

Selenium coprecipitated with barite as a new redox indicator

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Redox potential (Eh) is an important physico-chemical factor that can affect behaviors of various ions in water. A number of previous studies have suggested that Eh was estimated by the solid-water distribution of redox-sensitive elements based on the effect of change of the oxidation state such as relative enrichment-depletion profiles of particular elements such as iron and manganese. However, the estimation of redox conditions based on these profiles may not be reliable because (i) elemental concentrations are influenced by many factors such as secondary adsorption-desorption reactions and diagenesis and (ii) only the relative evaluation of the redox condition is possible by the depth profile of particular elements. Thus, the aim of this study is to propose a new redox indicator using the oxidation states of redox sensitive element itself in a certain mineral to estimate directly the particular redox condition at the time of the mineral formation. Here, we examined incorporation behavior of selenium (Se) species to barite as a redox indicator for oxic-suboxic condition.

Coprecipitation experiments of Se with barite coupled with determination of Se oxidation state both in barite and water phases were conducted to investigate the influence of the oxidation state on the coprecipitation of Se into barite. The oxidation state of Se in water and barite were determined by HPLC-ICP-MS and X-ray absorption near-edge structure (XANES) at Se K-edge, respectively.

It was found that the Se(VI)/Se(IV) ratio in barite reflects the Se(VI)/Se(IV) ratio in water, which suggests that the oxidization state of Se in barite can work as a redox indicator showing the redox condition at the time of barite formation. Selenium(IV) is incorporated into barite under suboxic condition below the redox boundary of Se(VI)/Se(IV). Selenium(VI), on the other hand, is incorporated under oxic condition above the redox boundary of Se(VI)/Se(IV). Based on the distribution behavior of Se to barite, we conclude that the Se(VI)/Se(IV) ratio in barite can be used as a redox indicator whether barite was precipitated below or above the redox boundary of Se(VI)/Se(IV), the Eh region of which is different from the Fe(III)/Fe(II) and Mn(IV)/Mn(II) boundaries often employed as a signature of redox condition.

Insights into mantle processes from water and trace elements in olivine

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Olivine continues to be neglected in most trace element studies of mantle rocks. This is in spite of the ability of modern analytical techniques to measure accurately and precisely a diverse and petrologically useful suite of elements and a burgeoning experimental interpretative framework of partition and diffusion coefficients.

We present the results of a detailed study of water and trace elements in olivine as evidence of their utility. Samples chosen for this study are harzburgite xenoliths dredged from volcanic cones close to Ritter Island in the West Bismarck Arc, Papua New Guinea. From textural observations, these samples are assigned to 'residual' or 'reacted' groups. 'Residual' samples display textures indicating an origin through melt extraction and sub-solidus cooling. Olivines have very low concentrations of all incompatible trace elements and water, consistent with the nominally cpx-free mineralogies. Concentrations of Al (0.5-9.1 ppm), Cr (5.0-19.9 ppm) and V (0.09-0.63 ppm) are exceptionally low due to the exsolution of Cr-spinel plates during cooling to temperatures of ~ 600 °C.

'Reacted' samples display textures consistent with melt-rock reaction. Olivines reflect this in significant water and trace element enrichment and disequilibrium, with over an order of magnitude variation in Y (0.08-23.8 ppb), Ca (22.3-793.0 ppm), Na (0.6-22.8 ppm) and Cr (7.2-252.4 ppm) concentrations among crystals in individual samples on a sub-cm scale. These concentrations overlap with and diverge from those measured in 'residual' olivines.

We interpret this as re-equilibration of olivine during percolation of hydrous mantle-derived melts. The extreme trace element disequilibrium requires that this reaction occurred on a very rapid timescale, shortly before magmatic entrainment. Olivine is the only phase that records this late-stage chemical exchange, due to its high modal abundance and more rapid rates of trace element diffusion. Similar studies on olivine from mantle and magmatic rocks can shed new light on the mechanisms and timescales of melt-rock reaction, transport, differentiation and magma mingling.