



USER MEETING 2016

24-25 NOVEMBER

National Centre for Synchrotron Science



Ansto



Contribution ID: 190

Type: Oral

XAS and XFM investigations of arsenic uptake in hydrothermal apatite

Thursday, 24 November 2016 11:00 (15 minutes)

Element substitution that occurs during fluid-rock interaction permits assessment of fluid composition and interaction conditions in ancient geological systems, and provides a way to fix contaminants from aqueous solutions. We conducted a series of hydrothermal mineral replacement experiments to determine whether a relationship can be established between arsenic (As) distribution in apatite and fluid chemistry. Calcite crystals were reacted with phosphate solutions spiked with As(V), As(III), and mixed As(III)/As(V) species at 250 °C and water-saturated pressure. Arsenic-bearing apatite rims formed in several hours, and within 48 hours the calcite grains were fully replaced. X-ray Absorption Near-edge Spectroscopy (XANES) data show that As retained the trivalent oxidation state in the fully-reacted apatite grown from solutions containing only As(III). Extended X-ray Fine Spectroscopy (EXAFS) data reveal that these As(III) ions are surrounded by about three oxygen atoms at an As-O bond length close to that of an arsenate group (AsO₄³⁻), indicating that they occupy tetrahedral phosphate sites. The three-coordinated As(III)-O₃ structure, with three oxygen atoms and one lone electron pair around As(III), was confirmed by geometry optimization using ab initio molecular simulations.

The micro-XANES imaging data show that apatite formed from solutions spiked with mixed As(III) and As(V) retained only As(V) after completion of the replacement reaction; in contrast, partially reacted samples revealed a complex distribution of As(V)/As(III) ratios, with As(V) concentrated in the center of the grain and As(III) towards the rim. Most natural apatites from the Ernest Henry Iron Oxide Copper Gold deposit, Australia, show predominantly As(V), but two grains retained some As(III) in their core. The As-anomalous amphibolite-facies gneiss from Binntal, Switzerland, only revealed As(V), despite the fact that these apatites in both cases formed under conditions where As(III) is expected to be the dominant As form in hydrothermal fluids.

Our study shows for the first time that As(III) can be incorporated into the apatite structure, although not as efficiently as As(V). Uptake of As(III) is probably highly dependent on the reaction mechanism. These results show that incorporation of As in apatite is a complicated process, and sensitive to the local fluid composition and kinetic effects during crystallization.

Keywords or phrases (comma separated)

hydrothermal apatite, mineral replacement, arsenic, XAS, XFM

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No

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No

Are you an ECR? (<5 yrs</br>since PhD/Masters)

No

What is your gender?

Male

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Session Classification: Concurrent Session 1: Earth & Environment

Track Classification: Earth and Environment