

Reconstructing Earth's surface oxidation across the Archean-Proterozoic transition

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ABSTRACT

The Archean-Proterozoic transition is characterized by the widespread deposition of organic-rich shale, sedimentary iron formation, glacial diamictite, and marine carbonates recording profound carbon isotope anomalies, but notably lacks bedded evaporites. All deposits reflect environmental changes in oceanic and atmospheric redox states, in part associated with Earth's earliest ice ages. Time-series data for multiple sulfur isotopes from carbonate-associated sulfate as well as sulfides in sediments of the Transvaal Supergroup, South Africa, capture the concomitant buildup of sulfate in the ocean and the loss of atmospheric mass-independent sulfur isotope fractionation. In phase with sulfur is the earliest recorded positive carbon isotope anomaly, convincingly linking these environmental perturbations to the Great Oxidation Event (ca. 2.3 Ga).

INTRODUCTION

Earth's atmosphere underwent a substantial increase in free oxygen during the early Paleoproterozoic Era (e.g., Holland, 2002; Farquhar et al., 2000), termed the Great Oxidation Event (GOE), when pO_2 likely rose from $<10^{-5}$ to $>10^{-2}$ PAL (present-day atmospheric level; Pavlov and Kasting, 2002). Consequently, oxidative weathering of sulfides would result in a concomitant rise in oceanic sulfate abundance (subsequently noted as $[SO_4]$). Higher sulfate levels would in turn stimulate bacterial sulfate reduction and amplify the magnitude of mass-dependent sulfur isotope fractionations (Canfield, 2001). This biological fingerprint was first imparted to sedimentary sulfides between 2320 and 2470 Ma (Cameron, 1982; Bekker et al., 2004). Notably, multiple S isotope (^{32}S , ^{33}S , ^{34}S , ^{36}S) data for the same units also indicate the transition from mass-independent to mass-dependent fractionation.

In the absence of bedded evaporite minerals, carbonate-associated sulfate has become the preferred proxy for reconstructing seawater sulfur isotope composition (e.g., Strauss, 2004). We determined the sulfur isotope abun-

dances of all four sulfur isotopes in chromium-reducible sulfide (i.e., sedimentary pyrite) as well as that of carbonate-associated sulfate in order to reconstruct the history of atmospheric oxygenation. To trace the rise of seawater sulfate and evaluate its effect on biological sulfur cycling in the late Neoproterozoic and early Paleoproterozoic, we examined carbonate-bearing strata from the Transvaal Supergroup in the Transvaal and Griqualand West subbasins, South Africa (Fig. 1). We focus specifically on samples from the glaciogenic Duitschland Formation, where on the basis of the carbonate carbon isotope record, Bekker et al. (2001) proposed that the transition from an anaerobic to an aerobic world would likely be archived.

ANALYTICAL METHODS AND SAMPLING

We collected 58 well-preserved carbonate samples from outcrop and drill core from the Transvaal Supergroup, a sedimentary succession deposited on the Kaapvaal craton of southern Africa between 2650 Ma and 2100 Ma (Eriksson et al., 2006). Radiometric constraints and basin-wide correlations of the Transvaal Supergroup define a chronostratigraphic framework for the sedimentary succession (see GSA Data

Repository Fig. DR1 and Table DR1¹), which includes two discrete positive carbon isotope anomalies (Bekker et al., 2001).

The extraction of carbonate-associated sulfate (CAS) and of chromium-reducible sulfur (CRS, largely sedimentary pyrite) involved wet-chemical procedures that are well established (Münster, Germany, and Maryland, USA, laboratories; outlined in detail in the Data Repository). The $\delta^{34}S$ values are presented in the standard delta notation against VCDT (Vienna Canyon Diablo troilite) with an analytical reproducibility of $\leq 0.2\%$. For multiple sulfur isotope analyses, extracted sulfur was fluorinated to produce SF_6 (Johnston et al., 2005). All multiple sulfur isotope measurements were performed at the University of Maryland. Uncertainties of $\Delta^{33}S$ and $\Delta^{36}S$ values by the SF_6 technique are ~ 0.01 and $\sim 0.2\%$. All data were generated from the same sample set.

Carbonate carbon and oxygen isotopes were measured using a ThermoFinnigan GasBench II interfaced via ConFlo III with a Delta Plus XL. Reproducibility as determined by replicate analyses is better than 0.2% for carbon and oxygen.

