Distinguishing biogenic from abiotic manganese minerals using EPR spectroscopy

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Terrestrial manganese minerals can form either abiotically or biogenically at low temperature, e.g., in deep-sea nodules, rock varnish, or diagenetic phases. Manganese silicates, oxides, and carbonates also form readily at high temperature in igneous and metamorphic environments. Manganese is an important trace element in critical enzymes in all branches of the Tree of Life, and the redox chemistry of manganese in the sedimentary record influences various earth history climate change and oxygenation debates.

Manganese is relatively abundant in the Martian regolith (commonly ~0.45% [1], rare rock samples reaching 6.7 wt% MnO [2]). It should be anticipated that manganese oxyhydroxides, or other manganese minerals, will eventually be identified on the Martian surface, and their potential biogenicity will be critically scrutinised.

Kim et al. [3] suggest that electron paramagnetic resonance (EPR) spectral signatures can distinguish between abiotic manganese oxides that produce broad linewidths ranging from 1200 to 3000 G and biogenic manganese oxides that exhibit narrower EPR spectral linewidths of about 500 G.

We extend this Mn-mineral EPR spectral database and analyse a variety of abiotic and likely biogenic samples. We also extend EPR characterisation to manganese sulphides and silicates in addition to manganese oxyhydroxides.

It is clear that ferromagnetic resonance effects of trace iron oxide components within all classes of manganese minerals have potential to confound the EPR manganese mineral signal. However, other magnetic measurements might account for and correct these effects.

Detailed EPMA study of deep-sea manganese nodules in context of EPR spectra suggests that EPR offers particular power for understanding manganese redox in the Earth's recent and ancient biosedimentary record.

[1] Kieffer et al. (1992) In: *Mars*, 1–33; [2] Lanza et al. (2015) *Lunar Planet. Sci.*, **46**, 3893; [3] Kim et al. (2011) *Astrobiology*, **11**, 775–786.