

Mass transfer during volatile exsolution in magmatic systems: Insights from the analyses of silicate melt and magmatic fluid inclusions

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We analyzed silicate melt and primary magmatic fluid inclusions in numerous granitic systems and in the basaltic andesites of the Villarrica volcano to quantify the distribution of several elements between silicate melts and magmatic volatiles.

LA-ICPMS analyses of co-existing silicate melt and fluid inclusions, entrapped in miarolitic quartz crystals, allowed direct quantitative determination of fluid/melt partition coefficients. Investigations of various granitic systems (peralkaline to peraluminous in composition, $\log f_{O_2} = \text{NNO} - 1.7$ to $\text{NNO} + 4.5$) exsolving fluids with various chlorinities (1 to 13 mol/kg) allowed us to assess the effect of these variables on the fluid melt partition coefficients (D). Partition coefficients for Pb, Zn, Ag and Fe show a nearly linear increase with the chlorinity of the fluid ($D_{\text{Pb}} \sim 6 \cdot M_{\text{Cl}}$, $D_{\text{Zn}} \sim 8 \cdot M_{\text{Cl}}$, $D_{\text{Ag}} \sim 4 \cdot M_{\text{Cl}}$, $D_{\text{Fe}} \sim 1.5 \cdot M_{\text{Cl}}$, where M_{Cl} is the molinity of Cl). This suggests that these metals are primarily dissolved as Cl-complexes and neither oxygen fugacity nor the composition of the melt affects significantly their fluid/melt partitioning. Partition coefficients of Mo, As, Sb and Bi are highest into low salinity (1-2 mol/kg Cl) fluids with maximum values of $D_{\text{Mo}} \sim 20$, $D_{\text{As}} \sim 10$, $D_{\text{Sb}} \sim 8$, $D_{\text{Bi}} \sim 15$ indicating dissolution as non-chloride (eg., hydroxy) complexes. Fluid/melt partition coefficients of copper are highly variable, but highest between vapor like fluids and silicate melt ($D_{\text{Cu}} \leq 2700$), indicating important role of ligands other than Cl. Fluid/melt partition coefficients of Sn and W show a weak positive correlation with the chlorinity of the fluid ($D_{\text{Sn}} = 0.3 - 42$, $D_{\text{W}} = 0.8 - 60$), but likely decrease with decreasing oxygen fugacity or melt peraluminosity.

In situ quantitative determination of fluid/melt partition coefficients in mafic systems with the use of natural samples is limited due to the lack of well preserved fluid inclusions. However, very high excess concentrations of Cu and Ag have been analyzed in plagioclase-hosted silicate melt inclusions in basaltic andesites compared to those in co-genetic pyroxene and olivine (up to 4800 ppm Cu vs. 40-200 ppm Cu in plagioclase vs. pyroxene and olivine hosted melt inclusions). The excess Cu is due to heterogeneous entrapment of a high temperature (~1000 °C) vapor phase rich in Cu, Ag and S. This suggests that high-temperature magmatic vapors may play an essential role in the transport of Cu, Ag and S from mafic to felsic magmas in complex magmatic reservoirs.

Geochemical fractionation and anthropogenic metal pollution in sediments of Nakagawa River in Tokyo, Japan

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Nakagawa River sediments were collected from the whole river and analysed for heavy metals in the less than 63 µm grain size fraction. The geochemical fractionation of heavy metals was examined with a sequential extraction scheme and the concentration of iron, manganese, lithium, cobalt, cadmium, chromium, copper, nickel, lead and zinc were measured in the liquid extracts by flame atomic absorption and inductively coupled plasma mass spectrometry. A certified reference stream sediment sample (JSd-2) provided by the Geological Survey of Japan was also analysed using the same procedure as a check. The association of Cr and Pb with oxides and Zn with carbonatic and oxides were comparatively higher. Nakagawa River sediment was considered to be polluted on the basis of unpolluted sediments and geochemical background values with respect to Cr, Pb and Zn, which were several times higher than the limiting concentration where toxicological effects are expected. The geoaccumulation index for most of the sampling points also lies above zero indicating contamination in Nakagawa sediment for the aforesaid metals. The pollution could be linked to anthropogenic activities such as industrialization, urbanization, deposition of industrial wastes and others. A final evaluation of the Nakagawa River sediments heavy metal pollution will be made from the study results.