Carbon isotope ($^{13}C/^{12}C$) composition of sedimentary carbonate (δ_{carb}, crosses) and of organic carbon corrected for postdepositional alteration (δ_{org}, circles) over Proterozoic time[1]. Note the relative constancy of the isotope age function for carbonate and pronounced time trend for organic carbon.

product $f_{org}\delta_{org}$ in the equation must have been constant through time).

Although decreasing isotope fractionations between C_{org} and C_{carb} could be accounted for by an assumed decrease of atmospheric CO_2 pressures, any causative link between the magnitude of biological fractionation and the quantity of carbon stored as sedimentary organic matter (so as to keep $f_{org}\delta_{org}$ constant) seems to involve a fair amount of teleology. In any case, a delicately tuned inverse relationship between biologically mediated carbon isotope fractionations and the size of the sedimentary C_{org} reservoir with the result of a near-stabilization of a single selected parameter of the system (δ_{carb}) remains shrouded in mystery.

Although a theoretically plausible (but not proven) decrease in atmospheric p_{CO_2} over the time interval in question might have provided the CO_2 concentration effect supposedly responsible for the δ_{org} increase of the revised age function, a large part, notably of the older values, clearly surpasses the average intrinsic maximum fractionations of some $-30\%_o$ of ribulose bisphosphate carboxylase[2] as the main carboxylating agent, suggesting instead an involvement of methylotrophic pathways.

For a final assessment of the proposed age trend in biological isotope fractionations, the buck probably has to be passed to enzymologists, who might be able to judge the feasibility of time-directed evolutionary changes in the isotope-discriminating properties of carboxylating enzymes. Further attention to these points, and perhaps other selected background parameters (including the

axiom that life, in its reckless striving for self-expression, always tends to sequester the maximum possible quantity of carbon permitted by nutrient availability), should help to test a possible conversion of the new concept from a captivating working hypothesis to an internally consistent cycling model.

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DES MARAIS ET AL. REPLY — We summarized the evidence that δ_{org} increased and that net isotope discrimination ($\delta_{carb} - \delta_{org}$) decreased substantially during the Proterozoic[1] (see figure left). These trends, which emerge from δ_{carb} and δ_{org} data obtained by several laboratories from hundreds of stratigraphic units, provide direct evidence that the carbon cycle changed. If δ_{carb} was relatively constant, as Schidlowski notes, then isotope mass balance requires that the fraction of carbon buried globally as organic matter, f_{org}, increased. Rather than interpreting the relative constancy of δ_{carb} or the decline in net discrimination, we explored instead the magnitude and episodicity of this increase in burial of organic matter, and its implications for the atmosphere and biosphere. We can, however, point out that no available evidence requires that the carbon cycle was unchanged during the 2 Gyr spanned by the Proterozoic. In fact, the trends we identified fit well with biological and environmental developments for which independent evidence exists.

How can the isotope trends for organic matter and carbonates be so different? The mass balance equation illustrates that δ_{org} and δ_{carb} respond differently to simultaneous changes in isotope discrimination and relative rates of organic matter burial. Specifically, decreasing discrimination and increasing organic burial both cause δ_{org} to increase, but they exert opposing effects on δ_{carb}. δ_{carb} can be evaluated over the interval 2.5 to 0.8 Gyr ago, using the trend in declining discrimination presented in our article[1], and estimating the increase in organic burial rate using the principle[3] that changes in the crustal organic matter reservoir are stoichiometrically coupled to changes in the oxidized reservoirs, and then assuming that the reservoirs of free oxygen and sulphate increased largely during the Proterozoic (see ref. 1). The net effect on δ_{carb} between 2.5 and 0.8 Gyr was less than $1\%_o$. This small, long-term trend is considerably less than the scatter of δ_{carb} values observed, therefore it is hard to detect. The δ_{carb} trend was insensitive to a significant long-term change in the

carbon cycle!

Actually, δ_{carb} has not been perfectly constant over time (see figure). The variations indicate that the isotope consequences of changing biogenic isotope discrimination and rates of organic burial often were not precisely balanced over timescales shorter than a few hundred million years. Mechanisms producing a tight linkage between isotope fractionation and organic burial are thus not required.

At least two mechanisms can be envisioned which plausibly linked isotope fractionation and organic burial over timescales longer than 100 Myr. First, in a low-O_2, late Archaean to early Proterozoic world, organic matter, already depleted in ^{13}C because of discrimination during photosynthetic carbon fixation, became even more depleted by globally significant recycling of ^{13}C-depleted biogenic methane[4]. Increased rates of organic matter burial caused an increase in environmental concentrations of O_2, sulphate and ferric iron. This in turn limited net discrimination because it suppressed methane recycling. Thus, changes in net discrimination might constitute additional evidence for oxidation of the environment. Second, increased rates of continental erosion augmented both rates of organic burial and rates of CO_2 removal from the atmosphere. Declining atmospheric p_{CO_2} would also have decreased isotope fractionation during photosynthetic carbon fixation[5-7].

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