

Impact of trace mineral phases on the total solute flux from andesitic volcanics

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Recent work on high standing islands (HSIs) shows weathering rates based on stream water chemistry in andesitic terrains are comparable to rates determined for basalts, indicating that these areas might be much more important in drawing down atmospheric CO₂ than previously recognized. We conducted batch dissolution experiments on andesitic material collected from ≤40,000 year old tephra deposits from Dominica and ash from the 1991 eruption of Mt. Pinatubo, Philippines, to determine the dissolution rates of major and trace mineral phases. Dissolution experiments of months duration were conducted over a range of pH (3–7) on bulk samples and mineral separates.

Dissolution rates at pH 4 based on Si release from the crystalline and glass-rich Dominica tephra separates were similar, ~4 to 8 *10⁻¹³ mol/g sec. Dissolution rates in water were lower, ~20–50% of rates measured at pH 4. Apatite, as inclusions within pyroxenes, composes only a few percent of the tephra but it contributes significantly to total solute flux. Solutes from apatite dissolution are ~1–6-fold greater than the solutes from silicate dissolution at pH 4, and ~0.1–1 times the solutes from silica dissolution in water.

TDS from dissolution of the Pinatubo ash is 2 orders of magnitude greater than for the Dominica samples. Silica dissolution rates for Pinatubo ash are about an order of magnitude greater than those for the Dominica tephra, from ~1 to 8 *10⁻¹² mol/g sec over pH 7–3. Apatite dissolution increases with increasing acidity, and is ~0.1–1 times silica dissolution. Over 90% of the solutes are derived from dissolution of trace amounts of CaSO₄.

Typically, the reactivity of Ca-bearing accessory minerals such as apatite or anhydrite has not been considered to contribute significantly to the overall Ca flux from weathering and subsequent CaCO₃ precipitation. However, in our experiments the release of Ca ions to solution is dominated by the reactivity of these phases. In areas that experience rapid physical weathering the reactivity of trace mineral phases may contribute significantly to the total chemical weathering flux.

'Invisible' Ag and Au in supergene Cu-sulfides: EMPA, SIMS and TEM constraints

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In this study, we used secondary ionization mass spectrometry (SIMS) and electron microprobe analyzer (EMPA) techniques to fully characterize the trace metal content of Ag-bearing supergene chalcocites from various Cu deposits in the Atacama Desert of northern Chile. SIMS and EMPA measurements reveal that, apart from hosting up to ~11,000 ppm Ag, supergene chalcocite can incorporate up to part-per-million contents of Au (~6 ppm) and associated metalloids such as As (~300 ppm), Sb (~60 ppm), Se (~96 ppm) and Te (~18 ppm).

The SIMS analyses show that Ag and Au concentrations strongly correlate with As, defining wedge-shaped zones in Ag-As and Au-As log-log spaces. SIMS depth profiling and high-resolution transmission electron microscopy (HRTEM) observations reveal that the anomalously high Ag/As and Au/As samples plotting above the wedge zone contain nanoparticles of metallic Ag and Au, while samples with lower ratios contain Ag and Au that is structurally bound to the Cu-sulfide matrix. The Ag-Au-As relations reported in this study strongly suggests that the incorporation of precious metals in Cu-sulfides formed under supergene conditions respond to the incorporation of a minor component, in this case As. Therefore, As might play a significant role by increasing the solubility of Ag and Au in supergene chalcocite and controlling the occurrence of Ag and Au nanoparticles. Considering the fact that supergene enrichment of Cu processes can be active from tens of millions of years (e.g. Atacama Desert), we conclude that As-bearing supergene chalcocite may play a previously unforeseen role in scavenging precious metals from undersaturated (or locally slightly supersaturated) solutions in arid to hyperarid areas.