Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.30776

Isotopic (Cu, Zn, Fe) and geochemical fingerprinting of Mn oxides for understanding low-temperature Mn deposits

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Manganese oxides are strong metal scavengers and significantly influence the composition and chemical behavior of mineral systems. In addition, they are highly reactive and engage in various oxidation-reduction and cation-exchange reactions. They are essential constituents of deep-sea polymetallic Fe-Mn nodules and play a crucial role in the critical zone. Main terrestrial Mn ore deposits can either be generated from karst through carbonates dissolution, or from regolith via chemical weathering of a Mn-rich bedrock, or hydrothermal fluid circulation in the upper parts of the system where oxidation rate increases (Fig. 1).

In this study, we investigate tunnel K-bearing Mn oxides as proxies for the process leading to ore concentration and use them to classify Mn oxide deposits. We analyzed trace element concentrations and stable isotopes of Cu, Fe, and Zn in 24 naturally occurring Mn oxide samples from the coronadite group and romanechite. The results show that each deposit type has a distinct geochemical fingerprint. Especially, plot of La/Lu vs (Co+Ni) (Fig. 2a) allows classification and the assessment of the potential enrichment in critical elements (e.g., W, Co, Ni). Regolith-hosted deposits exhibit a broader range of compositions, likely reflecting the strong influence of the protore (Fig. 2b). In contrast, karst-hosted and hydrothermal deposits show more constrained geochemical conditions, resulting in more systematic metal enrichment processes. Results in Cu ($-0.09 < \delta^{65/63}Cu < 1.04$) and Zn isotopes ($-0.18 < \delta^{66/64}Zn < 1.19$) suggest typical redox and pH conditions according to each deposit type, providing insights into the petrogenetic processes driving Mn oxide precipitation.