Experimentation to investigate volatile trace metal behaviour in volcanic gases and fumaroles

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Volatile trace metals (e.g. Pb, As, Cd, Cu) degas from volcanoes, forming sublimates in fumaroles and on ash particles on cooling. These processes impact the chemistry of volcanic plumes and the formation of some ore deposits. We systematically analyze the complexation effect of ligands (Cl, S) on the degassing and sublimation of such trace metals during volcanism in a 'benchtop fumarole' that degasses melts in the Na_2O-Al_2O_3-Fe_2O_3-SiO_2 system doped with trace elements (V, Cu, Zn, As, Mo, Cd, Sn, Y, Yb, Pb, Bi, Cl and S). Sublimates of trace metals form along a thermal gradient from 25-900°C in a silica tube suspended above the melt over week-long experiments. We chemically characterize and identify the sublimate phases using solution ICP-MS, SEM with EDS and microRaman spectroscopy. Results indicate that SiO_2 polymorphs form at all temperatures, whereas halite crystals form between 100-500°C. Chlorine concentrations are highest at <400°C, correlating with the occurrence of halite crystals. Bradaczekite [$NaCu_4(AsO_4)_3$], a fumarole mineral, is synthesized and hosts Cu and As. Chlorine-based analogues of szenicsite [$Cu_3(MoO_4)(OH)_4$] and molybdofornacite [$CuPb_2(MoO_4)(AsO_4)(OH)$] host Mo, As, Cu, Pb, Sn, Cr and W and form at ~ 500°C. Murdochite [$Cu_{12}Pb_2O_{15}Cl_2$] and Pt crystals occur at ~500°C. Solution ICP-MS results indicate that volatile trace metals sublimate in groups in our experiments. Rubidium, Pt and Tl sublimate in highest concentrations at <200°C; Ag and Pb at 200°C and 400°C; As, Mo, Cd, W and Bi at 200°C and 500°C; Cr and Zn at 500°C; Li and Pb at 400°C and 600°C; V at >500°C; and Cu and Sn at <200°C and >600°C. Our results can be compared to natural fumarole mineralogy and thermodynamic calculations to better quantify the behaviour of trace metals in the gas phase of plumes.