.70535
AH10	Quartz	Raul-Cond.	839	0.0003	34,551	93	5	+1.23	0.70605	4.6	100	0.70583
AH-114-1	Quartz	Raul-Cond.	1,011	0.0003	55,163	123	10	+1.08	0.70645	12	186	0.70615
AH-114-2a	Quartz	Raul-Cond.	1,170	0.0004	71,942	139	15	+0.99	0.70613	17	231	0.70578
AH-114-2b	Quartz	Raul-Cond.	891	0.0007	47,930	121	17	+2.10	0.70573	20	163	0.70515
B99216	Calcite	Sossego	932	bdl	27,282	66	bdl	+0.78	–	–	–	–
B99308	Quartz	Sossego	748	0.0332	82,470	248	1,467	+1.01	–	–	–	–
B99449	Quartz	Sossego	1,064	0.0038	99,141	210	201	+1.18	–	–	–	–
B99506	Calcite	Sossego	742	bdl	27,985	85	bdl	+1.53	–	–	–	–
B99536	Quartz	Sossego	1,131	0.0014	92,913	185	72	+0.94	–	–	–	–
B99540	Quartz	Sossego	1,786	bdl	188,260	237	bdl	+0.25	–	–	–	–
–	Tonalite	Raul-Cond.	–	–	–	–	–	–	–	–	–	0.70418±16 <sup>b</sup>
–	Composite pluton	Candelaria	–	–	–	–	–	–	–	–	–	0.70316±6 <sup>c</sup>
–	Diorite	El Romeral	–	–	–	–	–	–	–	–	–	0.703–0.704 <sup>d</sup>

Cation and anion concentrations are measured on diluted solutions and should not be taken as absolute values of concentrations in inclusion fluids. Dashes denote unanalysed samples

*bdl* Below detection limit

<sup>a</sup>Calculated at 115 Ma

<sup>b</sup>Average ( $\pm 1\sigma$ ) of the data from five samples of Tonalite 1 genetically associated with the mineralization (this study)

<sup>c</sup>Average ( $\pm 1\sigma$ ) of the data from nine samples of the Copiapó plutonic complex genetically associated with the mineralization (from Marschik et al. 2003)

<sup>d</sup>Inferred from data in McNutt et al. (1975)

dominantly from evaporites or from brines equilibrated with evaporites ( $\delta^{37}\text{Cl}\sim 0\text{‰}$ ; Cl/Br $\gg 50,000$ ). However, because evaporites usually have Cl/Br ratios and Cl concentrations several orders of magnitude higher than those of magmatic fluids, a magmatic fluid contribution in these deposits cannot be ruled out since it would be masked by as little as  $<5$  wt% of an evaporite contribution, depending on the actual Cl/Br value of the evaporitic source. The host sequence of El Romeral contains evaporites providing geological support to the above scenario. The evaporitic Cl and Cl/Br signatures of El Romeral fluids are also consistent with the crustal Os signatures of the ores, which may be the result of precipitation from a basin-derived, non-magmatic fluid (Mathur et al. 2002). In contrast, unless there are undiscovered evaporites in the host sequence or they have been obliterated by metamorphism, we cannot explain the evaporitic Cl/Br signature of the Gameleira fluid, which is at odds with the magmatic signature indicated by O, C and S isotopes, as well as by the high F/Cl values (although the mass balance argument noted above could explain this).

The fluid data of the Candelaria, Raúl-Condostable, and Sossego IOCG deposits define an inversely correlated trend in the Cl/Br vs  $\delta^{37}\text{Cl}$  space that is different from the trend defined by the Capitan Pluton, SW-England Pluton, Gameleira and El Romeral fluids and suggests mixing

between magmatic mantle-derived fluids and basinal brines (Fig. 1a).

Support to mixing between a mantle-derived magmatic and a crustal source in the fluids of the Cretaceous IOCG (Candelaria, Raúl-Condostable) and magnetite-apatite (El Romeral) deposits is provided by the fact that all of them plot along the same mixing trend in the  $\delta^{37}\text{Cl}$  vs Sr isotopic compositions space (Fig. 1b). This trend indicates mixing between a low radiogenic Sr and  $^{37}\text{Cl}$ -rich magmatic fluid and a radiogenic Sr and  $^{37}\text{Cl}$ -poor crustal source, which, according to Cl/Br values, is a basinal brine at Candelaria and Raúl-Condostable and evaporite at El Romeral. The fact that the Sr isotope compositions of the inclusion fluids of Candelaria, Raúl-Condostable, and El Romeral are significantly more radiogenic than those of the corresponding host magmatic rocks (Table 1) suggests that the magmatic fluids involved in the formation of these deposits have mixed with basinal brines or have leached evaporites after their exsolution from the magma.

