Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.29162

Rhodochrosite precipitation and the Mn cycle on early Earth.

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The availability of manganese (Mn) on early Earth bears significant implications for the co-evolution of early life and the environment. For instance, a Mn_4CaO_5 cluster constitutes the active site of photosystem II, a biological invention culminated in the Great Oxygenation Event that changed the fates of all redox elements, including Mn.

Due to its geochemical similarities to Fe, it has been assumed that the Mn cycle on early Earth was akin to the Fe cycle. However, the near-absence of large Mn deposit in the Archaean geologic record stands in stark contrast to the ubiquitous iron formations of similar ages. It, thus, falls on experimentation on Mn mineralisation to provide 1st order, robust geochemical constraints to fill the knowledge gaps.

This study investigates Mn^{2+} mineralisation and precipitation kinetics through three targeted experiments:

1. Spontaneous nucleation of rhodochrosite ($MnCO_3$) from oversaturated solutions.
2. Seeded $MnCO_3$ crystal growth rate as a function of solution chemistry.
3. Competing nucleation between $MnCO_3$ and Mn(II)-silicates in silica-rich solution.

Our laboratory observations demonstrate that:

1. Spontaneous nucleation of $MnCO_3$ requires significant solution supersaturation ($\Omega \geq 380$).
2. BET-surface area normalised crystal growth rates of $MnCO_3$ are similar to that of siderite ($FeCO_3$), but 6 orders of magnitude slower than that of calcite ($CaCO_3$).
3. Mn(II)-silicates do not nucleate in solution chemistry relevant to Precambrian seawater.

These quantitative constraints on Mn mineralisation and its sluggish kinetics explains the frequently reported rhodochrosite over-saturation in anoxic natural waters. The Mn cycle on early Earth was distinguished from the Fe cycle by its inactivity with SiO_2: whilst the level of Fe^{2+} in near-neutral, silica-rich Precambrian oceans was controlled by Fe(II)-silicate (e.g., greenalite) precipitation, Mn^{2+} could have accumulated up to 10s of mmol kg^{-1} without precipitating $MnCO_3$. Their distinct mineralisation pathways may offer an abiotic explanation for the spatial and temporal distribution of Mn and Fe in ancient marine sediments.