Miner Deposita (2009) 44:719–722
DOI 10.1007/s00126-009-0235-5

NOTE

Iodine-rich waters involved in supergene enrichment of the Mantos de la Luna argentiferous copper deposit, Atacama Desert, Chile

Martin Reich · Carlos Palacios · Macarena Alvear · Eion M. Cameron · Matthew I. Leybourne · Artur Deditius

Received: 30 January 2009 / Accepted: 4 March 2009 / Published online: 17 March 2009

Abstract Recent studies have suggested the involvement of highly saline deep formation waters that modified preexisting Cu assemblages to form atacamite during supergene oxidation of Cu deposits in the Atacama region. In this report, we document the occurrence of (Ag–I) inclusions hosted by supergene chalcocite from Mantos de la Luna, an argentiferous Upper Jurassic stratabound Cu deposit in the Coastal Range of northern Chile. The presence of this unusual mineral assemblage indicates that iodargyrite precipitated from reducing iodine-rich waters, suggesting that the fluids involved in supergene enrichment of Cu deposits in the Coastal Range were more complex than previously thought. This suggests the prevalence of hyperarid conditions during the latest stages of supergene enrichment of the Mantos de la Luna Cu deposit in the Atacama region, supporting the notion that supergene enrichment processes in hyperarid areas are dynamic in nature and do not exclusively require the presence of meteoric water.

Editorial handling: B. Lehmann

M. Reich (✉) · C. Palacios · M. Alvear
Departamento de Geología,
Facultad de Ciencias Físicas y Matemáticas,
Universidad de Chile,
Santiago, Chile
e-mail: mreich@ing.uchile.cl

E. M. Cameron
Eion Cameron Geochemical Inc.,
865 Spruce Ridge Road,
Carp, Ontario K0A 1L0, Canada

M. I. Leybourne
Ocean Exploration, GNS Science,
P.O. Box 30-368, Lower Hutt, New Zealand

A. Deditius
Department of Geological Sciences, University of Michigan,
Ann Arbor, MI, USA

Present address:
A. Deditius
CSIRO Division of Exploration and Mining,
26 Dick Perry Avenue,
Kensington WA 6151, Australia

Introduction

Argentiferous stratabound Cu ore deposits are typically found in volcano-sedimentary formations of Mesozoic age in the Coastal Range of the Atacama Desert, northern Chile (Fig. 1). These high-grade, low-tonnage deposits normally host 1–40 million metric tons of ore with 1–4% Cu and up to 30 g per ton of Ag (Maksaev et al. 2007). One of the most enduring questions about these deposits is the mineralogical form of Ag, as well as the time-scale relations between Ag precipitation and deposition of Cu ore. Recent studies show that this "invisible" Ag is present in solid solution, as well as in micro- to nanoinclusions of Ag minerals in the Cu and Cu–Fe sulfide hosts, although little knowledge exists about the nature of the process(es) that concentrate Ag (Reich et al. 2008a).

In this report, we document the occurrence of inclusions of a (Ag,I)-rich mineral, most probably iodargyrite, in supergene chalcocite from the Mantos de la Luna argentiferous stratabound Cu deposit in the Coastal Range of northern Chile. Iodargyrite (AgI) is highly insoluble, and its occurrence is restricted to Ag-bearing deposits in extremely arid environments such as desert areas of Nevada, Arizona, New Mexico, Kazakhstan, Australia, and Chile (Boyle

