Iodine remobilization and supergene enrichment of copper at Chuquicamata

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Abstract. Recent studies have suggested the involvement of highly saline deep formation waters that modified preexisting Cu assemblages to form Cu chlorides and iodides during supergene oxidation of Cu deposits in the Atacama region. Here, we present a new application of the iodine-129 isotopic method to iodine-rich samples from the world's largest supergene Cu profile at the Chuquicamata deposit in northern Chile, where anomalous concentrations of this element have been reported. Supergene marshites (CuI) from the oxide zone at Chuquicamata have $^{129}I/I$ isotopic ratios (~200-600x10^{-15}) that are significantly lower than the pre-anthropogenic surface water values (~1500 x10^{-15}), indicating that fluids involved in supergene enrichment were not exclusively meteoric in origin. Results from this study show that the occurrence of iodine at Chuquicamata was the result of a unique interplay between geological, hydrological and tectonic conditions that permitted deep basement fluids of marine origin to mix with meteoric water, modifying pre-existing supergene Cu assemblages and forming geochemical anomalies that have been preserved in a hyperarid climate.

Keywords: supergene enrichment, iodine, Chuquicamata

1 Introduction

Weathering of ore deposits can lead to several-fold increases in metal grades and produce supergene profiles that record the history of climate, groundwater flow and landscape evolution. The major Cu resources in the world occur in the hyperarid Atacama Desert of northern Chile, where supergene enrichment of Cu was driven by meteoric downward circulation during a long period extending from ~44 Ma to 14-9 Ma under a semi-arid to arid climate, followed by a late stage of oxidation under conditions of progressive aridification (Alpers and Brimhall, 1988; Sillitoe and McKee, 1996; Hartley and Chong, 2002; Arancibia et al., 2006; Reich et al., 2008, 2009a,b; Palacios et al., 2011).
Previous reports of anomalous concentrations of iodine and occurrences of Cu iodide minerals in the supergene zones of Cu deposits in the region are particularly enigmatic and remain unexplained, considering the fact that iodine is enriched in marine sediments pore fluids, and meteoric surface waters have exceedingly low concentrations of iodine, <50 ppb (Jarrell, 1944; Mortimer et al., 1978; Muramatsu and Wedepohl, 1998; Kelley et al., 2003; Fehn et al., 2007; Reich et al., 2009a; Cameron et a1., 2010). Here we present an isotopic analysis of iodine in supergene iodide minerals and iodine-rich soil from the Chuquicamata giant Cu deposit, where notable occurrences of this element have been reported.

2 Samples and methods

At Chuquicamata, anomalous concentrations of iodine have been reported in the supergene oxide zone, including historical accounts on the observation of small clouds of purplish smoke noted on several occasions during blasting of the (now mined-out) oxidation blanket, which was shown to contain significant iodine (Jarrell, 1939, 1944; Mortimer et al., 1978). Samples for this study came from the oxide zone of the deposit, and contain fine-grained (<2 mm) marshite crystals (CuI, pale orange) that occur intergrown with atacamite ($Cu_2Cl(OH)_3$, green) (Fig. 1), a Cu mineral that requires saline water to form and dissolves in the presence of meteoric water. In addition to the mineral samples, an anomalously iodine-rich soil sample (16,000 ppm I) obtained above the Ministro Hales (MM) deposit 10 km south of Chuquicamata was analyzed.

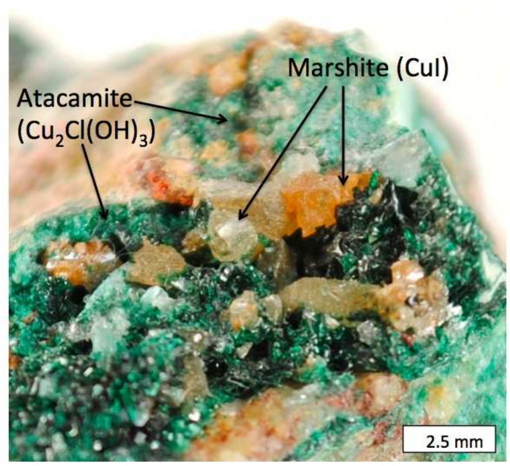

Figure 1. Marhsite and atacamite-bearing supergene assemblage from the Chuquicamata Cu deposit.

Iodine was extracted from mineral samples and soil using hydropyrolysis and anion exchange resin according to procedures by Schnetger and Muramatsu (1996). $^{129}I/^{127}I$ ratios, by convention expressed as $^{129}I/I$ ratios (x10^{-15}

atoms of ^{129}I over total I atoms), were determined by Accelerator Mass Spectrometry (AMS) at PRIME lab in Purdue University, Indiana.

3 Results

The $^{129}I/I$ ratios of supergene iodide minerals and soil are reported in Figure 2. Marshites from Chuquicamata are clustered within a narrow range of $^{129}I/I$ ratios, with values at 187.3 ± 17.3, 201.4 ± 13.6, 218 ± 72, and 562 ± 77 ($x10^{-15}$), similar to the ratio reported for the anomalous iodine-rich soil above the MM deposit, nearby Chuquicamata (472.7 ± 74.6 $x10^{-15}$) (Reich et al., accepted).

