Carbon isotope evidence for early life - correction of a model calculation

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Sir — The recent Letter by Mojzsis  $et\ al.^1$  on evidence for life on Earth before 3,800 million years ago was accompanied by a discussion of the effects of prograde thermal metamorphism on carbon isotope ratios. This discussion included an analysis of the effect an hypothetical Rayleigh-type distillation process might potentially have in reducing the  $\delta^{13}$ C of organic carbon that is residual to oxidation during diagenesis and metamorphism. The calculations presented in that discussion (including Fig. 3 and its caption, and text on page 58 of ref. 1) contained errors that contributed to the conclusion that it would have been physically impossible for such a process to produce the observed  $\delta^{13}$ C values of approximately -35‰ (PDB) from initial abiotic values of -10‰. The purpose of this correspondence is to correct the errors in this calculation and to discuss their significance for the interpretation of the data reported.

Two related errors are present in the Rayleigh distillation calculation as published in ref. 1: 1) the Rayleigh equation in the caption of Fig. 3 uses  $\delta^{13}$ C values where  $^{13}$ C/ $^{12}$ C ratios should be used, and 2) the direction of the equilibrium isotopic fractionation between CO<sub>2</sub> and graphite is opposite that necessary for use of the Rayleigh equation as it is commonly derived for stable isotopes, and its absolute magnitude differs substantially from that estimated by experimental studies of this process. The correct form of the Rayleigh equation for the distillation of CO<sub>2</sub> from residual graphite is:

$$R_f = R_i \cdot F^{(\alpha-1)}$$
 eqn. 1

Where R<sub>i</sub> is the isotope ratio <sup>13</sup>C/<sup>12</sup>C in the graphite prior to oxidation and distillation of CO<sub>2</sub>, R<sub>f</sub> is the same ratio in the residual graphite after this reaction, F is the mole fraction

of the residual phase (i.e. graphite) remaining after this reaction and  $\alpha$  is the equilibrium isotope fractionation factor between the evolved CO<sub>2</sub> and residual graphite at any given step in the Rayleigh distillation process, defined as  $\alpha = R_{CO2}/R_{graphite}$ . Translation of eqn. 1 into standard  $\delta$  notation yields:

$$\delta_f = 1000 \cdot (F^{(\alpha-1)} - 1) + \delta_i \cdot F^{(\alpha-1)}$$
 eqn. 2

Where  $\delta$  values are defined by the equation:

$$\delta = (R/R_{std} - 1) \cdot 1000$$
 eqn. 3

with R<sub>std</sub> being the <sup>13</sup>C/<sup>12</sup>C ratio of a reference standard (e.g. PDB).

The correct value for  $\alpha$  (CO<sub>2</sub>-graphite) at 400°C (the temperature appropriate for modeling prograde metamorphism of the samples in question) is 1.0111 (ref. 4), corresponding to an 11% difference in  $\delta^{13}$ C between CO<sub>2</sub> and graphite. Using this value for  $\alpha$ , an initial  $\delta^{13}$ C value of -10% pdb (the lower limit of 'abiotic' carbon from ref. 1), and eqn. 2, a  $\delta^{13}$ C value of -35% in residual graphite will, in this model, be attained when F = 0.1 (10% of the original carbon remains in the rock as graphite), different from the value of F = 2.5·10<sup>-11</sup> estimated by Mojzsis *et al.*<sup>1</sup> It was argued that the extreme value of F they calculated disproved the possibility that low  $\delta^{13}$ C was the result of oxidation during metamorphism because virtually no C would remain in the rock if it had experienced such extreme extents of reaction. The correct value of F = 0.1 (90% reaction) is not sufficiently extreme to offer such disproof, and instead the model calculation permits that under the assumed conditions the oxidation of carbonaceous matter during metamorphism could produce residual graphite with  $\delta^{13}$ C values in the range that is often regarded as diagnostic of biogenic carbon (i.e. less than -20%).

Resolving this issue requires that one prove or disprove the action of oxidation reactions that proceed by Rayleigh distillation, i.e. whether or not this mechanism takes place in nature. The debate over the C-isotope shifts that are expected to accompany diagenesis and metamorphism of carbonaceous matter is old (e.g., refs. 5,6), and

controversy as to the origin and initial isotopic composition of carbon in Archean rocks remains today (e.g., ref. 7). However, a number of studies have demonstrated that metamorphism of carbonaceous matter in sedimentary rocks leads to increases, not decreases, in  $\delta^{13}$ C due to the distillation of CH4 and exchange with high  $\delta^{13}$ C carbonate minerals<sup>8-12</sup>. Armoring of carbonaceous matter by crystals of a C-poor phase, such as is the case for the graphite analyzed by Mojzsis *et al.*, 1 tends to further reduce the opportunities for isotopic fractionation during metamorphism 13,14. For these reasons we support the initial interpretation by Mojzsis *et al.*<sup>1</sup>, that measured values of  $\delta^{13}$ C in graphite define maximum limits on the initial  $\delta^{13}$ C values of precursor carbonaceous matter.

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