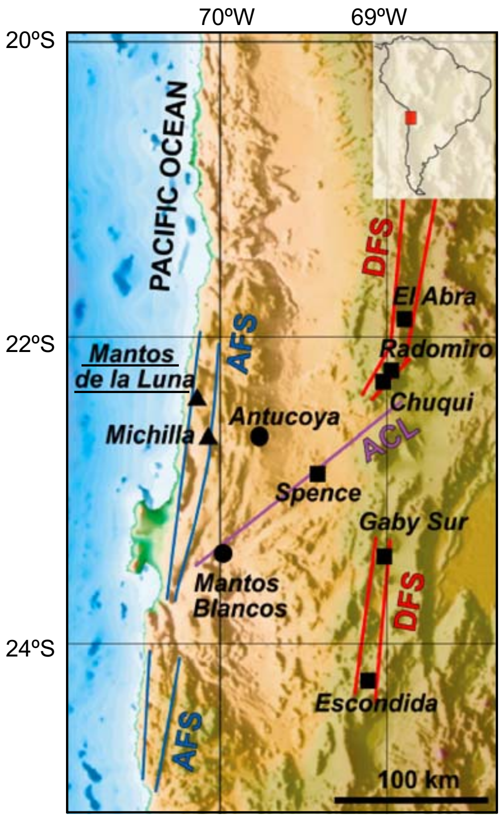

Fig. 1 Map of the Atacama Desert in northern Chile showing the distribution of Cu deposits. *Triangles*: stratabound Cu deposits, including Mantos de la Luna; *circles*: porphyry-like Cu deposits; *squares*: porphyry Cu deposits. The major structural features shown are the Atacama Fault System (*AFS*), the Antofagasta-Calama Lineament (*ACL*), and the Domeyko Fault System (*DFS*)

1997; Millsteed 1998). We explore the close association of iodargyrite and chalcocite in supergene zones and provide new constraints on the nature and source of the waters involved in supergene enrichment of Cu deposits in the Atacama region.

Geologic background, materials, and methods

Most of the stratabound Cu–(Ag) deposits in northern Chile are hosted by Jurassic basaltic to andesitic lavas from the La Negra Formation, and are commonly associated with unmineralized gabbroic to andesitic intrusive bodies interpreted as feeder conduits of Jurassic volcanism (Maksaev et al. 2007). The stratiform deposits occur as numerous tabular orebodies or "mantos" in the La Negra Formation, and primary Cu mineralization occurs preferentially in the porous parts of the host rocks such as amygdale fillings, veinlets, and disseminations, and they generally exhibit epigenetic features (Kojima et al. 2003). The mineral paragenesis in these deposits is relatively simple. The hypogene sulfide mineralization consists of chalcocite, digenite, bornite, and chalcopyrite that can contain up to ~2,000 ppm of "invisible" Ag (Kojima et al. 2003; Reich et al. 2008a). Supergene enrichment of these minerals has produced secondary, Ag-bearing chalcocite and covellite, and later oxidation has led to the replacement of hypogene and supergene sulfides by Cu-oxide minerals such as atacamite and chrysocolla.

Silver-bearing chalcocite samples were taken from the supergene enrichment zone of the argentiferous Mantos de la Luna deposit (Fig. 1). This deposit, located 30 km south of Tocopilla, consists of three small orebodies (Bloques Norte, Central, and Sur) that occur within a monoclinal volcanic sequence (N10°E, 30°E dip). The orebodies are delimited by the NWW- and EW-trending Sur and Albornoz faults, respectively (Kojima et al. 2003). At Mantos de la Luna, Cu mineralization occurs preferentially in the lower levels of amygdaloidal and porphyritic horizons. Mineral paragenesis is simple and composed exclusively of Ag-bearing supergene chalcocite (digenite), atacamite, and chrysocolla. The fine-grained aggregates of chalcocite and minor covellite occur disseminated and in veinlets, and are locally replaced by the oxide alteration assemblage (atacamite and chrysocolla). In contrast to other stratabound Cu deposits of the Coastal Range (e.g. Susana-Lince and Buena Esperanza), hypogene sulfides are not observed in this deposit, and extraction is exclusively reduced to the thick (~300 m) supergene/oxide zone.

Chalcocite samples from Mantos de la Luna were analyzed using a Cameca SX-100 electron microbe analyzer (EMPA) at electron microprobe analytical laboratory of the University of Michigan. The analytical conditions were accelerating voltage of 20 kV and a beam current of 20–40 nA. No beam-induced damage was observed during the sulfide analysis.

Results

EMPA observations reveal the presence of discrete, micron-sized inclusions of a Ag iodide mineral in 10 out of 13 supergene chalcocite samples analyzed. Figure 2a shows a backscattered electron image of a representative chalcocite grain containing two inclusions of 1 and 10 µm size, identified as iodargyrite by means of wavelength dispersive spectroscopy (WDS) elemental mapping (Fig. 2b–e, sample ML-1-08, see caption for sample details). The small size and the beam sensitivity of the Ag–I inclusions precluded the precise description of its chemical formula. The Ag concentrations in the inclusions vary from 1.0 to 67.6 wt%, and they are contaminated by Cu and S from chalcocite. However, the Ag and I elemental maps strongly correlate with the inclusions, whereas the WDS maps of Cu and S

