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Evidence from molybdenum isotopes for a transient and localized nature of free aquatic oxygen around 3 Ga.

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Evidence of early occurrences of low levels of free molecular oxygen has been reported from banded iron formations in the West Rand Group [1] (lower Witwatersrand Supergroup) as well as at the base of its more distal stratigraphic equivalent [2], the Mozaan Group. Here oxygenated conditions have been documented by Cr isotopes on a paleosol [3] and Mo isotopes in banded iron formation [4]. Mo systematics are a powerful in the study of oxygenation in early Earth history. In organic-rich shales and manganese oxide crusts, the combination of Mo concentrations >2 ppm and $\delta^{98/95}$Mo variations > 0.3‰ signal free oxygen at levels as low as 10^{-5} PAL or less [5], as long as these are present in a sufficiently large reservoir [6]. In order to explore the marine redox conditions at c. 2.95 Ma in a broader stratigraphic and spatial context, we have determined Mo contents and $\delta^{98/95}$Mo values of 20 (mainly carbonaceous) mudrock, banded iron formation (BIF) and manganese concretion samples throughout the West Rand Group as well as 3 samples from the Booysens Formation, Central Rand Group. Further, we analysed 8 similar samples from the Ntombe, Delfkom and Bangaspoort Formations in the Mozaan Group. Mn concretions occur as Mn^{2+} carbonate, but reflect original precipitation as MnO_2 [7], which requires some free O_2 even if bacterially mediated [8].

In mudrocks throughout the West Rand Group, we found Mo concentrations varying from 0.2 to 3 ppm and $\delta^{98/95}$Mo values from 0.1 to 0.45‰. Mostly, higher concentrations coincide with higher $\delta^{98/95}$Mo values. A carbonaceous mudrock sample from the Booysens Formation has 8 ppm Mo and δ^{98-95}Mo of 0.6‰. There is thus a weak but persistent signal that free O_2 affected the Mo isotopic mass balance in the shelf environment during West Rand Group times (2970-2910 Ma), and in the overlying Booysens Formation this signal is stronger. Three BIF samples from the lowermost West Rand Group and the Booysens Formation have <2ppm Mo but $\delta^{98/95}$Mo from -0.1 to +0.5‰. However, two Mn-concretions from the Brixton Formation have ~1 ppm Mo and δ^{98-95}Mo of 0.2‰. The samples from the Mozaan Group (mudrocks and Mn concretions alike) present Mo concentrations varying only between 0.2 and 1.5 ppm, with $\delta^{98/95}$Mo between 0.2 and 0.4‰, within the detrital range and thus not indicating free O_2. The Mn concretion data present an apparent paradox, since free O_2 is required for their formation [8]. However, this requirement is local only, whereas oxygenation on a basin-wide scale would be required for dissolved Mo to reach more distal sedimentation sites. We conclude that free O_2 was confined to 'oxygen oases' [4]. Further, an episode of strongly oxidizing conditions found at the base of the Mozaan Group [3,4] appears to have been transient.

References:

[1] Smith AJB, Beukes NJ and Gutzmer J. (2013) Econ Geol 108: 111-134.
[2] Beukes NJ and Cairncross B (1991) S Afr J Geol 94: 44-69.

[3] Crowe SA et al. (2013) Nature 501: 535-538.
[4] Planavsky NJ et al. (2014) Nature Geosc 7: 283-286.
[5] Siebert C et al. (2005) Geochim Cosmochim Acta, 69: 1787-1801.
[6] Wille M et al. (2007) Geochim Cosmochim Acta 71: 2417-2435.
[7] Smith AJB et al. (2014) Goldschmidt Conf 2014 Abstracts: 2332.
[8] Tebo BM et al. (2005) Trends Microbiol 13: 421-428.