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# Anoxic diagenetic recycling of organic carbon prior to 2.06 Ga: Evidence from diagenetic carbonates

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Postdepositional degradation of biologically produced organic carbon ($\delta^{13}C$ = -27‰) may be assigned to a number of processes which are marked by different isotopic compositions of generated $CO_2$ (*i*) microbial oxidation (-27‰), (*ii*) bacterial sulphate reduction (-27‰), (*iii*) microbial fermentation (up to +15‰), and (*iv*) abiotic decarboxylation (-15 to -20‰). $CH_4$ produced in the microbial fermentation can be oxidised to $CO_2$ (-50‰). Diagenetically derived $CO_2$ may be bound in carbonates with isotopic signatures which differ distinctly from those of the 'normal' marine carbonate, 0 ± 2‰.

If samples from 'red beds' and banded iron formations (BIF) are excluded, $\delta^{13}C$ values for sedimentary and diagenetic carbonates in the time interval from 3.7 to 2.06 Ga are near 0 ± 2‰. Diagenetic shifts of carbon-isotopic abundances are systematically lower for Archaean and Proterozoic carbonates. The first carbonates with diagenetic $\delta^{13}C$ values (-5‰ to -20.5‰) were formed immediately in the aftermath of the 2.33-2.06 Ga Lomagundi-Jatulian positive excursion of carbon isotopes in sedimentary carbonates, and coincide in time with the first abundant development of diagenetic carbonate concretions. The $\delta^{13}C$ of these carbonates, -5‰ to -21‰, reflects an input of $CO_2$ generated by the processes (*i*), (*ii*) or (*iv*). At least (*i*) requires oxygenic environments and (*ii*) depends on sulphate availability. Thus, abundant diagenetic carbonates with low $\delta^{13}C$ can be taken as evidence of redox gradients.

If currently available records on the early Precambrian diagenetic $\delta^{13}C$ are correct, then organic carbon recycling processes during much of Early Precambrian history differed from those observed in the later periods. The available $\delta^{13}C$ values of Early Precambrian carbonates do not reflect a significant contribution from $^{12}C$-rich $CO_2$ source. This may be partly attributed to the oxygen and sulphate lows which could suppress microbial oxidation and bacterial sulphate reduction, and consequently production of $CO_2$ with $\delta^{13}C$ < -5‰.. The temporal trend of $\delta^{13}C_{carb}$ indicates that prior to 2.06 Ga organic carbon was either very little recycled, or was recycled under anoxic environments with $CH_4$ as the main cycling product. Consequently, it is unlikely that the ratio of reduced/oxidised carbon sequestered in sediments remained constant trough time. The global carbon cycle must have been operating in the Early Precambrian under different conditions.

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# Purple sulfur bacteria in an intensely stratified Paleoproterozoic sea

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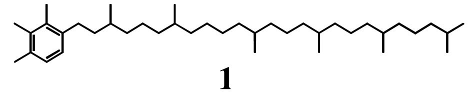
The distribution of redox-sensitive elements in the geological record indicates that the world's oceans remained almost entirely anoxic until ~1.8 billion years ago (1.8 Ga). However, for the interval from 1.8 Ga to the Neoproterozoic (1.0 to 0.54 Ga), ocean chemistry remains largely unconstraint and contested. One major hypothesis suggests the deep ocean became oxygenated 1.8 Ga ago and sulfate concentrations rose to essentially modern levels. A competing model proposes oceans remained largely anoxic and sulfate poor into the Neoproterozoic, but surface waters became oxygenated and deeper waters sulfidic. The existence of such a euxinic ocean would significantly alter our concepts of environmental and biological evolution in the mid-Proterozoic, but experimental evidence for or against the different models is limited.

Here we present hydrocarbon biomarker evidence for a euxinic and extremely stratified late Paleoproterozoic (2.5 – 1.6 Ga) marine basin. The 1.64 Ga Barney Creek Formation, McArthur Group, Australia, was predominantly deposited below storm wave base under marine conditions, covering a reconstructed minimum area of 50,000 $km^2$. Solvent extracts of dolomitic mudstones from the upper Barney Creek Formation yielded the aromatic carotenoids chlorobactane and okenane (**1**), revealing the presence of green sulfur bacteria (Chlorobiaceae) and purple sulfur bacteria (Chromatiaceae), respectively. The presence of these organisms indicates anoxic and sulfidic conditions below a chemocline at probably less than 20 meters water depth. High relative concentrations of 3β-methylhopanes point towards increased activity of methanotrophic bacteria and provide indirect evidence for low sulfate levels. Sterane biomarkers occur in extremely low concentrations or are absent, suggesting that even the upper oxygenated layer of the water column was hostile to eukaryotic algae and that stratification was sustained over extended periods of time. The biomarkers describe a marine environment unknown in the Phanerozoic (0.54 Ga to present) and support a Paleoproterozoic world with fundamentally different redox conditions.



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