

## Spectroscopic investigation of heavy metal incorporation into Hydroxylapatite

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Hydroxylapatite (HAP,  $[\text{Ca}_5(\text{PO}_4)_3\text{OH}]$ ) has been the subject of interest in geochemical and biological processes because of its high reactivity. Metal partitioning to HAP has been shown to be a key factor in controlling the fate and transport of metals as well as their bioavailability. The most effective mechanism for sequestration of a variety of heavy metals and radionuclides may be via coprecipitation. In this study we used EXAFS spectroscopy to examine the modes of incorporation of As, Se, and Zn with HAP.

As(V)-, Se(VI)- and Zn-doped HAP samples were synthesized at 75 °C to provide dopant concentrations up to 900 ppm for study by EXAFS. Fitting results for As-doped HAP show the local coordination of As is similar to that found in Johnbaumite ( $[\text{Ca}_5(\text{AsO}_4)_3(\text{OH})]$ ), with ~9 Ca atoms at distances of 3.25-3.68 Å. Se local coordination in Se-doped HAP samples yielded similar fitting results with ~8-9 Ca atoms at 3.17-3.65 Å. These results confirm that As(V) and Se(VI) substitute for P in HAP. Our results do not provide information regarding charge compensation for P substitution by Se.

Zn K-edge XANES spectra of Zn-doped HAP are found to differ from model compounds (hopeite, hydrozincite,  $\text{Zn}_3(\text{PO}_4)_2$ ,  $\text{Zn}(\text{OH})_2$ ,  $\text{ZnCO}_3$ , ZnO, and Zn-phosphate precipitate synthesized at similar experimental conditions), suggesting that precipitation of a Zn phase is unlikely. Best fit EXAFS results indicate that Zn occurs in tetrahedral coordination with O at ~1.96 Å. More distant shells were fitted with ~1 P at ~3.16 Å, ~1 P at ~3.58 Å and 1~2 Ca at ~4.05 Å, suggesting Zn incorporation into Ca sites in HAP with highly distorted local environments expected.

Results of this study also provide coprecipitation systematics, as well as insight to metal incorporation mechanisms in human bone and teeth.

## Taking the temperature of rhyolites from the Yellowstone hotspot track: Evaluation of the Ti-in-Quartz method

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Indirect insight into crustal thermal conditions and mafic magma fluxes associated with hotspot magmatism in continental settings can be gained by evaluating temperatures and volumes of associated crustal melts (rhyolites). Conditions of their formation provide critical constraints on the thermal structure of the underlying crust and on physical processes attending crustal modification by invasive basaltic magmas.

We have used Ti-in-quartz (TitaniQ) thermometry [1] to evaluate magmatic T for some 30 rhyolite lavas and ignimbrites from the Snake River Plain and Yellowstone based on LA-ICPMS analysis of quartz phenocrysts. Comparison of TitaniQ Ts with those (~750-1000°C) based on 'standard' thermodynamic equilibria between other mineral pairs (feldspars, pyroxenes, oxides) indicates best agreement with two-pyroxene thermometry (where applicable), but also illuminates potential problems in using some of the standard methods. TitaniQ Ts depend on assumptions regarding activity of Ti in the host magmas, which appears to vary significantly. If this problem is surmounted, the TitaniQ method potentially can provide a self-consistent thermometry for a wide variety of quartz-bearing rhyolites.

So far, the ignimbrites studied display relatively small diversity in quartz Ti contents, hence T, compared to associated lavas. Quartz geochemistry thus appears to be a useful tool for stratigraphic correlation between widespread ignimbrites. The lavas studied commonly are more diverse and often carry complexly zoned and resorbed quartz, indicative of complicated magmatic histories. Collectively, these data suggest that SRPY rhyolites form by anhydrous melting at crustal Ts near 1000°C or more. If melting occurs at mid-crustal levels or shallower, such high Ts imply time-integrated inputs of basaltic magma into the crust at volumes on the order of 1/4 to 1/3 of the present crustal thickness.

[1] Wark & Watson (2006).