RESULTS

CAS and CRS reveal wide ranges in $\delta^{34}S$ throughout the Transvaal Supergroup (Fig. DR4). A major change in $\delta^{34}S$ of CAS is recorded within the upper half of the Duitschland Formation ~ 700 m above glacial diamictites at the base of the unit and ~ 300 m above a conspicuous sequence boundary (Fig. 2; see also Coetzee,

¹GSA Data Repository item 2009101, stratigraphic profiles, and description of analytical methods and the modeling, is available online at www.geosociety.org/pubs/ft2009.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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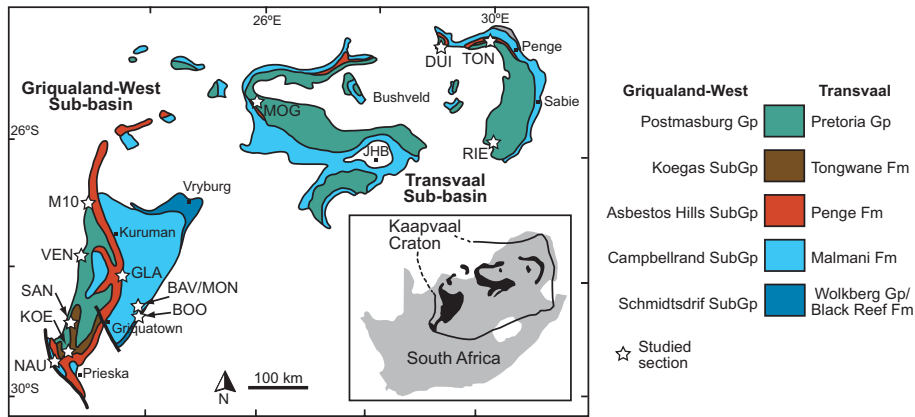


Figure 1. Simplified geologic map of Transvaal Supergroup outcrop area (modified from Sumner and Beukes, 2006). Colors correspond to stratigraphic units in Figure DR1 (see footnote 1). Stars indicate sampled sections: BOO—Boomplaas, MON—Monteville, BAV—Baviaanskrantz, NAU—Nauga, GLA—Gladstone, TON—Tongwane, KOE—Koegas, SAN—Sandridge, DUI—Deutschland, M10—Mooiiraai, VEN—Venn, MOG—Mogomane, RIE—Rietvalley, JHB—Johannesburg. Gp—Group, Fm—Formation.

2001). Below this level, $\delta^{34}\text{S}$ values range from +4.7‰ to +11.1‰, but above they display ^{34}S enriched sulfur isotope values, from +11.8‰ to as high as +42.3‰. Across the same interval CRS and CAS record a marked change in $\Delta^{33}\text{S}$, clearly exhibiting mass-independent fractionation (MIF) below and mass-dependent fractionation (MDF) above. The interpretation of MIF versus MDF is supported by our coupled

analysis of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ (Fig. 3) that shows that the data above and below the transition within the Deutschland Formation plot along significantly different isotopic arrays (Farquhar et al., 2007). Carbonates in the upper Deutschland Formation preserve evidence for a major positive carbon isotope excursion at the same stratigraphic level (this study; Bekker et al., 2001; see Table DR1).