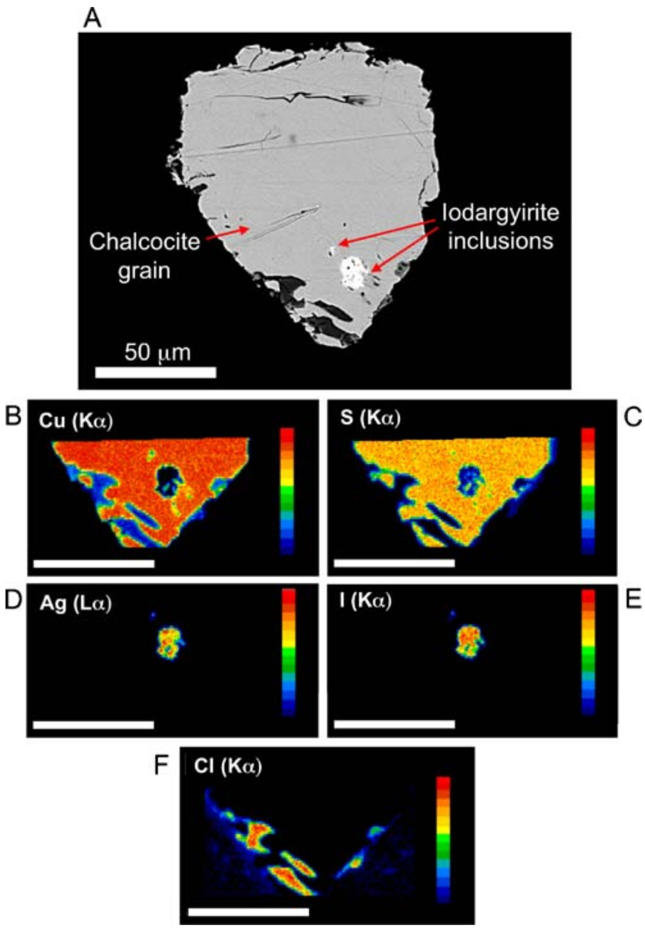

Fig. 2 **a** Back-scattered electron image of a representative chalcocite grain containing inclusions of iodargyrite (AgI), 1 and 10 µm in size (sample ML-1-08). **b**–**f** Elemental maps show the spatial distribution of Cu, S, Ag, I, and Cl in the selected area. The *color scale* indicates the relative concentration of the element analyzed (*red*: high, *blue*: low). The sample was taken from the southern wall of the main pit ("Rajo Principal") at the Mantos de la Luna deposit and corresponds to a N3°S-trending subvertical chalcocite vein occurring in the supergene enrichment zone (sample coordinates and altitude: 22°15′19″S/70°11′29″W, *h*=1027 m above sea level)

correlate well with the chalcocite sulfide host (formula $Cu_{1.85}S$, digenite, as determined by EMPA analysis) (Fig. 2a–e). The chalcocite (digenite) grain shows evidence of supergene oxidation to Cu-chloride [probably, atacamite, $Cu_2Cl(OH)_3$] in its rim, as noted in the WDS maps (Fig. 2a, f). No Ag-chloride or Ag-sulfide was observed in the analyzed samples.

Involvement of iodine-rich waters during supergene enrichment

The occurrence of iodargyrite inclusions in supergene chalcocite suggests the involvement of iodine-rich waters during supergene enrichment at the Mantos de la Luna Cu deposit. Iodine concentrations are typically low in the Earth's crust, and its distribution is dominated by accumulation in marine sediments (Muramatsu and Wedepohl 1998; Muramatsu et al. 2001). Iodine has concentrations in the low parts-per-billion range in igneous and metamorphic rocks, and its concentrations in fresh water and seawater are also exceedingly low, less than 50 ppb (Moran et al. 1999). However, iodine is strongly enriched in deep brines and pore waters, commonly exceeding 100 ppm (Muramatsu et al. 2001).

At the Spence porphyry Cu deposit in the Atacama Desert, Leybourne and Cameron (2006) have reported substantially higher concentrations of iodine in saline groundwaters (up to 65 ppm I) than in the meteoric waters (<1 to 7.3 ppm I). Iodine, along with Cl and Br, has been detected earlier in anomalies developed in gravels above Cu deposits in the Atacama Desert, including Cu deposits from the Coastal Range, suggesting the involvement of deep formation waters that have been pumped to the surface along active faults and/or fractures during seismic events (Cameron et al. 2002; Palacios et al. 2005). A similar source for iodine has been suggested for the iodine components of nitrate deposits occurring along the eastern slope of the Coastal Range in the Atacama Desert (Fehn et al. 2007). The ^{129}I isotopic signature of nitrate salts indicates that iodine might be derived from the release of iodine-rich fore-arc fluids along the continental margin (Fehn et al. 2007).

