

Uncovering Sulfur Redox Evolution via Mineral Chemistry Networks

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Sulfur (S) is a crucial element in global biogeochemical cycling and planetary redox evolution. Sulfur-containing minerals are important records of chemical speciation and redox that reflect the local environmental conditions at the time of their formation. However, the redox state of S in hundreds of mostly sulfide and sulfosalt minerals is unknown because of complex sulfur redox chemistry and associations with other redox sensitive elements. Here, we use mineral chemistry network analysis and the weighted Mineral Element Electronegativity Coefficient of Variation ($wMEE_{CV}$) metric to investigate the element interactions and localities of sulfur-containing minerals from the Mineral Evolution Database (MED) and infer the redox state of sulfur in minerals where it was previously unknown. Louvain community detection of the sulfur mineral chemistry redox network reveals that there are three main separate network communities that are separated by redox state. The S^{6+} community includes minerals that contain the S^{6+} redox state and a small number of S^{4+} and S^{2+} minerals, the S^{2-} community includes S^{2-} -containing minerals, and the S^u community includes minerals in which the redox state of sulfur is unknown. The $wMEE_{CV}$ values of the S^u community closely overlap with the $wMEE_{CV}$ values of the S^{2-} community, but do not overlap with the $wMEE_{CV}$ values of the S^{6+} community, indicating the S^u community minerals predominantly contain S^{2-} . The $wMEE_{CV}$ values of S^{6+} community minerals expand through time, coinciding with atmospheric oxygenation and lithospheric oxidation from the late Proterozoic to Phanerozoic. Assuming that S^u community minerals contain S^{2-} , as supported by their network chemical associations and $wMEE_{CV}$ values, then S^{2-} -containing minerals make up the majority (~74.9%) of all non-oxygen containing mineral localities in the MED. The abundance of S^{2-} -containing minerals illustrates the significance of reduced S in the geosphere as an important factor linked to organic matter diagenesis, a crucial substrate in microbial metabolic pathways, and as a widespread ligand for protein metal cofactors.