

## Response of the ancient anoxic biosphere to the oxidation of terrestrial environments

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An observation not previously reported is that although microbially-mediated, <sup>13</sup>C-depleted, carbonate, and <sup>34</sup>S-depleted, sulphide concretionary growths are common in ca. post-2.0 Ga sedimentary rocks, such features are largely absent in older rocks. Furthermore, 2.06 Ga is a watershed in global carbon geodynamic cycling, the end of the Lomagundi-Jatuli Event, a remarkable positive carbon isotope excursion often linked to the first establishment of stable free dioxygen in the planetary exosphere. Excluding banded iron formations,  $\delta^{13}\text{C}$  of sedimentary and diagenetic carbonates of the older rocks, including rare concretions, are  $-0 \pm 3\%$  VPDB and are not characteristic of microbially recycled organic matter (OM). We propose that ca. pre-2 Ga, the biosphere operated in a different mode compared to the modern. OM biogeochemical recycling was predominantly in the anoxic water column and sediment/ water interface; rarely within sediments. Isotopically distinctive CO<sub>2</sub> and CH<sub>4</sub> readily escaped to atmosphere leaving no vestige as diagenetic <sup>13</sup>C-depleted or <sup>13</sup>C-rich carbonates. Around 2 Ma, in response to the now oxic near-surface conditions, the anaerobic recycling microorganisms retreated deep into sediments to escape poisonous O<sub>2</sub>. Redox gradients developed in the sedimentary column and abundant <sup>13</sup>C-depleted carbonate concretions then formed using recycled organic matter, as observed in the Phanerozoic world. The creation of the new locus for OM recycling explains an intriguing yet unexplained feature of the Lomagundi-Jatuli carbon isotope positive excursion. There is no evidence for a subsequent compensating low  $\delta^{13}\text{C}$  excursion which is a characteristic feature of extinction events, ventilation or turnover of deep anoxic basins. Such an excursion might be anticipated to follow an episode of enhanced OM burial as recycling and remineralisation proceed. However, the lack of a compensating negative excursion emerges as a predictive consequence of the hypothesis, developed above, of the creation of a new locus for OM recycling. Because the active biomass reservoir within the sediments and crust endures, there was no net return of oxidised organic matter of low  $\delta^{13}\text{C}$  to the ocean-atmosphere system to become recorded by carbonates.

## Raman spectroscopic determination of the isotope composition of CO<sub>2</sub> inclusions

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The determination of the isotopic carbon composition of CO<sub>2</sub> trapped as inclusions in minerals can provide important information on the origin and global circulation of CO<sub>2</sub> in the Earth's lithosphere. In this contribution we evaluate the possibility to measure the <sup>13</sup>C-<sup>12</sup>C ratio of CO<sub>2</sub> inclusions in minerals by micro-Raman spectroscopy. The Raman spectrum of natural CO<sub>2</sub> is characterised by bands near 1286 and 1389 cm<sup>-1</sup> and 1265 and 1370 cm<sup>-1</sup> of <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub>, respectively, which result from Fermi resonance. The intensity ratios of the <sup>13</sup>CO<sub>2</sub> and the <sup>12</sup>CO<sub>2</sub> bands are directly related to the isotopic composition. Although the <sup>13</sup>CO<sub>2</sub> bands of natural CO<sub>2</sub> are hardly detectable at atmospheric pressure, the upper <sup>13</sup>CO<sub>2</sub> band can be measured precisely in dense CO<sub>2</sub> inclusions, if long counting times are used. To investigate the dependence of the intensity ratio between the <sup>13</sup>CO<sub>2</sub> and <sup>12</sup>CO<sub>2</sub> band on the CO<sub>2</sub> density and various instrumental parameters, we conducted Raman measurements on synthetic CO<sub>2</sub> gasses of different isotope composition (ranging from 51.7 at.% <sup>13</sup>C to <sup>13</sup>C contents in the range of natural variations) in an in-house made gas pressure cell at pressures from 90 up to 500 bar at 295 K. We will show that for the most precise results it is necessary to measure a standard gas with identical instrumental settings and, importantly, at the same density as the inclusion, which can be determined from the frequency difference between the upper and lower <sup>12</sup>CO<sub>2</sub> band of the Fermi diad. The power of the method will be demonstrated on recently discovered CO<sub>2</sub> inclusions in up to 4 Ga old detrital zircons from Jack Hills, Western Australia.