

## Carbon isotope evidence for early life

The Letter by Mojzsis *et al.*<sup>1</sup> 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 a Rayleigh distillation process might have in reducing the <sup>13</sup>C/<sup>12</sup>C ratio of organic carbon that is residual to oxidation during diagenesis and metamorphism. The calculations presented in that discussion (including Fig. 3, 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 δ<sup>13</sup>C values of approximately -35‰ (with respect to the PDB standard) from initial abiotic values of -10‰. Here we correct those errors and discuss the significance of the correct calculation.

Two related errors are present in the Rayleigh distillation calculation as published in ref. 1. First, the Rayleigh equation in the caption of Fig. 3 uses δ<sup>13</sup>C values where <sup>13</sup>C/<sup>12</sup>C ratios should be used. Second, the direction of the equilibrium isotopic fractionation between CO<sub>2</sub> and graphite is opposite to that necessary for the 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. The correct form of the Rayleigh equation for the distillation of CO<sub>2</sub> from residual graphite is:

$$R_f = R_i \times F^{(\alpha-1)} \quad (1)$$

where  $R_i$  is the isotope ratio <sup>13</sup>C/<sup>12</sup>C in the graphite before oxidation and distillation of CO<sub>2</sub>,  $R_f$  is the same ratio in the residual graphite after this reaction,  $F$  is the mole fraction of the residual phase (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  $\alpha = R_{\text{CO}_2}/R_{\text{graphite}}$  (ref. 2). Translation of equation (1) into standard  $\delta$  notation yields:

$$\delta_f = (1000 \times (F^{(\alpha-1)} - 1)) + \delta_i F^{(\alpha-1)} \quad (2)$$

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

$$\delta = (R/R_{\text{std}} - 1) \times 1000 \quad (3)$$

with  $R_{\text{std}}$  being the <sup>13</sup>C/<sup>12</sup>C ratio of a reference standard (for example PDB).

The correct value for  $\alpha$  (CO<sub>2</sub> - graphite) at 400 °C, the temperature appropriate for modelling prograde

metamorphism of the samples in question, is 1.0111 (ref. 3), corresponding to an 11‰ difference in δ<sup>13</sup>C between CO<sub>2</sub> and graphite. Using this value for  $\alpha$ , an initial δ<sup>13</sup>C value of -10‰<sub>PDB</sub> (the lower limit of 'abiotic' carbon from ref. 1), and equation (2), a δ<sup>13</sup>C value of -35‰ in residual graphite are obtained when  $F = 0.1$  (10% of the original carbon remains in the rock as graphite), substantially different from the value of  $F = 2.5 \times 10^{-11}$  estimated by Mojzsis *et al.*<sup>1</sup>

It was argued in ref. 1 that the extreme value of  $F$  that was calculated disproved the possibility that low δ<sup>13</sup>C was the result of oxidation during metamorphism because virtually no carbon would remain in the rock. The correct value for  $F = 0.1$  (90% reaction) is not sufficiently extreme to rule out the possibility, and instead the calculation permits that, under the assumed conditions, the oxidation of carbonaceous matter during metamorphism could produce residual graphite with δ<sup>13</sup>C values in the range that is often regarded as diagnostic of biogenic carbon (less than -20‰).

The debate over the carbon-isotope shifts that are expected to accompany diagenesis and metamorphism of carbonaceous matter is old (for example, refs 4, 5), and controversy as to the origin and initial isotopic composition of carbon in Archean rocks continues<sup>6</sup>. Resolving this issue for a given sample requires that the action of oxidation reactions that proceed by Rayleigh distillation during hydrocarbon maturation and metamorphism is proved or disproved. The requirements for such a process to lead to low δ<sup>13</sup>C residual carbon are that fluids in equilibrium with residual hydrocarbons and/or graphite must have a high ratio of CO<sub>2</sub>/CH<sub>4</sub>, and that isotopic exchange between residual hydrocarbons and/or graphite and fluids must be rapid. Under common oxygen fugacity ( $f_{\text{O}_2}$ ) conditions and mid-crustal pressures, and at temperatures less than 500 °C, C-O-H fluids are generally CH<sub>4</sub> dominated<sup>7</sup>. Thus, these requirements are not expected to be met unless metamorphic conditions are unusually oxidizing or if temperatures are higher<sup>7</sup>.

