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# GEOCHEMICAL MODELING OF THE EXOTIC MINERALIZATION OF THE EXOTICA DEPOSIT AT CHUQUICAMATA, CHILE

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## **ABSTRACT**:

The exotic copper mineralization at the Exotica deposit (now Mina Sur) located in a 6.5 km long paleo-channel southwards from the porphyry copper deposit Chuquicamata, Northern Chile, is characterized by a sequence of "copper-wad" associated to strongly kaolinized gravels, followed by atacamite (Cu<sub>2</sub>Cl(OH)<sub>2</sub>) associated to unaltered gravels, and of mainly chrysocolla (CuSiO<sub>2</sub>•nH<sub>2</sub>O) in the contact with the propylitic altered bedrock. It is generally believed that the exotic mineralization is a result of the lateral flow of acid solutions formed during the oxidation of the primary porphyry copper ore body from Chuquicamata and their interaction with the host-rock mineralogy (MÜNCHMEYER, 1996). The goal of this study is to simulate the mineral paragenesis by geochemical modeling in order to get further insight into the ore forming process. As it is impossible to obtain the pore water composition during the formation of the deposit, in this study, pore water from the actual oxidation zone of a porphyry copper mine tailings impoundment (Piuquenes/La Andina) was used as starting solution (pH 2.31, pe 12.2, 23.1 g/L SO<sub>4</sub>, 2080 mg/L Al, 1430 mg/L Mg, 1380 mg/L Fe, 910 mg/l Cu, 463 mg/L Ca, 92.9 mg/L Mn, 70.5 mg/L Cl, 50.9 mg/L Si, 11.5 mg/L K, 6.7 mg/L Na). The solution was titrated with calcite to simulate the neutralization reactions with the calcite baring propylitic altered metamorphic host-rock assemblage. The results show the same sequence of kaolinite, atacamite and chrysocolla with increasing pH (pH 3.12, 5.37, 6.8, respectively) as it is observed in the ore. This suggests that the observed mineral paragenesis is controlled by the neutralization potential of the host-rock mineralogy and the concentrations of Cl and Si. Therefore, Exotica is most likely the result of water-rock interactions between the host-rock and natural sulfide oxidation, what led to the formation of acid metal-rich solutions, similarly what nowadays is frequently observed in mine waste environments with the formation of acid mine drainage (AMD). Thus, the understanding of the formation of AMD also improves the understanding of supergene enrichment processes and exotic deposit formation and gives hints for exploration targets.

### METHODOLOGY

Hydrogeochemical data from the oxidation zone of the porphyry copper tailings impoundment Piuquenes from the La Andina mine (DoLD et al., 2005a; DoLD and FONTBOTÉ, 2001) was used as representative solution for acid rock drainage resulting from the oxidation of a porphyry copper mineralization, which is assumed to migrate laterally and react with the host-rock assemblage under oxic conditions. In a first step the Eh-pH diagrams of the Cu-Cl-Si system was calculated with the chemical equilibrium program MEDUSA. In the second step the modeling of the reactions of the acid rock drainage solution in contact with the host-rock was performed using PHREEQC2 (PARKHURST and APPELO, 1999) by titration with 0.5 moles calcite in 50 steps, in order to simulate the interaction of the acid solution and the calcite bearing propylitic zone of the metamorphic rocks.

#### **RESULTS AND DISCUSSION**

The pH-Eh diagram for the Cu-Cl-Si system with 14.3 mM Cu, 1.99 mM Cl, and 1.81 mM Si at  $T = 25^{\circ}$ C and 1 bar for the solution from the oxidation zone of Piuquenes is shown in Figure 1a. Under oxidizing low-pH conditions, the Cu<sup>2+</sup> cation is stable in the solution. When a pH of 4.8 is reached due to the neutralization reactions, atacamite becomes oversaturated and will precipitate. Chrysocolla will not precipitate in this solution. Therefore, an adaption of the Cl and Si concentration was applied. The Cl concentration was increased in Fig. 1b and 1c to 2000 mg/L. Such concentration are measured actually in the Talabre tailings impoundment (DoLD et al., 2005b) and are the mean Cl concentrations encountered in the Chuquicamata area (ROMERO et al., 2003). The higher concentrations of Cl result in an over-saturation of atacamite at lower pH (4.3). The stability field of chrysocolla appears when the Si concentration is increased to a minimum of 70 mM, where the solution will be oversaturated at pH 6.7. At higher Si concentrations (e.g. 181 mM in Fig. 1c) chrysocolla starts to precipitate at lower pH (5.8). The titration of the acid pore water shows that the saturation index (SI) for kaolinite will be oversaturated at pH 3.1, suggesting its precipitation (Fig. 2). This corresponds in the exotic ore to the area of the strongly kaolinized gravels and bedrock, relatively close to the acid



**Figure 1:** Eh-pH diagrams for the system Cu-Cl-Si. A) representing the system from the oxidation zone at Piuquenes. B) and C) show the stability fields with adapted Cl concentration and increasing Si concentration.



**Fig. 2:** Modeled titration of the pore water solution from the oxidation zone at Piuquenes by the addition of 0.5 moles of calcite in 50 steps. Round dots represent the SI for atacamite with 2000 mg/ 1 Cl in solution. For discussion see text.

source of the Chuquicamata ore deposit. Atacamite will reach over-saturation starting at pH 5.4 in this solution. If the Cl concentration is adapted to 2000 mg/L, as it is typical for the waters in the Chuquicamata area, atacamite will be oversaturated at pH 4.8. When then the pH still increases towards pH values over 6.8, chrysocolla will precipitate, mainly in direct contact with the propylitic zone of the methamorphic host-rock, where still enough calcite is available to buffer the near neutral pH values. If the host-rock assemblage does not contain calcite (e.g. no propylitic alteration) near

neutral pH conditions cannot be reached and therefore atacamite is favored, as it is most likely the case for the unaltered gravels.

## CONCLUSIONS

The exotic mineral paragenesis found at the Exotica deposit, Chuquicamata could be modeled by the water-rock interaction process of acid rock drainage with the specific host-rock mineralogy. The paleo solution, which formed Exotica were most likely acid rock drainage with elevated Cl and Si concentrations. The Cu2+ was mobilized in low-pH conditions in the paleo channel from the source, the Chuquicamata porphyry copper deposit. When these acid solutions came in contact with neutralizing bed-rock a pH increase was triggered, resulting in the over-saturation and subsequent precipitation of kaolinite. When the pH increased further towards pH 4.8-5.6 (depending on the Cl concentrations), due neutralization reaction with the host-rock, atacamite precipitated. Mainly in the contact with the propylitic altered metamorphic rocks, which contain calcite to buffer to near neutral pH, chrysocolla precipitated. Therefore, the neutralization potential of the host-rock controls whether atacamite or chrysocolla will form.

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