

## The first truly oxic sub-basin in Earth's history: The Paleoproterozoic Hotazel Formation, South Africa

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The Hotazel Formation is part of the Voëlwater Subgroup of the Transvaal Supergroup, South Africa, and shows a well-preserved succession of chemical sediments comprising iron-formation (IF), manganese-formation (MnF) and minor carbonate. Its depositional age is ill-defined but bracketed by a 2.32 Ga Re-Os age for the Timeball Hill Formation and by a 2.25 Ga age for the start of the Lomagundi Event. The lithostratigraphy is characterized by three symmetrical cycles of IF and MnF, the lithologies of which are dominated by Fe oxides and carbonates and by Mn oxides and carbonates, respectively. It should be emphasized that the MnF in the Hotazel Formation constitutes the first *large-scale* sedimentary deposit of Mn oxides in the geological record.

The REY distribution of both, IF and MnF, shows HREE enrichment and positive anomalies of La, Gd, Lu and Y, i.e. super-chondritic Y/Ho ratios. All these features can also be seen in the 2.5 Ga old Kuruman IF and are clear evidence of a marine origin of these chemical sediments.

However, in contrast to the Kuruman IF, REY patterns of the Hotazel samples do not show positive Eu anomalies, which suggests that high-temperature hydrothermal "black-smoker-type" REY input into Hotazel seawater was very limited. Low <sup>87</sup>Sr/<sup>86</sup>Sr values between 0.7028 and 0.7057 [1] are similar to those of the underlying Ongeluk basaltic andesite, and are compatible with hydrothermal Sr input from mantle-derived igneous sources. The εNd(t) values, too, are similar to those of the Ongeluk lava, but also to those of contemporaneous shales. These observations are in marked contrast to what is seen in the older Kuruman IF and suggest that REY and probably iron and manganese were supplied by "local" low-temperature hydrothermal fluids from the Ongeluk lava, by porewaters from terrigenous sediments elsewhere in the Hotazel sub-basin, and/or by continental run-off.

Some of the chemical sediments in the Hotazel Formation display negative Ce anomalies indicating Ce depletion of Hotazel seawater. Decoupling of redox-sensitive Ce from the strictly trivalent REY requires Ce oxidation, i.e. highly oxygenated conditions. The Hotazel Formation, therefore, indicates the onset of the modern-style redox-controlled biogeochemical cycle of Ce and Mn.

### References

E.A. Schneiderhan *et al.*, (2006), *S. Afr. J. Geol.* **109**, 63-80

## Kinetics and thermodynamics of redox reactions between humic substances, microorganisms and iron(II) and iron(III) minerals

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Humic substances (HS) are natural organic polymers present in most environmental systems. They are redox-active and participate in microbially catalyzed redox reactions. Iron-reducing and many fermenting bacteria can use HS as an alternative electron acceptor in their metabolism. The reduced HS transfer electrons in a chemical reaction to electron acceptors like metal ions or organic pollutants, thus functioning as an electron shuttle between microorganisms and these terminal electron acceptors. So far the kinetics and thermodynamics of redox reactions of HS with iron(II) and iron(III) minerals as well as with microorganisms are poorly understood.

In order to tackle these knowledge gaps, the kinetics of microbial reduction of various HS by Fe(III)-reducing bacteria (*Geobacter* and *Shewanella* sp.) was quantified and compared to i) the direct microbial reduction of iron(III) minerals and ii) the reduction of iron(III) minerals by reduced HS. We determined the minimum concentration of HS necessary for observable electron shuttling.

The thermodynamics of redox reactions between HS and dissolved and solid iron(II) and iron(III) compounds was evaluated. Since O<sub>2</sub> is the most important electron acceptor in nature, redox reactions of HS with iron compounds possessing different redox potentials were compared to HS oxidation by O<sub>2</sub>. We applied electron spin resonance (ESR) spectroscopy in order to quantify radical formation during HS redox reactions. As the contribution of HS-complexed iron to HS redox reactions is unclear, we extracted different iron fractions from HS by sequential extraction and quantified the redox properties of HS after each extraction step.

Our results showed that HS can react with several iron(II) and iron(III) minerals and efficiently catalyze biogeochemical processes in the environment. The fact that during these processes a variety of reactive HS species such as semiquinone radicals are formed suggests that HS have the potential to be an important player in the redox cascade in natural environments.