

Evidence for dissimilatory manganese reduction and availability of free molecular oxygen during deposition of Mesoarchean Witwatersrand-Mozaan strata

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Marine shelf deposits, with an age of between 2.96 Ga and 2.92 Ga, in the lower part of the Witwatersrand-Mozaan succession [1] host several laterally extensive beds of manganiferous magnetic mudstone. The manganese occurs in early diagenetic kutnahorite and/or rhodochrosite concretions, set in a matrix of magnetic chlorite-quartz mudstone with wave-rippled siltstone laminae indicating deposition in shallow water above storm wave base. The Mn-carbonates have varied and highly depleted $\delta^{13}\text{C}$ values of -12 to -21‰. It is suggested that this enrichment of ^{12}C in the concretions relates to dissimilatory Mn (III and/or IV) reduction in presence of organic matter. However, this process requires a flux of free molecular oxygen as there is currently no process known that would oxidise significant quantities of Mn (II) to Mn (III and/or IV) in sedimentary environments under strictly anaerobic conditions.

Facies reconstructions indicate that the manganiferous units represent middle shelf strata that interfinger shoreward with inner shelf grey-green interlaminated mudstone and siltstone and offshore with outer shelf magnetic mudstone and starved shelf iron formation. This facies architecture with iron in deeper and manganese in shallower water is in agreement with a shallow water source of oxygen i. e. a population of oxygen-producing microbes in the photic zone. The indications for dissimilatory manganese reduction and the prerequisite of a flux of free oxygen in water of the Witwatersrand-Mozaan basin is in line with recent findings that denitrification reactions requiring free oxygen may also have developed during the Mesoarchean [2].

[1] Beukes & Cairncross (1991) *Trans. Geol. Soc. S. Afr.* **45**, 44–69. [2] Godfrey & Falkowski (2009) *Nature Geoscience* **2**, 725–729.

Ectomycorrhizal weathering, evidence from the field?

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Ectomycorrhizal fungi have been put forward as important agents in soil mineral weathering. Indeed, many laboratory experiments confirm the ability of these fungi to enhance mineral dissolution. But field evidence is still lacking.

Here we present field measurements of apatite weathering in a vegetation gradient in southern Norway. A natural occurring lead contamination, probably present since the last glacial, caused a gradient from bare soil, via sparse grass to healthy spruce forest. Because of the absence of a host tree, ectomycorrhizal fungi were absent in the bare soil and grass patches. We measured apatite content and soil solution chemistry in soil profiles in the different vegetation zones of the gradient.

To our surprise apatite loss for each soil depth could be described by the same, simple proton-based, dissolution function over the whole vegetation gradient:

$$(1) \quad r = K \cdot (H^+)^n$$

The parameters n and K increased with soil depth. The reaction order (n) increased from 0.18 in the top soil to 0.6 at 30–40 cm depth. It indicates changes in weathering mechanisms with depth, but constant over the vegetation gradient. Lower n and K values could indicate apatite surface interactions with simple and complex organic complexants. In the vegetation gradient, we found considerable amounts of spruce litter over the whole gradient, including on top of the bare soil. Our data indicate that it is the breakdown of dead organic matter, rather than ectomycorrhizal actions as major source or organic weathering agents.