The relatively heavy chlorine isotope signatures ( $\delta^{37}\text{Cl}=+0.2\text{--}2.1\text{‰}$ ) of the investigated IOCG deposits (Candelaria, Raúl-Condostable, Sossego) contrast with the  $\delta^{37}\text{Cl}=0\pm 0.5\text{‰}$  values of porphyry copper fluids (Fig. 1a). This could indicate a greater contribution from a mantle-derived chlorine component in IOCG deposits compared with porphyry copper deposits. A similar relationship, which indicates a significantly higher

mantle Os component in IOCG deposits than in the porphyry Cu and magnetite–apatite deposits of the Central Andes (Fig. 2), is implied by the Os isotope data of the ore minerals from IOCG, porphyry Cu, and magnetite–apatite deposits (Mathur et al. 2002). Alternatively, the high  $\delta^{37}\text{Cl}$  values could indicate a chlorine isotope fractionation process in IOCG fluids leading to  $\delta^{37}\text{Cl} > 0$  (e.g. Lüders et al. 2002) before mixing with the  $\delta^{37}\text{Cl} \sim 0\%$  basinal brine, which is absent in porphyry–Cu fluids ( $\delta^{37}\text{Cl} = 0$ ).

## Conclusions

We have presented the first stable Cl isotope data, combined with Cl/Br ratios and radiogenic Sr isotopes, of selected deposits of the iron oxide (Cu–U–Au–REE) class in South America. Our results indicate that the fluids of the IOCG deposits of Candelaria, Raúl–Condestable, and Sossego are distinctive from those of the other variants in the iron oxide (Cu–U–Au–REE) class (Gameleira, El Romeral) concerning Cl/Br and, to some extent, also  $\delta^{37}\text{Cl}$  values. The fluids of Gameleira, a deposit classified as a magmatic end member of the IOCG class of deposit (Lindenmayer et al. 2001; Pimentel et al. 2003), and of the magnetite–apatite deposit of El Romeral are characterised by high molar Cl/Br ( $\geq 4,000$ ), near 0‰  $\delta^{37}\text{Cl}$  values, and, at least at El Romeral for which Sr isotope data are available, high crustal Sr contributions ( $> 80\%$ ). These characteristics indicate a dominantly evaporitic Cl and Sr contribution in these deposits. However, due to the significantly higher Cl and Sr contents in evaporites than in magmatic fluids, this does not exclude the possible participation of magmatic

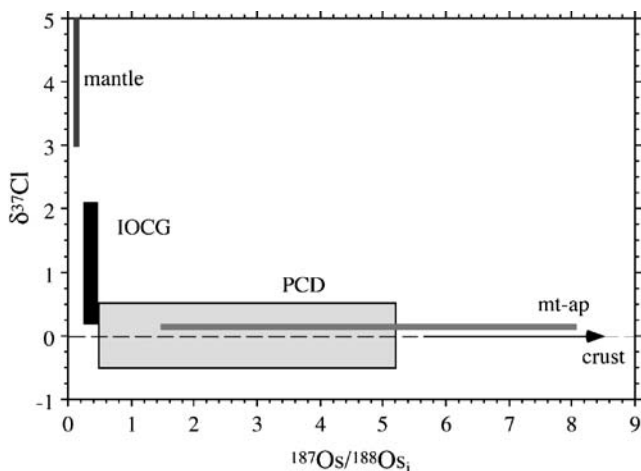
fluids in forming these deposits, which other stable isotope systematics (S, O, C) suggest to be dominant at Gameleira.

In contrast, the fluids of the IOCG deposits (Candelaria, Raúl–Condestable, Sossego) have Cl/Br (800–1,500),  $\delta^{37}\text{Cl}$  (+0.2 to +2.1‰) and Sr isotope values that indicate mixing of a mantle-derived magmatic fluid with basinal brines. This result, based on different stable and radiogenic isotope systematics, reinforces the conclusions of previous studies, which indicated a mixed source model for these deposits. The investigated IOCG deposits (Candelaria, Raúl–Condestable, Sossego) are characterised by positive  $\delta^{37}\text{Cl}$  values (+0.2 to +2.1‰), thus differing from the near 0‰  $\delta^{37}\text{Cl}$  values of porphyry copper deposit fluids, which have nevertheless a similar range of Cl/Br values. These positive  $\delta^{37}\text{Cl}$  values may result from a higher mantle chlorine contribution (an argument that would also be supported by Os isotope data) or from fractionation during hydrothermal processes (e.g. phase separation) before mixing with the basinal brines.

**Acknowledgements** A previous version of this manuscript has benefited from the critical reviews by Mark Barton and Peter Pollard. RM thanks Phelps Dodge Exploration Corp. and C.C. Minera Candelaria for their support. We thank V. Lüders for profitable discussions and Bernd Lehmann for editorial handling and useful comments. This work was supported by NERC through JIF award NER/H/S/2000/00853.

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**Fig. 2**  $\delta^{37}\text{Cl}$  vs  $^{187}\text{Os}/^{188}\text{Os}_i$  plot for IOCG, magnetite–apatite (*mt-ap*), and porphyry copper (*PCD*) deposits of the Andes. The fields are based on available  $\delta^{37}\text{Cl}$  values from this study and from Eastoe and Guilbert (1992) and on Os isotope values of Mathur et al. (2000) and Mathur et al. (2002). Because a limited number of deposits define these fields and often combined data of Cl and Os isotopes on the same deposit are not yet available, the fields drawn should be considered as provisional. IOCG Iron oxide–Cu–Au deposits, PCD porphyry copper deposits, *mt-ap* magnetite–apatite deposits



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