Advances in crustal geochronology of shales and sulfide minerals using ^{187}Re-^{187}Os

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Analytical advances over the last 15 years are primarily responsible for the recent widespread application of the ^{187}Re-^{187}Os isotope system. The element pair has important geochemical differences compared to systems like Rb-Sr or Sm-Nd, which permits geochronology in crustal matrices not otherwise amenable for dating. Despite Re and Os being among the rarest elements in Earth's crust, the development of high-yield, high ionization efficiency, ultra low-blank analytical methods allows high-precision crustal geochronology to be explored. It is now clear that the Re-Os geochronometer has large advantages over other isotope methods for some specific matrices. These include determination of depositional ages for organic-rich mudrocks like black shales and direct dating of sulphide minerals. Direct determination of depositional ages from shales has widespread application for geological timescale calibration, stratigraphic correlation and basin analysis studies; determined Re-Os ages can be $< \pm 1\%$ uncertainty (2σ), and are demonstrably accurate. The Re-Os shale geochronometer appears unaffected by metamorphism up to chorite grade, but is readily disturbed by fluid flow events, typically evidenced as veining, after deposition. For sulphide minerals, we have investigated Re-Os systematics in the common sulfide minerals pyrite, arsenopyrite, pyrrhotite, chalcopyrite, sphalerite and galena. We find that pyrite and arsenopyrite, although containing low ppb levels of Re and ppt level of ^{187}Os*, can provide precise age determinations in various ore deposit types. These minerals appear robust to post-formational disturbance to at least 500ºC based on case studies. Arsenopyrite Re-Os geochronology is of particular significance for determining the timing of formation of many gold deposits, given the common genetic association between arsenopyrite and gold. We find that pyrrhotite and sphalerite are not robust minerals for preserving primary Re-Os age information, and that galena rarely contains measurable Re.

Molecular modelling of metal speciation in aqueous solution and at the mineral surface

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Molecular dynamics simulations and spectroscopic techniques are often used to examine the structure of water and the coordination of ions at a mineral surface. In this study, both approaches are first validated by investigating aqueous speciation. Molecular simulations were performed to examine if a flexible SPC water model with a consistent set of ion force field parameters can reproduce experimental trends in aqueous speciation for the alkaline earth metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) and chloride (Cl^-). Solvent-shared ion pairs (SSHIPs), in which the ions are separated by one water molecule, were calculated to have lower potential energy minima than contact ion pairs (CIPs) for $MgCl^+$, $CaCl^+$, and $SrCl^+$. In contrast, the CIP for $BaCl^+$ appears to be slightly more stable than the SSHIP. Calculated free energy profiles for the adsorption of these metal cations to the gibbsite (001) surface suggest that they adsorb as outer-sphere complexes. However, the larger the cation, the more readily a mixture of inner- and outer-sphere surface complexes forms.

Free energy profiles for aqueous species MNO_3^+ (M = metal) were calculated to support Raman studies of aqueous metal-nitrate solutions. For Ca^{2+}, Sr^{2+}, and Pb^{2+}, the calculations suggest CIPs are more stable than SSHIPs. The free energy profile for $MgNO_3^+$ is very different from those for the other cation-nitrate pairs and suggests that the $MgNO_3^+$ CIP is highly unstable. These calculations corroborate spectroscopic results that show that CIP formation decreases with increasing cation charge density: $Pb^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$.

For Mg^{2+}, the studies of both aqueous ion-pairing and adsorption suggest that the energy required to remove a water of hydration strongly controls its binding properties. To investigate this further, adsorption experiments and simulations over a range of temperatures are underway. Initial results suggest that with increasing temperature, Mg^{2+} will adsorb to gibbsite as an inner-sphere complex.

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