European Mineralogical Conference
Vol. 1, EMC2012-511, 2012
European Mineralogical Conference 2012

Hydrothermal controls on metal distribution in porphyry systems

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Porphyry Cu systems are defined as large volumes of hydrothermally altered rocks initiated by injection of fluid-saturated oxidized magma from cupolas of subjacent parental plutons in the upper part of the crust. Porphyry and associated skarn and epithermal deposits supply most of the world's copper, molybdenum and rhenium, as well as important amounts of gold, silver, bismuth, lead, and zinc. These systems are the best studied of all hydrothermal deposits and an extensive research over the 20th century has revealed their major geodynamic, petrological, geochemical, mineralogical and structural features. Nowadays, it is largely accepted that the porphyry and associated deposits form from sulfur- and metal-rich supercritical aqueous fluids of moderate salinity (2-10 wt. % NaCl eq.) exsolved from the magma and subjected to various phenomena leading to ore precipitation. However, until recently, the metal transport and fractionation during this post-magmatic fluid evolution has remained insufficiently quantified owing to the lack of direct data on metal contents in the fluid phase.
In the last 15 years, advances in novel micro analytical techniques particularly for individual fluid inclusion characterization, such as laser ablation-inductively coupled plasma mass-spectrometry (LA-ICP-MS), proton-induced X-ray emission spectroscopy (PIXE), synchrotron radiation X-ray fluorescence (SR-XRF), infrared, Raman, and fluorescence spectroscopy, provide direct evidence for the chemical and phase composition and metal content of ore-forming fluids that have allowed metal budgets and sources in porphyry systems to be determined. In addition, recent progress in experimental approaches and physical-chemical modeling of hydrothermal fluids allowed the generation of more accurate data on the identity and stability of dissolved metal-bearing species, and far improved prediction of ore-mineral solubilities, metal vapor-liquid partitioning, and depositional mechanisms
In this contribution, we review a dataset of published fluid inclusion compositions from more than 30 deposits of the porphyry-epithermal suite and we provide an overview of the current knowledge of the chemical speciation of ore metals (Cu, Au, Ag, Mo) and accompanying elements (S, Fe, Zn, Pb) in various types of fluids under the conditions relevant to porphyry formation. This knowledge, coupled with available mineralogical and fluid inclusion data that provide constraints on key intensive parameters (temperature, pressure, acidity, redox potential, and sulfur fugacity), has improved our understanding of factors related to ore deposition and metal fractionation in porphyry Cu-Au-Mo and associated (skarn, epithermal) deposits.