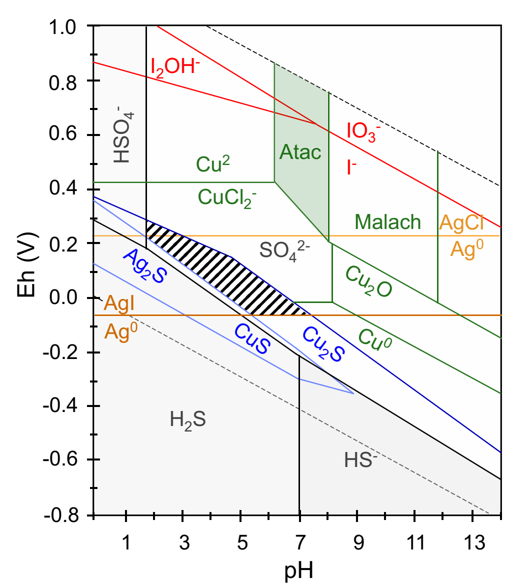

Fig. 3 Eh–pH stability diagram for Cu and Ag minerals and dissolved species of Cu, Ag, S, Cl, CO_2, and I, at 25 °C and 1 bar. *Dashed lines* show the stability field of water. The *hatched area* shows the stability field of the iodargyrite + chalcocite mineral association. The *green-colored area* shows the stability field of atacamite. Data based on McNeil and Little (1992), and Welham et al. (1993)

Recent studies by Cameron et al. (2007) and Reich et al. (2008b) have suggested the involvement of highly saline, deep-formation waters that modified preexisting Cu assemblages to form atacamite during supergene oxidation of Cu deposits in the Atacama Desert. Chlorine-36 and U-series disequilibrium ages in atacamite/gypsum assemblages indicate that the formation of these products of supergene oxidation is an ongoing process that has occurred intermittently since the onset of modern hyper-aridity (Reich et al. 2008b, 2009). In the context of this model, we propose that saline, iodine-rich deep formation waters and/or fore-arc fluids, forced to the surface by seismic pumping along faults and fractures, passed up through the argentiferous Cu deposit of Mantos de la Luna, leaching preexisting Cu sulfides. After each pulse, Cu hydroxy-chlorides such as atacamite formed under oxidizing conditions in the upper parts of the system by replacement of primary and secondary Cu assemblages (Fig. 3, green field). The resulting chlorine-depleted, iodine-rich solutions infiltrated and leached Cu and Ag from the previous generations of Cu assemblages (e.g., formed during the main peak of supergene enrichment, 14–21 Ma, Alpers and Brimhall 1988; Sillitoe and McKee 1996; Mote et al. 2001), to finally precipitate iodargyrite under near-neutral to acidic, moderately reducing conditions (Fig. 3, hatched field).

Considering the fact that the occurrence of iodargyrite is restricted to extremely arid environments (Boyle 1997), our observations strongly suggest the prevalence of hyperarid conditions during the latest stages of supergene enrichment of the Mantos de la Luna argentiferous Cu deposit in northern Chile. This suggests that supergene enrichment processes of Cu deposits in the hyperarid Atacama Desert are dynamic in nature and do not exclusively require the presence of meteoric water. Further studies are needed not only to address the isotopic signature (and age) of iodine-rich waters involved in supergene enrichment of these deposits, but also to constrain the origin of iodine in the extensive nitrate deposits occurring in the eastern flank of the Coastal Range.

Acknowledgements Support for this study was received from FONDECYT grant # 11070088 to Martin Reich. We acknowledge Larry Meinert, Chris Gammons, and John Muntean for suggestions that helped improve an earlier version of this manuscript. We thank Jorge Pizarro at *Compañía Minera Mantos de la Luna* for logistical assistance in the field and Carl Henderson at the University of Michigan for his valuable help with EMPA measurements. Review and editorial comments by Bernd Lehmann are greatly appreciated.