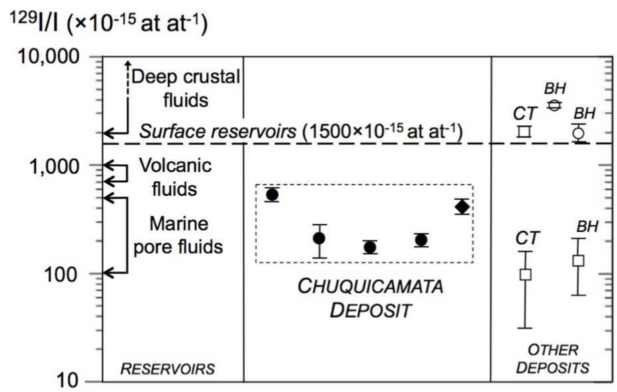

Figure. 2. $^{129}I/I$ ratios of marshite samples from Chuquicamata (black circles) and a soil sample from MM south of Chuquicamata (black diamond). Isotopic data for iodide minerals (CuI, AgI) from Chañarcillo, Chile, (CT) and Broken Hill, Australia (BH) are shown on the right side.

4 Discussion and Conclusions

The ratios of individual samples are compared to known ranges for the $^{129}I/I$ system (Fig. 2). All samples from Chuquicamata have low ratios (~200-600$x10^{-15}$) that are typical of deep fluids of marine origin, and plot below the pre-anthropogenic meteoric surface waters (horizontal segmented line, Fehn et al., 2007; Reich et al., accepted). These low ratios suggest that iodine at Chuquicamata was most likely derived from the sedimentary rocks that form part of the low Jurassic to mid Cretaceous marine basement in the Chuquicamata/Calama area. Although the exact age of precipitation of the supergene iodides cannot be constrained from the $^{129}I/I$ ratios, they do provide valuable information regarding the supergene history of the region. The non-meteoric iodine signature reported here, when coupled with previous ^{36}Cl and U-Th desequilibrium data from Chuquicamata and other Cu deposits nearby indicating young ages (<2 Ma) and marine sources for chlorine (Arcuri and Brimhall, 2003; Reich et al., 2008, 2009b), strongly suggests that iodides precipitated from saline ground waters under well-established hyperarid conditions (Reich et al., accepted).

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References

Alpers, C.N., Brimhall, G.H., 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.

Arcuri, T., and Brimhall, G., 2003, The chloride source for atacamite mineralization at the Radomiro Tomic porphyry copper deposit, Northern Chile: Economic Geology, v. 98, 1667–1681.

Arancibia, G, Matthews, S.J., and De Arce, C.P., 2006, K-Ar and Ar-40/Ar-39 geochronology of supergene processes in the Atacama Desert, Northern Chile: tectonic and climatic relations. J. Geol. Soc. London 163: 107–118.

Cameron, E.M., Leybourne, M.I., Reich, M., and Palacios, C., 2010, Geochemical anomalies in northern Chile as a surface expression of the extended supergene metallogenesis of buried copper deposits. Geochem. Explor. Env. Anal. 10: 1-14.

Fehn, U., Moran, J.E., Snyder, G.T. and Muramatsu, Y., 2007, The initial I-129/I ratio and the presence of 'old' iodine in continental margins. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms 259: 496-502.

Hartley, A.J., Chong, G., 2002, Late Pliocene age for the Atacama Desert: Implications for the desertification of western South America. Geology 30: 43-46.

Jarrell, O., 1939, Marshite and other minerals from Chuquicamata, Chile. Am. Mineral. 24: 629-635.

Jarrell, O., 1944, Oxidation at Chuquicamata, Chile. Econ. Geol. 39: 251-286.

Kelley, D.L., Hall, G.E., Closs, G., Hamilton, I.C. and McEwen, R.M., 2003, The use of partial extraction geochemistry for copper exploration in northern Chile. Geochem. Explor. Env. Anal. 3: 85-104.

Mortimer, C., Munchmeyer, C., and Urqueta, I., 1978, Emplazamiento del yacimiento Exótica, Chile. Rev. Geol. Chile 6: 41-51.

Muramatsu, Y., and Wedepohl, K.H., 1998, The distribution of iodine in the earth's crust. Chem. Geol. 147: 201-216.

Palacios, C., Rouxel, O., Reich, M., Cameron, E., and Leybourne, M.I., 2011, Pleistocene recycling of copper at a porphyry system, Atacama Desert, Chile: Cu isotope evidence. Miner. Deposita 46: 1-7.

Reich, M., Palacios, C., Parada, M.A., Fehn, U., Cameron, E.M., Leybourne, M.I., and Zúñiga, A., 2008, Atacamite formation by deep saline waters in copper deposits from the Atacama Desert, Chile: evidence from fluid inclusions, groundwater geochemistry, TEM, and 36Cl data: Miner. Deposita 43: 663-675.

Reich, M., Palacios, C., Alvear, M., Cameron, E.M., Leybourne, M.I., and Deditius, A., 2009a, Iodine-rich waters involved in supergene enrichment of the Mantos de la Luna argentiferous copper deposit, Atacama Desert, Chile. Miner. Deposita 44: 719-722.

Reich, M., Palacios, C., Vargas, G., Luo, S., Cameron, E.M., Leybourne, M.I., Parada, M.A., Zúñiga, A., and You, C.F., 2009b, Supergene enrichment of copper deposits since the onset of modern hyperaridity in the Atacama Desert, Chile. Miner. Deposita 44: 497-504.

Reich, M., Snyder, G.T., Alvarez, F., Perez, A., Palacios, C., Vargas, G., Cameron E.M., Muramatsu, Y., and Fehn, U. Using iodine isotopes to constrain supergene fluid sources in arid regions: insights from the Chuquicamata oxide blanket. Econ. Geol. (accepted).

Schnetger, B. and Muramatsu, Y., 1996, Determination of the halogens, with special reference to iodine, in geological and biological samples using pyrohydrolysis for preparation of inductively coupled plasma mass spectrometry and ion chromatography for measurement. Analyst 121: 1627-1631.

Sillitoe, R.H., and McKee, E.H., 1996, Age of supergene oxidation and enrichment in the Chilean porphyry copper province. Econ. Geol. 91: 164-179.