

## Evaluation of sources of error in $^{186}\text{Os}/^{188}\text{Os}$ measurements via NTIMS

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The  $^{190}\text{Pt}$ - $^{186}\text{Os}$  decay system may be useful for monitoring signals of core/mantle interaction in plume-derived lavas [c.f., 1]. However, the total natural variation in  $^{186}\text{Os}/^{188}\text{Os}$  is small (~150 ppm), requiring the highest levels of accuracy and precision in  $^{186}\text{Os}/^{188}\text{Os}$  measurements to discern natural variations that may reflect such interaction. Previous studies have examined several potential sources of systematic and non-systematic error in  $^{186}\text{Os}/^{188}\text{Os}$  measurements deriving from uncertainties in the O-isotope composition of  $\text{OsO}_3^-$ , potential interferences from  $\text{PtO}_2^-$ ,  $\text{PtO}_3^-$ , and  $\text{WO}_3^-$ , and departures from exponential mass fractionation [2]. We have undertaken a  $^{186}\text{Os}/^{188}\text{Os}$  study of both laboratory Os standards and natural samples to better quantify the primary sources of analytical error in  $^{186}\text{Os}/^{188}\text{Os}$  measurements and refine analytical procedures to minimize these errors.

Inter- and intra-run variations in oxygen isotope composition of measured  $\text{OsO}_3$  peaks produce correlated errors in  $^{186}\text{Os}/^{188}\text{Os}$ ,  $^{189}\text{Os}/^{188}\text{Os}$ , and  $^{190}\text{Os}/^{188}\text{Os}$  ratios. Although significant O-isotope variation is observed between analyses, intra-run variation is sufficiently small that O-isotope composition determination through pre- and post-run measurement of  $^{192}\text{Os}^{16}\text{O}_2^{18}\text{O}$  and other high-mass oxide peaks is sufficient. Uncertainties derived from oxide corrections can be further reduced by utilizing the  $^{189}\text{Os}/^{188}\text{Os}$  ratio for mass fractionation corrections rather than  $^{192}\text{Os}/^{188}\text{Os}$ , but the reduced error from oxygen isotope uncertainties is offset by increased error in the fractionation factor. However, the excellent reproducibility of  $^{189}\text{Os}/^{188}\text{Os}$  measurements (<10ppm  $2\sigma$ ) using  $^{192}\text{Os}/^{188}\text{Os}$  for mass fractionation indicates that these uncertainties are not the primary sources of error in  $^{186}\text{Os}/^{188}\text{Os}$  measurements.

For the quantities of Os and beam intensities utilized in previous  $^{186}\text{Os}/^{188}\text{Os}$  studies (several 10s of ng Os, ~80-120 mV  $^{186}\text{Os}$  with a  $10^{11}$  ohm resistor), the largest source of analytical error is shown to be Johnson Noise on interblock baseline measurements, which significantly exceeds error derived from counting statistics. Because  $^{186}\text{Os}$  is a relatively minor isotope of Os (~1.6%), it is affected by Johnson Noise error propagation to a much greater extent than higher abundance isotopes. Analytical precision on the smaller Os-isotope peaks can be significantly improved without increasing sample size simply by increasing the duration of baseline measurements in proportion to signal measurement time [3]. Further improvement is obtained by utilizing a  $10^{12}$  ohm resistor for measurement of  $^{184}\text{OsO}_3$  and  $^{186}\text{OsO}_3$  peaks. Finally, several  $^{186}\text{Os}/^{188}\text{Os}$  analyses previously reported in the literature appear to be compromised by an as-yet unidentified, possibly organic interference that impacts both the  $^{186}\text{Os}/^{188}\text{Os}$  and  $^{184}\text{Os}/^{184}\text{Os}$  ratios. We present an improved method for monitoring potential interferences in future  $^{186}\text{Os}/^{188}\text{Os}$  studies.

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## Reactivity of $\text{U}^{\text{VI}}$ with pure, oxidized, and Ti-substituted magnetites

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Reduction of  $\text{U}^{\text{VI}}$  to  $\text{U}^{\text{IV}}$  through coupled biotic-abiotic processes can significantly decrease uranium mobility in subsurface environments. To understand the abiotic factors contributing to this process, we investigated the reduction of  $\text{U}^{\text{VI}}$  to  $\text{U}^{\text{IV}}$  by magnetite, a common rock forming mineral and product of microbial  $\text{Fe}^{\text{III}}$  respiration.  $\text{U}^{\text{VI}}$  reactivity with pure, stoichiometric magnetite ( $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$ ,  $\text{Fe}^{2+}/\text{Fe}^{3+} = 0.5$ ) is compared to that with a series of oxidized ( $\text{Fe}^{2+}/\text{Fe}^{3+} < 0.5$ ) and Ti-substituted magnetites.  $\text{Ti}^{4+}$ -for- $\text{Fe}^{3+}$  substitution is common in natural magnetite [1, 2] and results in a solid solution ( $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ ,  $0 < x < 1$ ) where  $\text{Ti}^{4+}$  incorporation is charge balanced by proportional increases in  $\text{Fe}^{2+}$ .

Using x-ray absorption spectroscopy (XANES and EXAFS) at the  $\text{U L}_{\text{III}}$ -edge we observe that the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio in magnetite is a major control on its ability to reduce  $\text{U}^{\text{VI}}$ . Stoichiometric and partially oxidized magnetites ( $\text{Fe}^{2+}/\text{Fe}^{3+} \geq 0.38$ ) reduce  $\text{U}^{\text{VI}}$  to uraninite ( $\text{U}^{\text{IV}}\text{O}_2$ ) nanoparticles, whereas more oxidized magnetites ( $\text{Fe}^{2+}/\text{Fe}^{3+} < 0.38$ ) adsorb  $\text{U}^{\text{VI}}$  as an inner-sphere complex without transferring electrons. The observed redox reactivity between magnetite and  $\text{U}^{\text{VI}}$  can be correlated with measured reduction potentials for magnetite and with published thermodynamic parameters for  $\text{U}^{\text{IV}}/\text{U}^{\text{VI}}$  redox couples [3].

Titanomagnetite nanoparticles with Ti formula contents up to  $x = 0.5$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios between 0.5 and 1.2 can also reduce  $\text{U}^{\text{VI}}$  to  $\text{U}^{\text{IV}}$ . EXAFS spectra indicate that the reduced  $\text{U}^{\text{IV}}$  atoms are *not* incorporated in uraninite. The speciation of  $\text{U}^{\text{IV}}$  appears to be controlled by Ti-content and not by the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio, as the reduction of  $\text{U}^{\text{VI}}$  by partially oxidized  $x = 0.5$  titanomagnetite results in the same non-uraninite  $\text{U}^{\text{IV}}$  species.

This work highlights previously unexplored thermodynamic and geochemical factors that may influence the speciation and solubility of uranium in the subsurface. The observation of non-uraninite  $\text{U}^{\text{IV}}$  species in this study, as well as in carbonate and phosphate bearing systems in previous studies [4-6] suggests the need for a better understanding of the stability of reduced  $\text{U}^{\text{IV}}$ .

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