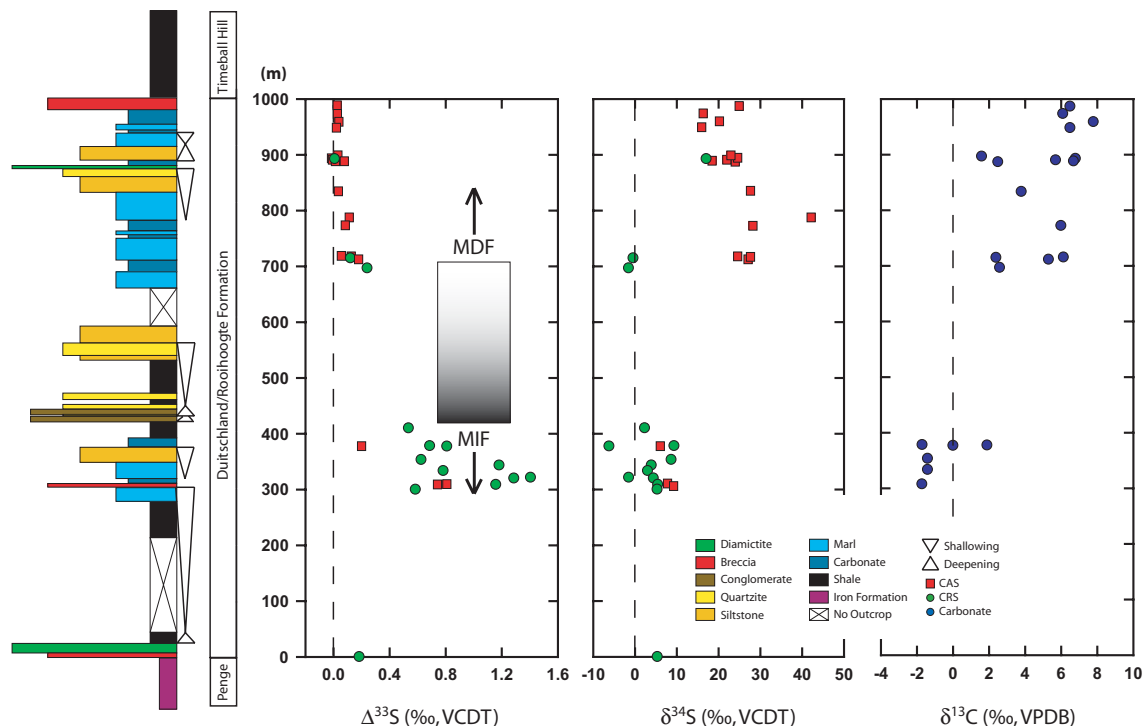


Figure 2. Temporal variations in $\Delta^{33}\text{S}$, $\delta^{34}\text{S}$, and $\delta^{13}\text{C}$ values for carbonates and of $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$ values of sulfides from Deutschland Formation (geology after Coetzee, 2001). Sequence boundary at ~430 m separates lower and upper parts of the succession. Transition from mass-independent fractionation (MIF) to mass-dependent fractionation (MDF) is shown as gradational zone that encompasses the sequence boundary. CAS—carbonate-associated sulfate, CRS—chromium-reducible sulfur. VCDT—Vienna Canyon Diablo troilite; VPDB—Vienna Peedee belemnite.

DISCUSSION

These unique and novel observations (i.e., the coincident change in $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$ of CAS and CRS and of $\delta^{13}\text{C}$ in carbonates) strongly point to a coupled change in the sulfur and carbon cycles across the transition from an anoxic to an oxic world. The disappearance of MIF in the upper Deutschland Formation indicates that atmospheric O_2 levels rose to $>10^{-5}$ PAL through this transition. The highly positive $\delta^{34}\text{S}$ values of the upper Deutschland Formation samples are consistent with suggestions that $[\text{SO}_4]$ rose with atmospheric $p\text{O}_2$ (cf. Bekker et al., 2004; Papineau et al., 2007), but also that progressive bacterial sulfate reduction, imparting a ^{34}S depletion on the product sulfide (e.g., Canfield, 2001), resulted in the ^{34}S enrichment of the residual oceanic sulfate; hence the amplified $\delta^{34}\text{S}$ values of CAS and CRS in the upper Deutschland Formation.

In order to evaluate the transition from a sulfur cycle with MIF to a sulfur cycle with a higher $[\text{SO}_4]$ and bacterial sulfate reduction (BSR), we constructed a basic box model (see the Data Repository). In the model, $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ change as a result of dilution during ingrowth of the sulfate pool, and in response to larger isotope fractionations of BSR at higher sulfate concentrations. As a result, the response of the system does not yield straight-line trajectories from MIF compositions to MDF composi-

tions, but instead yields a hooked trajectory, that begins with the loss of the MIF signal (principally as smaller $\Delta^{33}\text{S}$, $\delta^{34}\text{S}$, and $\Delta^{36}\text{S}$) as a result of dilution, and is followed by the establishment of the characteristic mass-dependent signal (large variations for $\delta^{34}\text{S}$, and smaller variations for $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ with a characteristic relationship between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$). These variations are broadly consistent with the sulfur isotope variations observed in this study.

