

Increase of oxygen in the Earth's atmosphere and hydrosphere between -2.5 and -2.4 Ga B.P.

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Currently, two competing concepts that both are based on (amongst others) the Fe-Ti systematics of palaeosols, try to describe the evolution of the oxygen content of the Precambrian Earth's atmosphere. One model favours a rapid and significant increase of atmospheric oxygen levels during the Palaeoproterozoic (summarized in Holland, 1994), whereas another suggests that only minor changes of less than $\pm 50\%$ occurred throughout Earth's history (summarized in Ohmoto, 1997). Although the former is currently more widely accepted than the latter, it suffers from two shortcomings: (i) the validity of the conclusions derived from the palaeosol record rely heavily on the assumption of absence of organic matter from Archaean and Palaeoproterozoic weathering profiles, and (ii) the time of the postulated increase of atmospheric oxygen is rather poorly constrained due to large uncertainties of some palaeosol ages; nevertheless, however, the rapid increase is suggested to have occurred between *c.* 2.2 and 1.9 Ga B.P. (Holland, 1994). Thus, there is need for (i) other redox-indicators that are able to provide at least qualitative evidence for a rather constant or an increasing redox-level of the Precambrian atmosphere-hydrosphere system, but which are rather insensitive to the presence or absence of organic matter, and (ii) evidence from samples that originate from well-dated profiles with a (for Precambrian standards) reasonably good time resolution.

Hence, we studied the distribution of Mn and rare-earth elements (REEs) in only slightly metamorphosed chemical platform sediments from the Kuruman and Griquatown Iron-Formations (IFs) and the Hotazel Manganese-Formation (MnF), and in palaeo-weathering products in the Transvaal Supergroup, South Africa. While the only abundant primary oxide minerals in the Kuruman and Griquatown IFs are Fe(III) oxides, the Hotazel MnF is the oldest large-scale deposit of Mn(III) oxides in the geological

record. The results bear clear evidence for a rapid increase of the oxygen content of both, the Earth's ocean and atmosphere between ~ 2.5 and ~ 2.4 Ga B.P.

Age constraints

While the age of the Kuruman and Griquatown IFs in the lower Transvaal Supergroup are well-constrained by U-Pb zircon ages of 2521 ± 3 Ma for a tuff from the base of the Kuruman IF (Sumner and Bowring, 1996) and 2432 ± 31 Ma for a tuff from just below the contact of Kuruman IF and overlying Griquatown IF (Trendall *et al.*, 1990), the assumed age of the Hotazel MnF is exclusively based on a Pb-Pb whole-rock age of 2222 ± 13 Ma for the Ongeluk basaltic andesite (Cornell *et al.*, 1996) that underlies the Hotazel Formation. However, this age could not be confirmed by discordant U-Pb SHRIMP zircon data that yield widely scattering apparent ages between ~ 500 and 2140 Ma (Gutzmer and Beukes, 1997), indicating that the Pb systematics of the Ongeluk lava is not suited for geochronology due to initial isotopic heterogeneity of its Pb and a poly-stage evolution. Hence, we decided to study the Pb systematics in drill core samples from the Moidraai Dolomite which is a silicified micritic marine shallow-water dolomite overlying the Hotazel Formation. In a $^{208}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ diagram, the carbonate-bound Pb (determined on acetic acid and 2 M HCl leachates) differs significantly from the silicate-bound Pb (determined on the residues), indicating that bulk Pb was derived from two separate sources, but that there was no exchange between these components during or after silicification. Hence, we determined a secondary-Pb isochron from the acetic acid and the 2 M HCl leachates, that defines an (diagenetic) age of the Moidraai Dolomite of 2394 ± 26 Ma (2σ , MSWD = 1.8, $n = 22$). This age is about 200 My older than previously thought, but

compatible with the 'normal' $^{13}\text{C}_{\text{carb}}$ values of the Mooirdraai Dolomite. Thus, while an age of ~2.5 Ga can be assigned to the Kuruman and Griquatown IFs, the Hotazel MnF was deposited only about 100 my later at ~2.4 Ga B.P.

Ce as a qualitative palaeo-redox-indicator

In contrast to La and Pr, i.e. its strictly trivalent neighbours in the *REE* series, Ce^{3+} may be oxidized in oxygenated (near-)surface environments and 'fixed' in insoluble Ce(IV) compounds. This results in decoupling of Ce from its *REE* neighbours and in positive or negative Ce anomalies in *REE* patterns. This decoupling of Ce is typical of the present-day biogeochemical cycle of the *REEs*, and hence, Ce anomalies are commonly found in modern seawater (and marine precipitates) and soil profiles. Absence of Ce anomalies from *REE* patterns of ancient chemical sediments and products of terrestrial palaeoweathering, therefore, is qualitative evidence for a low oxygen content of the ocean and atmosphere, respectively, while presence of Ce anomalies indicates a higher redox-level.

Ce anomalies in chemical sediments from the Transvaal Supergroup

All studied chemical sediments from the Transvaal Supergroup display *REE* patterns typical of marine IF and MnF precipitates that are free from detrital aluminosilicates, i.e. they show enrichment of the heavy over the light *REEs*, positive La and Gd anomalies, and super-chondritic Y/Ho ratios. The Kuruman and Griquatown IFs, however, do not show any Ce anomaly, indicating that decoupling of Ce from its trivalent *REE* neighbours did not occur at 2.5 Ga B.P. (Bau and Dulski, 1996). In marked contrast, however, the Hotazel MnF is not only the oldest large-scale deposit of Mn(III) oxides, but is also the first chemical sediment that is characterized by ubiquitous negative Ce anomalies. This suggests that just 100 my after the deposition of the Kuruman IF, the modern redox-controlled biogeochemical cycles of Ce (and Mn) were in operation. Since in both, the IFs and the MnF, the *REE* distribution is controlled by marine surface water as evidenced by heavy *REE* enrichment, positive La and Gd anomalies, and super-chondritic Y/Ho ratios, the negative Ce anomalies in the Hotazel MnF marks the onset of the present-day biogeochemical cycle of Ce

(and Mn), and indicates a significant and rapid increase in the oxygen content of marine surface waters.

Ce anomalies in products of palaeoweathering in the Transvaal Supergroup

Iron-oxides from the giant Sishen iron-ore mine, that are the residues of a Palaeoproterozoic episode of oxic weathering of the Kuruman IF display strong positive Ce anomalies. In contrast, the lower oxidized zone of the Drakenstein palaeoweathering profile that developed simultaneously on the Ongeluk lava shows pronounced negative Ce anomalies. Similar to the present-day environment, Ce was oxidized in the uppermost soil horizons and fixed in insoluble cerianite. Depletion of the more soluble trivalent *REE* by soil solutions and continental runoff led to a positive Ce anomaly in the residual Fe-oxides, whereas *REE* input from such Ce-depleted descending soil solutions from above generated negative Ce anomalies in the lower soil horizons. This is evidence for the oxidation of Ce in terrestrial (near-)surface environments in the early Palaeoproterozoic. The contrast between the Archaean (2760 Ma) Mt.Roe palaeosol that shows no Ce anomalies (Macfarlane *et al.*, 1994) and the early Palaeoproterozoic residual Sishen Fe-oxides and Drakenstein palaeosol suggests that the oxygen content of the atmosphere increased rapidly and significantly.

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