

Mo-W-Re-Au-Cu partitioning between vapor, brine and felsic melt: Super-solidus to sub-solidus

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The exsolution of metal-bearing “proto-ore fluids” from magmas initiates at super-solidus conditions and continues throughout cooling and decompression to solidus conditions for the parental magma. The range of exsolution conditions for a particular magma will affect the efficiency by which each ore metal is removed from the melt, the metal ratios in the exsolved fluid(s), the mass of metals available for transport, and ultimately the grade of the deposits.

Experiments performed at a range of P-T conditions across the solidus for a given magma composition provide insight into the behavior of these metals that is not readily accessible by study of natural samples. We have performed exploratory experiments to investigate the effect of the super-solidus to sub-solidus transition on metal partitioning between melt and volatile phases under ore-mineral saturated conditions. These experiments examine Mo-W-Re-Au partitioning, and wolframite-molybdenite solubility, at super-solidus (800°C 100 MPa), near-solidus (725°C 100MPa) and sub-solidus (700°C 75MPa) conditions. New techniques are in development to refine data reduction and account for the complex behavior of our Mo-Fe-W-bearing fluid inclusions. However, the early results may be broadly interpreted as showing that Mo and W partitioning between vapor, brine and melt is strongly influenced by the super-solidus to sub-solidus transition.

The impact of the transition is more pronounced for W ($D^{v/m} = 11 \pm 5$ and 210 ± 120) compared to Mo ($D^{v/m} = 10 \pm 4$ and 50 ± 25) as the temperature drops from 800°C to 725°C. These data are consistent with fractionation of Mo from W across the super-solidus to sub-solidus transition. The molybdenite- and wolframite-saturated fluids have W/Mo ratios that increase from 20 to 30 to 60 in the brine and 15 to 25 to 50 in vapor, for 800°C-100MPa to 725°C-100MPa to 700°C-75MPa, respectively. While these results are tentative, new experiments are in progress that include Mo, W, Re, Au, and Cu. These new experiments and new data analysis techniques will provide further insight into the effect of the super-solidus to sub-solidus transition on the composition and ore-mineral solubility limits of proto-ore fluids.

The silicon isotope record of early silica diagenesis

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During diagenesis, silica is converted to quartz through dissolution-reprecipitation reactions which are likely influenced by isotope fractionation effects.

To assess the impact of diagenesis on the silicon isotope composition of chert, we explored the silicon isotope record of Plio- and Pleistocene siliceous sediments of the South Atlantic that are hosting the youngest products of the incipient stages of silica diagenesis found to date.

High $\delta^{30}\text{Si}$ values of $2.26 \pm 0.18 \%$ (n= 5) and $1.97 \pm 0.06 \%$ (n= 4) characterize two bulk porcelanite (opal-CT) layers found in two drill cores from Maude Rise and the Southwest Indian Ridge, respectively. Bulk $\delta^{30}\text{Si}$ values of surrounding siliceous oozes are lower and range between $-0.34 \pm 0.08 \%$ (n= 4) and $0.60 \pm 0.08 \%$ (n= 7), and $0.16 \pm 0.08 \%$ (n= 4) and $1.45 \pm 0.11 \%$ (n= 6), respectively.

Within these types of siliceous sediments, diatoms constitute both the compartment most prone to dissolution and heaviest in $\delta^{30}\text{Si}$ consistent with [1]. Their dissolution together with isotope fractionation through rapid precipitation of inorganic opal (opal A') during the ascent of pore fluids can produce isotopically heavy diagenetic fluids.

From these fluids porcelanite is precipitated only in narrow ranges of the host sediment characterized by extremely low detrital mineral contents.

High-spatial resolution analyses along profiles through two porcelanite layers by fs LA-MC-ICP-MS show opposing trends of $\delta^{30}\text{Si}$ and Al/Si ratios and indicate a kinetic control on the isotope fractionation factor, varying in response to the chemical composition of the fluid.

We identified processes of fluid generation, isotope fractionation, and chemical controls on precipitation during early stages of silica diagenesis that can well be extrapolated to conditions of ancient chert formation. The understanding of these processes can help discerning diagenetic fingerprints from source signals in the silicon isotope record of chert.

[1] Egan *et al.* (2012) *Geochim. Cosmochim. Acta.* **91**, 187-201.