

Rhenium geochemistry under sulfidic conditions: When the sulfide acts as both ligand and reducing agent

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Rhenium is a rare critical element fundamental to high-tech products and emerging innovations industries, with limited possible substitution¹. This element is mainly used in high-temperature superalloys to manufacture turbine blades for jet engines, in power generation applications, and in platinum-rhenium catalysts for the petrochemical industry. Rhenium (Re) is soluble in a redox state VII as highly soluble perrhenate ion (VII) - ReO_4^- and in reduced and little soluble form as rhenium (IV) oxide - $\text{ReO}_{2(s)}$ and rhenium sulfide $\text{ReS}_{2(s)}$.

The geochemical behavior of redox-sensitive trace metal rhenium (Re) has been postulated to record information about the extent of low oxygen depositional conditions in the oceans. In modern oxygenated oceans, Re speciation is thought to be dominated by the geochemically inert perrhenate anion at concentrations of $\sim 40 \text{ pM}^2$. In rocks, the highest enrichment of Re is found in sulfide-rich euxinic settings, e.g., black shales, where concentrations of hundreds of ppb of this trace element are found³. However, our understanding of the mechanism leading to these Re deposits is not precise, while it is critical to explain Re geochemistry. In the presence of sulfide, the oxyanion perrhenate is transformed by a step-wise substitution of O atoms by S atoms, forming thioperrhenate species ($\text{Re(VII)O}_{4-x}\text{S}_x$) in a similar way to Mo^4 , and then Re is reduced, but the later pathway is unknown.

In our study, we prepare high sulfide solutions with different Re concentrations at different pH. Re(VII) is gradually thiolated and finally precipitated by S atoms, forming $\text{Re(IV)S}_{2(s)}$ or $\text{Re}_2\text{S}_7(s)$ particles. We characterized for the first time the reduction pathway and grew Re-S nanoparticles from a few nanometers to hundreds of nanometers after the thiolation species formation. The discovery of this research system helps to expand our understanding of the geochemistry of the sulfur-rhenium system and the stability and bioavailability of rhenium species in the past and present natural environments, as well as in environments relevant to pharmaceutical and mining industries. Furthermore, by considering the reductive mineralization of Re on a near-atomic scale level, this work opens the field to new studies in trace elements crystallization in highly oversaturated sulfide environments.