A number of previous studies have demonstrated that metamorphism of carbonaceous matter in sedimentary rocks commonly leads to increases, rather than decreases, in δ<sup>13</sup>C owing to the distillation of CH<sub>4</sub> and exchange with high δ<sup>13</sup>C carbonate minerals<sup>8,9</sup>. Armouring of carbonaceous matter by crystals of a C-poor phase, such as is the case for the graphite analysed by Mojzsis *et al.*<sup>1</sup>, would tend further to reduce the opportunities for isotope fractionation during metamorphism<sup>10</sup>. For these reasons the authors of the original paper<sup>1</sup> support the initial interpretation

that measured values of δ<sup>13</sup>C in graphite define maximum limits on the initial δ<sup>13</sup>C values of precursor carbonaceous matter.

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## Clouds, precipitation and temperature range

The daily range of surface air temperature has decreased worldwide since the 1950s, with an increase in night-time minimum temperature ( $T_{\text{min}}$ ) exceeding the increase in daytime maximum temperature ( $T_{\text{max}}$ )<sup>1–3</sup>. Coincident increases in total cloud cover found in many locations<sup>1</sup> have been cited as a plausible cause<sup>1,4,5</sup>. Clouds have a damping effect on diurnal temperature range (DTR), aiding cooling of the Earth's surface by reflecting sunlight and heating the surface by increasing downward longwave radiation, as confirmed by model studies<sup>6,7</sup>. Increasing aerosol concentrations have been suggested as a possible cause of the observed increase in cloudiness<sup>4</sup>, but we suggest that greenhouse gas-induced increases in thick precipitating clouds and precipitation are better candidates to explain the decrease in DTR.

DTR has been negatively correlated with both total cloud cover and precipitation throughout this century, over all regions for which data are available (Fig. 1). In particular, the correlation is remarkable for the long-term trends, especially over mid-latitude Canada and Australia. Available surface and ship observations<sup>8</sup> indicate that, during the 1952–81 period, cumulonimbus, nimbostratus and cirriform clouds increased substantially over Australia, Europe and the United States, but there was little change in low-altitude cumulus and stratus clouds over northern mid-latitude oceans. Consistent

with the cumulonimbus and nimbostratus increase, clouds with low bases showed the largest increase from 1948–87 over the United States<sup>9</sup>. However, available data are insufficient to determine whether thin cumulus and stratus clouds have also increased over the United States.

Satellite observations (Fig. 2), which are good for studying clouds with high tops, show that monthly anomalies of only optically thick and high-topped clouds are strongly correlated with precipitation anomalies over a 66-month period of coincident observations. As the correlation between cloud cover and precipitation is independent of the timescale of variation<sup>10</sup>, the correlated secular trends of precipitation and cloud cover shown in Fig. 1 indicate that it was the thick precipitating clouds that increased during the past 4 or 5 decades.

Thick precipitating clouds such as cumulonimbus and nimbostratus have low cloud bases, which radiate back to Earth at temperatures close to ground temperature, and high cloud tops with large column-integrated condensate which reflect back most of the sunlight. These two properties make these clouds very effective in damping DTR, consistent with a general circulation model (GCM) study<sup>7</sup>. Over the contiguous United States and Europe, the correlation between DTR and precipitation is substantially higher than that between DTR and total cloud cover (Fig. 1), suggesting that DTR decreases are more likely to be related

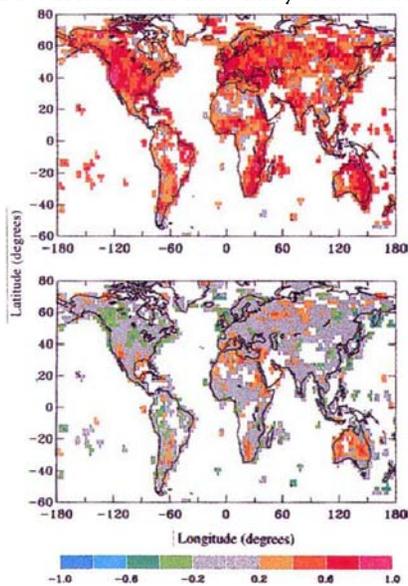


Figure 2 Maps of correlation coefficients (–1.0 to +1.0) between surface observed monthly precipitation anomalies and the ISCCP<sup>15</sup> cloud cover anomalies of nimbostratus, cirrocumulus/cirrostratus and deep convective clouds (upper panel) and other types of clouds (lower panel). Seasonal variations were removed by subtracting out the monthly means. The systematic error in ISCCP clouds due to changes of satellites was corrected. The data are for July 1983 to December 1988.