References

Alpers CN, Brimhall GH (1988) Middle Miocene climatic change in the Atacama Desert, northern Chile: evidence from supergene mineralization at La Escondida. Geol Soc Am Bull 100:1640–1656

Boyle DR (1997) Iodargvrite as an indicator of arid climatic conditions and its association with gold-bearing glacial tills of the Chibougamau-Chapais area, Quebec. Can Mineral 35:23–34

Cameron EM, Leybourne MI, Kelley DL (2002) Exploring for deeply covered mineral deposits: Formation of geochemical anomalies in northern Chile by earthquake-induced surface flooding of mineralized groundwaters. Geology 30:1007–1010

Cameron EM, Leybourne MI, Palacios C (2007) Atacamite in the oxide zone of copper deposits in northern Chile: involvement of deep formation waters? Miner Depos 42:205–218

Fehn U, Moran JE, Snyder GT, Muramatsu Y (2007) The initial ^{129}I/I ratio and the presence of 'old' iodine in continental margins. Nucl Instrum Methods B 259:496–502

Kojima S, Astudillo J, Rojo J, Trista D, Hayashi K (2003) Ore mineralogy, fluid inclusion, and stable isotopic characteristics of stratiform copper deposits in the coastal Cordillera of northern Chile. Miner Depos 38:208–216

Leybourne MI, Cameron EM (2006) Composition of groundwaters associated with porphyry-Cu deposits, Atacama Desert, Chile: Elemental and isotopic constraints on water sources and water-rock reactions. Geochim Cosmochim Acta 70:1616–1635

Maksaev V, Townley B, Palacios C, Camus F (2007) Metallic ore deposits. In: Moreno T, Gibbons W (eds) The geology of Chile. The Geological Society, London, pp 179–199

McNeil MB, Little BJ (1992) Corrosion mechanisms for copper and silver objects in near-surface environments. J Am Inst Conserv 31:355–366

Millsteed PW (1998) Marshite-miersite solid solution and iodargyrite from Broken Hills, New South Wales, Australia. Mineral Mag 62:471–475

Moran JE, Oktay S, Santschi PH, Schink DR (1999) Atmospheric dispersal of iodine from nuclear fuel reprocessing facilities. Environ Sci Technol 33:2536–2542

Mote TI, Brimhall GH, Tidy-Finch E, Muller G, Carrasco P (2001) Application of mass-balance modeling of sources, pathways, and sinks of supergene enrichment to exploration and discovery of the Quebrada Turquesa exotic copper orebody, El Salvador district, Chile. Econ Geol 96:367–386

Muramatsu Y, Wedepohl KH (1998) The distribution of iodine in the Earth's crust. Chem Geol 147:201–216

Muramatsu Y, Fehn U, Yoshida S (2001) Recycling of iodine in fore-arc areas: evidence from the iodine brines in Chiba, Japan. Earth Planet Sci Lett 192:583–593

Palacios C, Guerra N, Townley B, Lahsen A, Parada M (2005) Copper geochemistry in salt from evaporite soils, Coastal Range of the Atacama Desert, northern Chile: an exploration tool for blind Cu deposits. Geochem Explor Environ Anal 5:371–378

Reich M, Chryssoulis S, Palacios C (2008a) Nanoscale mineralogy of Ag in sulfides from Cu deposits in northern Chile: Implications for ore genesis, exploration, and metallurgical recovery. Geochim Cosmochim Acta 72(12):A783

Reich M, Palacios C, Parada MA, Fehn U, Cameron EM, Leybourne MI, Zúñiga A (2008b) Atacamite formation by deep saline waters in copper deposits from the Atacama Desert, Chile: evidence from fluid inclusions, groundwater geochemistry, TEM, and ^{36}Cl data. Miner Depos 43:663–675

Reich M, Palacios C, Vargas G, Luo S, Cameron EM, Leybourne MI, Parada MA, Zúñiga A, You CF (2009) Supergene enrichment of copper deposits since the onset of modern hyperaridity in the Atacama Desert, Chile. Miner Depos (in press) DOI: 10.1007/s00126-009-0229-3

Sillitoe RH, McKee EH (1996) Age of supergene oxidation and enrichment in the Chilean porphyry copper province. Econ Geol 91:164–179

Welham NJ, Kelsall GH, Diaz MA (1993) Thermodynamics of Ag–Cl–H_2O, Ag–Br–H_2O, and Ag–I–H_2O systems at 298 K. J Electroanal Chem 361:39–47