

## Ecology and Evolution of Manganese Minerals: Implications for the Redox History of Earth and Life

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Manganese is a widespread redox sensitive transition element with three naturally occurring oxidation states and 560 mineral species, making it a useful proxy for the redox state of Earth's crust. Network analysis of Mn minerals using large mineral databases (mindat.org), which graphically displays the coexistence of mineral species, reveals three distinct clusters: (1) a central cluster composed of primary  $Mn^{2+}$  silicates, oxides, and carbonates formed in igneous intrusions, hydrothermal ores, and skarns, together with secondary  $Mn^{3+}$  and  $Mn^{4+}$  oxidative weathering products, (2) a side cluster of predominantly  $Mn^{2+}$  phosphates and oxides arising in granitic pegmatites, and (3) a side cluster of predominantly  $Mn^{2+}$  silicates arising in aegaitic intrusives. Clusters 2 and 3 display some co-occurrence with minerals in cluster 1, but not with each other.

Ages of first appearance reveal that common, primary igneous and metamorphic minerals of clusters 1 and 2 appear early in the geologic record, at or before 2.0 Ga. Oxidative weathering products in cluster 1 predominantly appear after photosystem-II initiated the Great Oxidation Event at ~ 2.3 Ga. Minerals of cluster 3 are geologically recent, appearing in the last 1.2 Ga as a result of further reworking and differentiation of the crust. The increasing prevalence of oxidized Mn minerals during the last 1 billion years raised the average oxidation state of crustal Mn in a pattern mirroring reconstructions of atmospheric oxygen, documenting the oxidation of Earth's crust in response to photosynthetic oxygen.

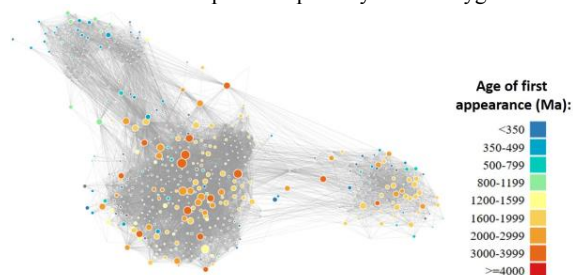


Fig. 1: A network diagram for Mn minerals – nodes represent Mn mineral species, colored by age of first appearance.