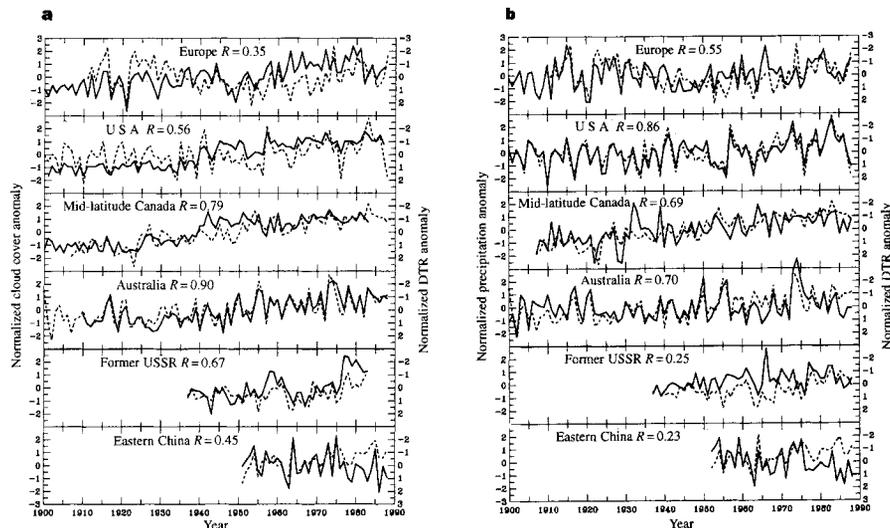


Figure 1 Variations of annual anomalies of diurnal temperature range (dashed line) with a, total cloud cover<sup>11–14</sup>, and b, precipitation (solid lines), over various regions during this century. Note that the scale for DTR anomalies on the right side decreases upwards. The DTR data are derived from the NOAA National Climatic Data Center GHCN v2 data set. Correlation coefficient *R* between the curves is given.

to increases in precipitating clouds.

Given the high correlation between DTR and precipitation (Fig. 1), the increased precipitation itself may have contributed to the DTR decrease through surface evaporative cooling (especially over dry areas).  $T_{max}$  is more sensitive to water availability than  $T_{min}$  owing to the existence of an unstable surface layer (thus higher turbulent mixing) and larger potential evapotranspiration during the day<sup>9</sup>. This mechanism is likely to be most effective from late summer to autumn when soil moisture levels are low in northern mid-latitudes, consistent with the seasonal signal of DTR changes, which show largest decreases in the northern autumn<sup>1,3</sup>. The mechanism should also work under clear-sky conditions, which is in agreement with the finding that the DTR of clear skies has decreased in the United States<sup>5</sup>, although increased greenhouse gas concentrations (including water vapour)<sup>2</sup> may also contribute to the DTR decrease. (GCM results<sup>6</sup> suggest that the direct effect of industrial aerosols on DTR is small compared with the concurrent CO<sub>2</sub> forcing.)

Because anthropogenic aerosols may increase the concentration of cloud condensation nuclei and reduce mean cloud-droplet sizes, thus inhibiting precipitation, the increases in precipitation and precipitating clouds are likely to be related to other forcings such as the enhanced greenhouse effect<sup>2</sup>. The increases in precipitation and precipitating clouds are consistent with GCM experiments with increasing CO<sub>2</sub> which generally produce increased precipitation (mostly in winter) and increased convective cloud amounts over northern mid-latitude land areas<sup>2</sup>. Simulated changes in mid-latitude nimbostratus, a dominant precipitating cloud there, are more model-dependent by comparison and therefore not conclusive.

Consistent with our argument, model simulations<sup>6</sup> with increasing CO<sub>2</sub> concentrations reproduce DTR changes comparable to the observations through mechanisms similar to those mentioned above. However, more detailed analyses of changes of cloud types are needed before a definite conclusion can be reached.

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