

## **Biogeochemical co-evolution reflected in large Mn mineral database.**

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As the second most abundant transition metal on Earth, Mn is particularly sensitive to environmental redox states with its three different oxidation states in crustal minerals. The total categories of Mn minerals (476 mineral species) far exceed those containing most other redox-sensitive metals such as Ce (168 mineral species) and Cr (109 mineral species) (statistics from RRUFF database). Their compositional and structural diversity implies their great potential to reflect a broad range of complex environmental changes. By employing large mineralogical databases, it has been shown that the crystal chemical evolution of Mn minerals through geologic age was closely correlated with the evolution of biogeochemistry, oxygenation of atmosphere and oceans, and tectonic activities. Specifically, 1) During the transformation from Columbia to Rodinia supercontinent (1.8-0.8 Ga), relatively stable continents brought steady Mn fluxes (as a functional element for life) and nutrients (e.g., P, as a nutrient element for life) through weathering, which could be conducive to the expansion of the ecological niche of oxygenic photosynthetic organisms and the increase of oxygen source. 2) During 1.8-0.8 Ga, the frequent deposition and gentle increase in new Mn minerals may indicate the moderately active redox cycling and evolution of the Earth's internal and external environment even during the period of "orogenic quiescence". 3) Two depositional discontinuities were observed in the mineralization frequency of Mn minerals around GOE and NOE, which may be caused by the dramatic changes in the Earth's environment, including but not limited to the atmospheric oxygen levels. Therefore, the evolutionary records of Mn minerals could provide insights into the complex history of Earth's oxygenation and the underlying geological drivers.