The observation that rising $\delta^{34}\text{S}_{\text{CAS}}$ values overlap with the disappearance of nonzero $\Delta^{33}\text{S}$ values suggests a coupling of atmospheric and oceanic processes. We suggest that this overlap is expected where a mass-independent sulfate pool is displaced by a mass-dependent pool that grows in with higher concentration. Rising atmospheric O_2 levels and formation of an ozone shield may have attenuated and ultimately terminated the photolytic production and transfer of sulfate and elemental sulfur with their MIF sulfur isotope signatures to surface environments (Farquhar et al., 2000; Pavlov and Kasting, 2002). This is also supported by the relationship between $\Delta^{36}\text{S}$ and $\Delta^{33}\text{S}$ values. In the lower half of the Transvaal Supergroup (Boomplaas to lower Duitschland formations) the $\Delta^{36}\text{S}$ - $\Delta^{33}\text{S}$ array defines a slope of -0.96 ($r^2 = 0.98$; Fig. 3A), which is in agreement with previous multiple sulfur isotope studies of Neoproterozoic successions (Kaufman et al., 2007; Ono et al., 2003), as well as the products of ultraviolet (UV) photolysis experiments with SO_2 in the absence of oxygen (Farquhar and Wing, 2003). In contrast, samples from the upper Duitschland Formation and stratigraphically younger units (i.e., Mooidraai, Silverton, Lucknow, and Houtenbeck formations) define a data array with a much steeper mass-dependent slope (Ono et al., 2006), which is similar to younger Proterozoic and Phanerozoic samples. A few samples from the Koegas and Tongwane formations, which were expected to show MIF, plot slightly off of the characteristic $\Delta^{36}\text{S}$ - $\Delta^{33}\text{S}$ array (Fig. 3B). These samples were collected from brecciated and iron-rich carbonates, suggesting that post-depositional factors may have complicated the preservation of their sulfur isotope abundances.

The contemporaneous rise in $[\text{SO}_4]$ and the termination of MIF provide strong evidence for the geologically rapid build up of oxygen in the atmosphere (cf. Bekker et al., 2004). The coincidence of Earth's oldest positive carbon isotope anomaly with the upper Duitschland oxygenation event suggests that increases in atmospheric O_2 and oceanic sulfate relate to the enhanced burial of organic matter, providing a plausible causal link for the oxidative transition (Bekker et al., 2001). The age of this event, which is now identified in the upper Duitschland stratigraphic record, is best defined by a Re-Os age of 2316 ± 7 Ma from the basal Rooihooft

Formation, from which the absence of MIF was recorded in sedimentary pyrite (Bekker et al., 2004). The Rooihooft Formation is considered to be a facies equivalent of the carbonates in the Duitschland Formation (Coetzee et al., 2006). Our study differs, however, insofar as we identify the rock interval where the atmospheric oxygenation event occurred, and provide additional evidence that this stimulated oxidative weathering and changes in seawater chemistry, as well as Earth's oldest recorded perturbation in the exogenic carbon cycle.

Coevolution of Paleoproterozoic Life and Environment

While alternative models have been proposed to explain strong positive carbon isotope anomalies in the Paleoproterozoic (e.g., Melzhik et al., 1999; Hayes and Waldbauer, 2006), we find the coupled stratigraphic events a novel and persuasive argument for oxygenation of the atmosphere to be associated with a greater proportional burial of organic carbon in sediments (Hayes et al., 1983). Insofar as nutrient supply to the shallow ocean was enhanced by the onset of oxidative weathering (cf. Holland, 2002), high relative burial rates of organic carbon might reflect high primary productivity sustained by the progressive increase in $p\text{O}_2$. Furthermore, as photosynthetic rates are proportional to light intensity (Falkowski and Raven, 1997), the development of a substantial ozone layer at this time would amplify primary productivity by allowing UV-sensitive photoautotrophs to migrate upward to the surface ocean.

While speculative, the linkage of early Paleoproterozoic surface oxidation with enhanced nutrient supply and development of stratospheric sunscreen suggests that the upper Duitschland carbon cycle anomaly could also be associated with the rapid expansion of single-celled photosynthetic eukaryotes (Knoll and Carroll, 1999). Both sterol synthesis in eukaryotes (Summons et al., 2006) and aerobic respiration require significant levels of O_2 in the ambient environment. The lowermost limit of O_2 required for microbial oxygen respiration is difficult to ascertain, but in the ocean the switch point between oxygen respiration and nitrification occurs around $3 \mu\text{M}$ (Codispoti et al., 2001; Canfield, 2005). If catabolism is limited only by O_2 concentrations, the Monod equation constrained by laboratory studies of modern aerobic respirers (Jin and Bethke, 2005) may be used to determine minimal required concentrations for this metabolism. The calculated minimum value required by aerobic microbes $[\text{O}_2]_{\text{min}}$ is $6.7\text{E-}11$ mol/L, which is $\sim 8.8\text{E-}8$ atm of O_2 . It is notable that the rise in respiration rate occurs at O_2 levels consistent with our observations of the disappearance of MIF in the geological record ($\sim 10^{-5}$ PAL or $\sim 2 \times 10^{-6}$ atm; Fig. 4) and the earliest recorded carbon cycle anomaly.

