

Organic Carbon Oxidation State (C_{ox}): A new proxy for the Earth's C and O cycles

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Carbon oxidation state (C_{ox}) is a basic property of the Earth's carbon pools, and has the potential to be used as a tracer in a broad range of ecological and Earth system questions. It is relevant to questions such as the controls on our planetary greenhouse, the history of life, the history of our atmospheric gas composition, and the processes which drive petroleum formation. C_{ox} is simple to define ($C_{ox} = (2z - y + 3z)/x$ for any organic molecule $C_xH_yO_zN_w$), and its natural biochemical variation is large (Fig. 1).

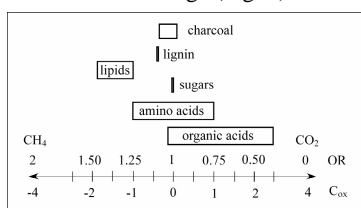


Fig. 1: Natural variation in C_{ox} values (lower axis) and oxidation state values (OR, upper axis, assuming N from NH_3).

C_{ox} varies with 1) initial form of organic matter (e.g. marine vs terrestrial organisms) and 2) degree of diagenesis. On short timescales (decades) precursor organism controls organic pool C_{ox} values. Organism C_{ox} values are themselves likely controlled at a fine scale by ecosystem N status and CO_2 concentration at the time of C fixation, as well as the history of ecosystem disturbance (Randerson *et al.*, 2006). On longer timescales, degree of diagenesis is at least as important as precursor organism in controlling C_{ox} values.

The utility of C_{ox} is enhanced by its linear relationship with another C cycle parameter, oxidative ratio (OR), defined as ratio of mols O_2 released/mols CO_2 fixed by photosynthesis. Currently, the global terrestrial OR value is both unconstrained and required in calculations of the fate of fossil fuel CO_2 in the environment (Manning and Keeling, 2006). On both long and short timescales, organic matter OR values record the efficiency of the biosphere's production of O_2 .

References

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Sulfur isotopes in barite deposits from the lower Onverwacht Group, Barberton Greenstone Belt: Evidence for microbial sulfate reduction at >3.5 Ga?

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Convincing stable isotopic evidence for microbial sulfate reduction is limited to only one locality in the early Archaean rock record at the 3.48 Ga North Pole dome in the Pilbara Block (Shen *et al* 2001), even though molecular phylogeny suggests it to be one of the most ancient metabolic processes on Earth. Here we studied some of the oldest barite-rich deposits of both hydrothermal and sedimentary origin in the Barberton Greenstone Belt, South Africa, where excess sulfate could have led to significant $\delta^{34}S$ fractionation. We focus on samples from the Theespruit formation of the lower Onverwacht group (3.54-3.50 Ga, Kroner *et al.* 1996). The rocks, from localities at Londozi and Stentor, contain massive barite, chert- and re-worked barite-rich layers of sedimentary origin with abundant pyrite that in places shows petrographic evidence for detrital deposition. Trace elements within the sedimentary pyrites support a low temperature origin with Co/Ni of 0.1 to 1 and low Se/S of $<5 \times 10^{-5}$.

$\delta^{34}S$ in bedded and fine grained barite varies between +4 and +6‰, that could represent the isotopic composition to sulfate derived from seawater or an enclosed basin. Pyrite included within and closely associated with the barite, measured by both bulk and *in situ* techniques, shows $\delta^{34}S$ that varies between -4 and -13‰. Individual pyrite grains reveal mass independent fractionation ($\Delta^{33}S$) of up to -2‰ consistent with an atmospheric-derived sulfate component. If both barite and pyrite were in isotopic equilibrium then the shift recorded here would match enrichment factors for microbial sulfate reduction in modern sediments (Canfield, 2001). The variations we show here represent the largest amount of fractionation yet found in early Archaean sedimentary sulfides outside the North Pole locality.

References

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