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Mo and Re-PGE signatures of black shales as a proxy for a rise of oxygen event within the Transvaal Supergroup, South Africa

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We report Mo concentrations and isotopic compositions as well as Re-PGE data from black shales of the Transvaal Supergroup (Schmitdrift/Campbellrand Subgroup, 2.64-2.5Ga, and Pretoria Group, 2.45-2.15Ga). Such data are important proxies for changes in redox conditions of the early atmosphere and oceans. In particular the Mo isotopic sea-water signal is an indicator not only of palaeoredox conditions, but also of contiguity with the palaeo-ocean (Arnold et al.,2004; Siebert et al.,2005). This is so because a heavy Mo isotope signal in ocean water is built up by Mo fractionation during scavenging/precipitation in oxic and suboxic sediments. The Mo isotopic sea-water signal is approximately mirrored in anoxic sediments.
A general increase in Mo concentration and fractionation as well as an enrichment in Re compared to the continental crust can be seen within the Campbellrand Subgroup. In one Campbellrand black shale oxygen was even high enough to mobilize Os. These data indicate a general rise of oxygen. However, Mo concentrations and $\delta^{98/95}$Mo values fluctuate strongly in the upper Campbellrand Subgroup. Small scale ($\sim$1Ma) Mo fluctuations can be explained by changing local sedimentary circumstances (change in redox and input conditions). Long scale ($\sim$50MA) Mo fluctuations are better explained by global oxic/anoxic oscillation.
Samples of the overlying Pretoria group show Mo concentrations and isotopic compositions often below the continental input while Re-PGE abundance pattern are quite similar to those for the Campbellrand. The apparent contradiction between the Mo and Re-PGE values can be resolved assuming an oxidizing upper ocean with almost

total scavenging of Mo. Total scavenging can result from enhanced biological sedimentation between and especially after glacial events. This extensive Mo scavenging coincides in time with the Lomagundi-Jatulin carbon isotope excursion, which indeed signals very enhanced organic carbon burial.