

Redox controls on the fractionation of chalcophile and siderophile elements

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Virtually all chalcophile and siderophile elements exist in more than one valence state over the range of redox conditions inferred for solar system materials. Thus, a complete understanding of the geochemical behaviour of these elements during planetary differentiation process (e.g. core-mantle-crust formation) requires knowledge of both (i) the effect of fO_2 on their solubilities and partitioning between metal, sulfide, silicate melts and minerals; and (ii) the range of redox conditions prevailing during these processes.

Some chalcophile/siderophile elements are especially important because they belong to radiogenic isotope decay systems and, therefore, can provide clues about the timing of planetary differentiation processes. The ^{182}Hf - ^{182}W decay has been widely used to constrain the time of core-mantle differentiation in the Earth-Moon system due to the contrasting geochemical properties of Hf (lithophile) and W (siderophile). Tungsten has always been regarded as a multivalent element, although XANES studies indicate that up to redox conditions approaching IW-3 (IW= iron-wüstite), 6+ is the dominant W valence state. Mineral/melt partitioning studies, however, reveal that even tiny proportions of W^{4+} are sufficient to increase the bulk partitioning of W between basalt and peridotite ~2 orders of magnitude from IW+3 to IW-3. The fractionation of Re from Os, which are part of the ^{187}Re - ^{187}Os decay system that is widely used to trace crust-mantle evolution, is strongly dependent on fO_2 since oxidizing conditions make Re increasingly more lithophile.

The redox-controlled fractionation of key elements like W, Re and Os have profound implications for understanding core-mantle-crust differentiation processes. However, the redox state of the Earth's upper mantle, particularly concerning the more oxidized nature of the mantle beneath subduction zones, remains unresolved. New approaches to estimate fO_2 in mineral-rock assemblages, such as XANES spectroscopy in minerals and melts, and trace-element partitioning relations, such as V-in-olivine, may provide extra clues which are relevant for interpreting the geochemical behaviour of chalcophile and siderophile elements.