Evidence for a gradual rise of oxygen between 2.6 and 2.5 Ga from Mo isotopes and Re-PGE signatures

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The question of how and when oxygen began to accumulate in the early atmosphere is still a point of debate. To address this question 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). This time range covers the period between the first strong evidence of cyanobacteria at 2.7Ga and the disappearance of sulfur MIF at 2.32Ga. Due to the redox dependent solubility of Mo, Re and Os, such data are important proxies for changes in redox conditions of the early atmosphere and ocean. In particular the Mo isotopic signal is an indicator of palaeoredox conditions [1][2]. Significant Mo isotope fractionation requires Mo in solution and thus sufficiently oxidizing conditions to allow Mo oxyanions to exist.

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. These data indicate a gradual rise of oxygen between 2.64 and 2.5Ga. However, Mo concentrations and $\delta^{98/95}$Mo values fluctuate strongly in the upper Campbellrand Subgroup. Small term (~1Ma) Mo fluctuations can be explained by changing local sedimentary circumstances (changes in redox and input conditions). Whereas long term (~50Ma) Mo fluctuations probably reflect global oxic/anoxic oscillations.

Samples of the overlying Pretoria Group (2.45-2.25Ga) show Mo concentrations and isotopic compositions often below the continental input, while Re-PGE abundance patterns are quite similar to those for the Campbellrand. The apparent contradiction between the decoupled Mo and Re-PGE values can be resolved assuming a stratified ocean with almost total scavenging of Mo. Such an increased scavenging can result from enhanced biological sedimentation between and especially after glacial events. This coincides with the Lomagundi-Jatulian carbon isotope excursion, which indeed indicates very enhanced organic carbon burial.

References

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