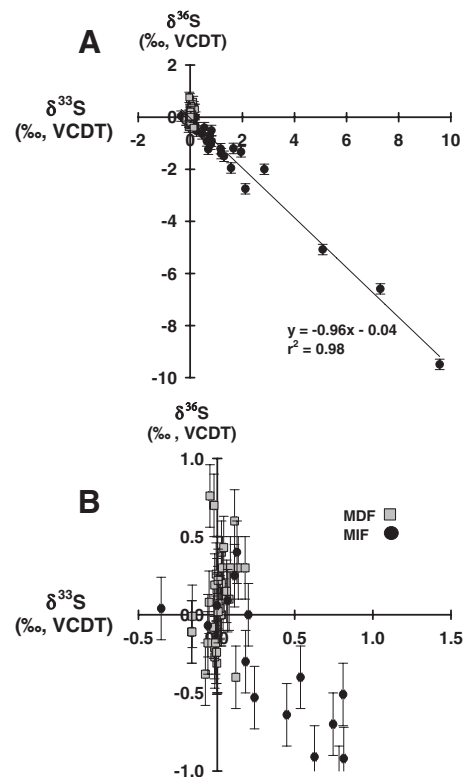


Figure 3. A: Plot of $\Delta^{36}\text{S}$ versus $\Delta^{33}\text{S}$ for mass-independent fractionation (MIF) and mass-dependent fractionation (MDF) data from Transvaal Supergroup. **B:** Enlargement of $\Delta^{36}\text{S}$ versus $\Delta^{33}\text{S}$ plot around origin. VCDT—Vienna Canyon Diablo troilite.

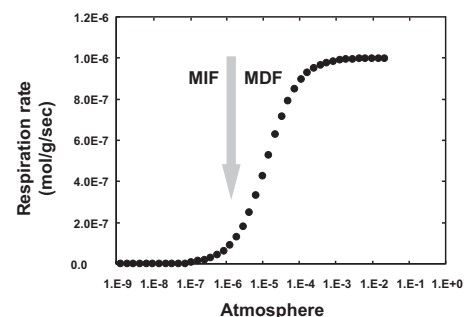


Figure 4. Plot of O_2 concentrations and minimum value required by aerobic metabolism to be dominant on Earth. MDF—mass-dependent fractionation, MIF—mass-independent fractionation.

CONCLUSIONS

Our detailed isotopic examination of the Duitschland Formation (Fig. 2) clearly captures the significant rise of atmospheric oxygen (as well as the protective ozone layer) and its subsequent consequences for ocean chemistry and biology. The MIF signal disappears in a poorly exposed interval between the lower and upper successions separated by a prominent sequence boundary. Biomarker evidence for the presence

of cyanobacteria and eukaryotes already at 2.7 Ga (Summons et al., 1999; Brocks et al., 1999) led to speculation on the ~300 m.y. delay of the GOE; however, a recent study indicates that the critical biomolecules are younger contaminants (Rasmussen et al., 2008).

The emergence of cyanobacteria and oxygenic photosynthesis may then be associated with a geochemical “whiff of oxygen” recorded in 2.5 Ga sediments (Kaufman et al., 2007; Anbar et al., 2007). If true, the delay in the GOE can then be understood in terms of a finite sink for molecular oxygen–ferrous iron, which was abundant in deep Neoproterozoic seawater and sequestered in a worldwide episode of iron formation deposition ending shortly before accumulation of the glaciogenic Duitschland Formation. Insofar as early Paleoproterozoic glaciation is associated with oxygenation of a methane-rich atmosphere (Kopp et al., 2005; Bekker and Kaufman, 2007), we conclude that Earth’s earliest ice age(s) and the onset of a modern and far more energetic carbon cycle are directly related to the global expansion of cyanobacteria that released oxygen to the environment, and of eukaryotes that respired it.

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