Redox evolution during magmamixing: Implications for Cu/Au ratios of porphyry deposits

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Mafic magma intrusions are believed to contribute significantly to the volatile (H_2O , Cl, S) and (chalcophile) metal budgets of porphyry ore deposits. We performed magma-magma diffusion-couple experiments that reveal remarkable redox gradients near the magma-magma interface, which potentially explain the formation of Cu-rich vs. Au-rich porphyry deposits [1].

The experiments were conducted by using samples from Volcán Quizapu, representing the dacitic host magma, and basaltic andesite re-charge magma, respectively. Crystalbearing (spinel, \pm plagioclase, \pm opx, \pm cpx) and volatileenriched (H₂O, Cl, S) dacitic and andesitic cylinders were synthesized at 150 MPa, 900°C (dacite) or 1030°C (andesite) in cold seal pressure vessels (fO₂ ~ FMQ+4). The cylinders were sliced, and dacite-andesite mixing experiments were performed at temperatures of 950 and 1000°C, FMQ+4 and 150 MPa. The samples were rapidly quenched after 1 to 80 h.

The andesite shows a high crystallinity of ~85% that decreases slowly near the interface with increasing run duration, while the dacite contains only a small fraction of spinel. The andesite has reached volatile saturation at mixing temperatures as indicated by the presence of vesicles, while the dacite is bubble-free. The vesicles remain within the mafic phase, indicating that the transport of S and chalcophile metals from the mafic to the felsic magma may be controlled by diffusion. Analyses of major (EPMA) and trace elements (LA-ICP-MS) as well as WDS/EDS mapping show that the exchange of the major and trace elements (incl. S) is further limited by the crystal dissolution rate. Here, cpx dissolution is followed by opx, plag and spl. Fe µ-XANES analyses reveal a strong drop of Fe³⁺/Fe_{tot} near the interface, which is explained by the dissolution of predominantly Fe^{2+} -rich minerals in the basaltic andesite. The Fe^{3+}/Fe_{tot} gradient is equivalent to a drop of fO2 by ~1.5 log units. Considering the strong influence of fO2 on Au and Cu solubility in melts and on Au and Cu fluidmelt partitioning [2-3], we suggest that the formation of such redox gradients during magma-mixing can explain the contrasting Au/Cu ratios of porphyry deposits.

[1] Vila and Sillitoe (1991) *Econ. Geol.* **86**, 1238-1260; [2] Zajacz *et al.* (2012) *GCA* **91**, 140-159; [3] Zajacz *et al.* (2013) *GCA* **112**, 288-304.