Reliability of LA-MC-ICP-MS Hf isotope analyzes: Insights from natural and synthetic zircons

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In situ Hf isotopic measurements by LA-MC-ICP-MS typically require significant Lu and Yb isobaric interference corrections. To assess the viability of atomic isobaric corrections on Hf isotopic measurements, we prepared synthetic zircons with variable REE contents. Analyses of these zircons and natural zircons (91500, BR266, MAD, SAME, FC-1, and R33) using our Nu Plama show that accuracy and precision of Hf isotopic measurements decrease systematically with increasing REE/Hf ratios. The synthetic zircon experiments indicate that at Lu-Yb/Hf ratios resulting in around 20 percent or less correction between uncorrected and Lu-Yb corrected ^{176}Hf/^{177}Hf ratios, we can routinely obtain accurate and precise Hf isotopic data. Systematically more inaccurate and imprecise Hf isotopic data are observed at progressively higher correction levels. Our experiments show that at lower REE/Hf the REE oxide interferences on the masses of interest are, to a certain extent, self-cancelling and do not affect the Hf measurements at the 1 eHf level (2s). Above the ~20% correction threshold, however, the REE oxides differentially affect a number of ratios used in the Hf isotope data reduction protocol. As a result, Lu-Yb peak stripping based on atom % of the constituent isotopes becomes a progressively less adequate proxy for all isobaric interferences. For example, R33, which has relatively high REE/Hf ratios compared to FC-1, suffers in both accuracy and precision (± 2 eHf 2s, on average) vs. FC-1 (1 eHf 2s). Our experiments support previous suggestions of the ~20% correction limit and directly tie this limit to REE oxide formation. Unfortunately, the formation of these oxides appears to be too irregular to apply accurate corrections at higher correction percentages, which suggests that their production reflects multiple modes (e.g. during ablation, ionization, and transfer from the plasma to the mass spectrometer). Consequently, the extent of oxide production and limit of viable correction is likely to be dependent to some degree on instrumental and experimental conditions as well as target composition.

Mechanism of selenite sequestration by low-soluble phosphate minerals

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Selenium-79 (the half-life of 6.5×10^4 yrs) in high-level radioactive waste needs to be safely disposed in geological repository. However, Se has low affinity against various sorbents due to the common anion species such as selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}). On the other hand, apatite was proposed as an efficient sorbent for anion species as well as Pb salt of Se oxoacid with low solubility. In order to understand the mechanism of Se sequestration by apatite and pyromorphite in the Se-Pb-P-O system, we have conducted sorption experiments under four conditions: (*i.*) hydroxylapatite (HAP, Ca_5 $(PO_4)_3OH$) reacted in 0.5 mM Na_2SeO_3 solution at initial pH of 5.0 or 9.5; (*ii.*) hydroxypyromorphite (HPY, Pb_5 $(PO_4)_3OH$) reacted in 0.5 mM Na_2SeO_3 solution at initial pH of 5.0; (*iii.*) HAP reacted in the solution with 0.5 mM Na_2SeO_3 and 0.5 mM Pb $(NO_3)_2$ at initial pH of 5.3. All experiments were carried out at room temperature for 30 min. to 30 d. Analytical technique includes an inductively coupled plasma-atomic emission spectrometry (ICP-AES), a powder X-ray diffraction analysis (XRD), and transmission electron microscopy (TEM).

In the condition (*i.*), Se concentration in solutions did not change significantly during the reaction and the XRD shows no peak besides HAP peaks at both pHs, indicating that Se sorption proceeds by surface adsorption in addition to anion exchange. HAP seems not effective sorbent under this experimental condition due to its limited number of Se adsorption site on the HAP surface. In case of (*ii.*), XRD patterns show peaks of molybdomenite, $PbSeO_3$, $P2_1/m$, z = 2. The concentration of Se decreased from 0.49 mM to 0.30 mM in 30 d, while P concentration gradually increases to 0.06 mM, indicating the formation of $PbSeO_3$ as a consumption of Pb^{2+} released from HPY dissolution. In the condition (*iii.*), $PbSeO_3$ with structure of $P2_1/c$ (z = 8) precipitated in the solution prior to contact with HAP. Both Se and Pb concentrations decreased from 0.05 mM and 0.10 mM to under detection limit. Moreover, TEM reveals that Pb and Se nano-needles (40 × 10 nm) formed epitaxially on the tip of HAP.

These results suggest that the form of sequestered Se is largely dependent of the combination of the initial form of Pb^{2+} and the template crystals. Consequently, Se sequestration is constrained by complex kinetic processes between different forms of Pb selenite in the presence of low-soluble Pb-phosphate.