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Synthesis of small aqueous rhodium clusters for kinetic studiesJ.R. HOUSTON¹, B.L. PHILLIPS² AND W.H. CASEY^{1,3}¹Department of Chemistry, University of California, Davis, CA, 95616 USA (jrhouston@ucdavis.edu)²Department of Geosciences, State University of New York, Stony Brook, NY 11794 USA³Department of Land Air and Water Resources, University of California, Davis, CA 95616 USA (whcasey@ucdavis.edu)

Small aqueous rhodium complexes are ideal geochemical models for the polymers that form on mineral surfaces and for dissolution. They are structurally similar to geochemically relevant surface functional groups and metal clusters such as the aluminum polyoxocations, but are substitutionally inert. Slow exchange of bound water molecules and hydroxyl bridges from the rhodium metal allow the oxygen exchange kinetics to be studied using spectroscopic techniques such as oxygen-17 NMR, since ¹⁷O can be added to specific sites in the molecules. Additionally, these small rhodium clusters can be used to validate computational models that predict rates of geochemical reactions.

Our research efforts focus on synthesizing small aqueous rhodium clusters, both in solution and in the solid phase, in order to ultimately investigate the oxygen exchange-kinetics using O-17 NMR. Rhodium multimers were synthesized by aging a pure solution of the rhodium monomer at high pH. The isolation of the various oligomers generated during the polymerization process was accomplished using ion exchange chromatography. The solid phase of each rhodium oligomer was prepared by precipitating the rhodium multimer out of solution as the “active hydroxide”. Characterization of these various rhodium clusters was accomplished using a variety of techniques, CE, UV-vis, Rh-103 and O-17 NMR. The ¹⁷O-label can be added at distinct steps in the synthesis procedure, resulting in molecules with specific atoms that are isotopically enriched for spectroscopy.

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Transition metal isotope fractionation on sulfide mineral precipitationI.B. BUTLER¹, C. ARCHER², S. ERLICH³, D. VANCE⁴, A. MATTHEWS⁵ AND D. RICKARD¹¹School of Earth, Ocean and Planetary Sciences, Cardiff University, U.K. (Butler@earth.cf.ac.uk)²Dept. of Geology, Royal Holloway, University of London, U.K.³Geological Survey of Israel, Jerusalem, Israel.⁴Department of Earth Sciences, University of Bristol, U.K.⁵Institute of Earth Sciences, Hebrew University of Jerusalem, Israel.

The isotopic fractionation of Fe and Cu on FeS and CuS precipitation was studied at acid pH and 2–40°C. Both FeS and CuS follow Ostwald step rule behaviour, and the first precipitate is the most soluble and least thermodynamically stable phase. The formation of a condensed phase proceeds from discrete Cu(II)_(aq), Fe(II)_(aq) and S(-II)_(aq) species through complexes to multinuclear aqueous clusters which are the building blocks of the nanoparticulate solid [1]. Cu(II)_(aq) precipitates as Cu(I)S (covellite) and Fe(II)_(aq) precipitates as Fe(II)S (mackinawite). Cu(I) forms in solution [1] during Cu-S bond formation and the condensation of higher order clusters from Cu₃S₃ which is associated with release of Cu(II) back to solution [1]. The mechanism of FeS precipitation proceeds via two competing processes which are dependent upon S(-II) speciation and consequently pH [2]. These processes may be described by Eigen-Wilkins kinetics with the H₂S mechanism proceeding via clusters and the HS⁻ mechanism proceeding via a more rapid direct route [2] to produce two end-member mackinawite phases [3]. On precipitation of FeS, we recorded ⁵⁷Fe kinetic isotope fractionations of ΔFe(II)-FeS = 0.96‰ IRMM, which reduced to 0.29‰ on ageing in contact with Fe(II)_(aq) for 168 hours at 20°C. No effect of temperature was observed in the range 2–40°C. On precipitation of CuS we recorded mean ⁶⁵Cu kinetic isotope fractionations of ΔCu(II)-CuS = 3.06‰ NIST SRM 976, and this fractionation also reduced on ageing. There is a distinct dependence of fractionation factor on temperature in the 2–40°C range. The observed data are consistent with precipitation mechanisms described above. ⁶⁵Cu depletion of the precipitated phase may be associated with electron transfer and ejection of Cu(II) during cluster condensation. ⁵⁷Fe depletion of the condensed phase is consistent with rapid exchange of inner sphere H₂O molecules with H₂S [2]. Thus isotope fractionations recorded in sulfide phases are the product of aqueous phase reactions which precede the formation of the condensed phase.

References

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