Supergene enrichment of copper deposits since the onset of modern hyperaridity, Atacama Desert, Chile

Reich, M.1, Palacios, C.1, Vargas, G.1, Cameron, E.M.2, Leybourne, M.I.3, Fehn, U.4, Zúñiga, A.5, Luo, S.6, You, C.F.6

(1) Departamento de Geología, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago, Chile.
(2) Eion Cameron Geochemical Inc., Carp, ON, Canada.
(3) Ocean Exploration, GNS Science, Lower Hutt, New Zealand.
(4) Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY, USA.
(5) Departamento de Ingeniería Mecánica, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago, Chile.
(6) Earth Dynamic System Research Center & Department of Earth Sciences, National Cheng-Kung University, Tainan, Taiwan, Republic of China.

mreich@ing.uchile.cl

Introduction

Supergene enrichment of Cu deposits in the Atacama Desert of northern Chile has played a critical role in making this the prime Cu producing province of the world. Previously, this has been believed to have occurred exclusively over a long period from the middle Eocene to the Late Miocene, which ended when climate conditions changed from arid to hyperarid. However, there is no consensus about the onset of hyperaridity, which may have commenced as early as 25 Ma [1], or 19-13 Ma [2], or as late as 3-4 Ma [3, 4]. Furthermore, it is debatable if supergene processes ceased completely as a result of hyper-aridification. The green mineral atacamite (Cu₂Cl(OH)_3) is the major component of oxide zones of many Cu deposits in the Atacama Desert. As atacamite requires saline water for its formation and dissolves rapidly when exposed to meteoric water, hyperarid climate conditions are necessary for its preservation in supergene zones.

In this study we couple geochemical, mineralogical, and isotopic data from atacamite-bearing supergene assemblages to show that supergene oxidation of Cu deposits did not cease after the onset of hyperaridity, but extended at least until the late Pleistocene. We
provide a new conceptualization on both the supergene enrichment process and the onset of extreme hyperaridity in the Atacama Desert.

Copper deposits from the Atacama Desert

The Atacama Desert of northern Chile is the driest desert on Earth and hosts the world’s largest known accumulation of Cu, the primary Cu sulfide hydrothermal mineralization having formed during Late Jurassic to Early Oligocene time as part of the geological evolution of the southern segment of the Central Andes [5]. Supergene oxidation and leaching processes have led to significant enrichment of porphyry and stratabound (“manto-type”) Cu deposits, and the economic viability of these deposits is typically dependent on the size and quality of the supergene enrichment blanket that overlies the hypogene Cu-sulfide zones [5, 6]. Notable occurrences of atacamite (with variable proportions of other oxide minerals) are found in several Cu deposits in northern Chile, e.g., Chuquicamata, Radomiro Tomic, Spence, Escondida, Mantos Blancos, and many others.

Atacamite assemblages: groundwater geochemistry, fluid inclusions, chlorine-36 and U-series data

Atacamite typically occurs as complex, fine-grained polycrystalline aggregates associated with gypsum in veinlets in supergene zones. Transmission electron microscopy (TEM) observations in selected samples from atacamite/gypsum veinlets reveal that atacamite is in close association with gypsum at all scales. The presence of atacamite and gypsum at the nanoscale was confirmed using energy-dispersive spectrometry (EDS) spot analyses during TEM observation [7, 8].

In the Spence and Mantos Blancos deposits, the salinities of fluid inclusions in atacamite are comparable to those measured in saline groundwaters sampled from drill holes. The average salinity of fluid inclusions in atacamite for the Mantos Blancos and Spence deposits (~7-9 and 2-3 wt% NaCl_{eq}, respectively) are strongly correlated to the salinities at which gypsum supersaturates from groundwaters in both deposits (total dissolved solids (TDS*) ~5-9 and 1-3 wt% NaCl_{eq}, respectively). This correlation is consistent with the intimate association between atacamite and gypsum observed at all scales [7].

All atacamite samples show very low 36Cl/Cl ratios as measured by accelerator mass spectrometry (AMS), comparable to previously reported 36Cl/Cl ratios of saline deep formation waters and old groundwaters. The (U+Th) vs. 36Cl/Cl correlation indicates subsurface production of fissionsgenic 36Cl in secular equilibrium with the solutions involved in the atacamite origin. Atacamite does not contain U or Th itself, therefore the production of 36Cl is not longer supported once Cl enters the structure and the 36Cl/Cl ratio starts to decrease with age. The fact that we still found measurable 36Cl in atacamite indicates that the formation of atacamite was relatively recent. The 36Cl data strongly
suggest that Cl in the saline waters related to atacamite formation is old in origin (>1.5 Ma), but that the atacamite formation occurred less than 1.5 Ma ago, which is approximately five times the half-life of $^{36}\text{Cl}$ [7].

The young ages of atacamite assemblages are confirmed by U-series disequilibrium data obtained by multi-collector ICP-MS in the associated gypsum. $^{234}\text{U}-^{230}\text{Th}$ ages of gypsum intergrown with atacamite in veins from Cu deposits cluster at ~ 240 ka (Chuquicamata), 130 ka (Mantos Blancos, Spence) and 80 ka (Mantos de la Luna, Michilla). U-series dating of gypsum-atacamite-bearing assemblages shows that supergene oxidation processes in Cu deposits were active during the middle and late Pleistocene when hyperarid climate conditions prevailed in the Atacama Desert [8].

Conclusions

Groundwater geochemistry, fluid inclusions, and TEM data show that atacamite formation is associated with gypsum saturation. All atacamite assemblages show very low $^{36}\text{Cl}/\text{Cl}$ ratios, comparable to previously reported $^{36}\text{Cl}/\text{Cl}$ ratios of deep formation waters. The presence of low but detectable $^{36}\text{Cl}$ of fissiogenic origin in atacamite from supergene zones indicates that the hyperarid conditions necessary for its preservation were already established at 1.5 Ma.

Chlorine-36 and U-series disequilibrium data in atacamite-bearing assemblages show that supergene enrichment of Cu deposits did not cease after the onset of hyperaridity. We propose that supergene enrichment in the Atacama Desert developed in two stages: (i) The main phase, caused by downward circulation of meteoric waters in a semi-arid setting, was active from 45 until ~9 Ma. Meteoric waters do not permit the creation of atacamite-bearing assemblages, because atacamite requires saline water for its formation and rapidly dissolves when in contact with meteoric water. (ii) This was followed by a second “atacamite formation” stage, starting at ~2-1.5 Ma and continuing until at least the late Pleistocene, when saline deep formation waters derived from the basement ascended by seismic pumping [9-11], passing up through the deposits and modified the pre-existing supergene assemblages [8].

Acknowledgements

Financial support for this study was provided to Martin Reich and Carlos Palacios by the Chilean Fund for Science and Technology, Fondecyt Grant # 1070736.

References


