EXAFS characterization of poorly crystalline ferric arsenate undergoing transformation to scorodite

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The removal of arsenic from hydrometallurgical process solutions and waste streams continues to be a critical technology in a number of industries. The mineral scorodite ($FeAsO_4.2H_2O$) is often the focus of attention because of its ability to fix arsenic in a stable crystalline phase. As such, the physical and chemical conditions necessary for scorodite formation from related species are a major concern in arsenic removal technologies. In this investigation, we follow the transformation of a poorly crystalline ferric arsenate to scorodite in an acidic (pH 2) nitrate medium at 80 ºC for 24 hours using, in part, As and Fe K-edge Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. EXAFS shows a consistent change in the As-Fe bond distance, As coordination number and As-Fe Debye-Waller factor during the transformation to scorodite. Large changes in EXAFS parameters occur around 9 hours of aging, which is consistent with x-ray diffraction measurements. No evidence was observed to suggest an adsorbed arsenate intermediate. It is likely that the transformation to scorodite occurs through heterogeneous nucleation and crystallization within the poorly crystalline precursor material.

Mineral water concentration and H isotope evidence for decompressional dehydration during exhumation of deeply subducted continental crust

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Diverse water species, including molecular water (H_2O), hydroxyl groups (OH^-), and structurally incorporated hydrous complexes (e.g., Si-OH or Al-OH), can flux in or out both hydrous and anhydrous minerals in the processes of prograde or retrograde metamorphism, making important contributions to fluid regime and chemical geodynamics of continental subduction and exhumation. In terms of the study of H and O isotopes in minerals from ultrahigh-pressure (UHP) eclogite and garnet amphibolite associations, it was hypothesized that the decompression exsolution of hydroxyl from nominally anhydrous minerals in UHP metamorphic rocks can form an important source of retrograde fluid.

Mineral H isotope and total water concentration were analysed by the TC/EA-MS continuous flow technique for garnet and omphacite from UHP eclogites in the Sulu orogen, China. The results show δD values of −116 to −64‰ for garnet and −104 to −82‰ for omphacite. Both equilibrium and disequilibrium H isotope fractionations were observed between coexisting garnet and omphacite, suggesting fluid-assisted H isotope exchange at local scales during amphibolite-facies retrogression. Total water concentrations are 522 to 1584 ppm for garnet and 1170 to 20745 ppm for omphacite. In particular, negative correlations occur between δD value and water concentration for both garnet and omphacite, demonstrating the decompression exsolution of hydroxyl during exhumation in the light of experimental results that solubilities of hydroxyl in nominally anhydrous minerals increase with pressure.

The observations supporting the internal origin of retrograde fluid also include: (1) measured similarities in the O isotope composition of minerals between eclogite and garnet amphibolite and between vein and host eclogite, (2) measured disequilibria in H isotope fractionation between phengite and zoisite in eclogite and between biotite and epidote in gneiss as well as in O isotope fractionation between omphacite and garnet in eclogite, and (3) measured U-Pb ages for HP veining, fluid-facilitated HP eclogite-facies recrystallization and amphibolite-facies retrogression relative to the peak UHP metamorphic event. There is a growing body of evidence for the origin of retrograde fluid from the UHP rocks themselve.