The effect of oxygen fugacity and melt composition on As-Sb fluid-melt partitioning in the granite-H_2O system at 800°C and 200 MPa

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The partition coefficients of arsenic and antimony between aqueous fluids and granitic melts have been studied in the system SiO_2-Al_2O_3-Na_2O-K_2O-H_2O at 800 °C and 200 MPa. The experiments were conducted in rapid-quench cold-seal pressure vessels and the concentrations of As were measured in both quenched glasses and fluids. By contrast in the Sb experiments, a solid phase crystallized on quenching and partition coefficients were calculated from glass compositions and mass balance. Forward and reverse experiments were also conducted to confirm that the measured values represent equilibrium. The fluid-melt partition coefficient of As ranges from 0.6 ±0.2 to 2.3 ±0.3 with a mean of 1.4 ±0.5. This value was found to be constant over an ASI range of 0.63 to 1.31 and a SiO_2 concentration of 60.62 wt% to 72.96 wt%. The As fluid-melt partition coefficient is also constant at oxidized conditions, over a log oxygen fugacity range of -12.2 to -8.4 bars (NNO + 1.6 to NNO + 5.4). The fluid-melt partition coefficient of Sb between aqueous fluid and melt ranges from 0.10 ± 0.03 to 1.3 ± 0.2 and the average for hydrous haplogranite is 0.8 ± 0.5. The fluid-melt partitioning of Sb is independent of oxygen fugacity over a log oxygen fugacity range of –16.8 to –7.9 (NNO – 3.0 to NNO + 5.9), and of the SiO_2 melt concentrations of 55.21 wt% to 72.59 wt%. However, ASI has a strong effect on Sb partitioning and for peralkaline melt (0.1 ± 0.01) is much smaller than that for metaluminous and peraluminous melts (0.8 ± 0.4).

As(III) is most likely dominant in aqueous fluid at 800 °C and 200 MPa and XPS analysis of run product glass indicate that only As(III) exists in melt. This is consistent with the finding that oxygen fugacity does not affect As fluid-melt partitioning. By contrast XPS analyses of glasses indicate Sb(V) dominates in melts at oxidized conditions.

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^{13}C-^{18}O bonds in dissolved inorganic carbon: Implications for carbonate clumped isotope thermometry

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Carbonate clumped isotope thermometry is based on a homogeneous thermodynamic equilibrium that orders ^{13}C and ^{18}O into bonds with each other within the carbonate lattice. To improve understanding of this new geothermometer and advance its application to natural environments, we present here theoretical predictions of the equilibrium and kinetic (including CO_2 hydration, hydroxylation, and reverse reactions) fractionations of 'clumped' isotopic species in dissolved inorganic carbon (DIC), and tests of these predictions based on measurements of both synthetic and natural carbonates.

Despite the significant differences in equilibrium carbon and oxygen isotope compositions between dissolved HCO_3^- and CO_3^{2-}, we predict only a subtle (~0.02‰) difference in their proportions of ^{13}C-^{18}O bonds, and thus weak pH dependence for carbonate clumped isotope thermometry. We are testing this prediction by analyzing carbonates precipitated from solutions having a range of pH.

Kinetic isotope effects associated with irreversible reactions can influence ^{13}C-^{18}O ordering in DIC and thus that in precipitated carbonate minerals. For example, kinetic isotope fractionations during rapid CO_2 degassing from aqueous solutions are predicted to increase the $\delta^{13}C$ and $\delta^{18}O$ but decrease the proportion of ^{13}C-^{18}O bonds in the residual DIC species, and thus lead to an apparent overestimation of carbonate formation temperatures as determined by carbonate clumped isotope thermometry (~10°C overestimation for every 1‰ kinetic enrichments in carbonate $\delta^{18}O$). This predicted effect is corroborated by isotopic measurements of synthetic cryogenic carbonates and natural modern speleothems (Villars cave, France). We suggest that this kinetic model can be used to quantitatively reconstruct paleotemperatures when the $\delta^{18}O$ of water is known.