

## Enhanced CO<sub>2</sub> greenhouse to compensate for reduced solar luminosity on early Earth

CURRENT models for the evolution of the Sun require an increase in solar luminosity by 25% since the formation of the Solar System<sup>1</sup>. Such an increase in the solar constant should have profound effects on the terrestrial climate, but there is no evidence from the fossil record of a corresponding change in the Earth's global mean temperature<sup>2</sup>. This apparent conflict cannot be explained by the apparent inability of solar models to account for the low observed neutrino flux<sup>3</sup>. Even models that are forced to fit the neutrino data require a similar increase in the solar luminosity. As Newman and Rood<sup>1</sup> state: "a faint young Sun is one of the most unavoidable consequences of stellar structure considerations". We discuss here whether CO<sub>2</sub>-H<sub>2</sub>O in a weakly reducing atmosphere could have caused this change in the early Earth's temperature by the so-called greenhouse effect.

Sagan and Mullen<sup>4</sup> suggested that the solution must lie in a more efficient atmospheric greenhouse effect on Earth during the period when the solar luminosity was low. To increase the greenhouse effect, it is necessary to change the atmospheric composition, or density, or both. Sagan and Mullen<sup>4</sup> postulated that the atmosphere was reducing during the early history of the Earth and found that a small amount of ammonia in the atmosphere (mixing ratio 10<sup>-5</sup>-10<sup>-6</sup>) would provide the necessary opacity to outgoing infrared (IR) radiation to increase the mean surface temperature. In this model, the transition from reducing to oxidising conditions with the replacement of the NH<sub>3</sub>-H<sub>2</sub>O greenhouse by a CO<sub>2</sub>-H<sub>2</sub>O greenhouse comes about as a result of the development of widespread green plant photosynthesis 1,000-2,000 Myr ago. A similar route was invoked by Hart<sup>5</sup>, who developed a more detailed model for the evolution of the atmosphere.

We agree that an enhanced greenhouse effect caused by a change in atmospheric composition is a good solution to the solar constant dilemma, but we think the NH<sub>3</sub>-H<sub>2</sub>O model is unrealistic. Current thinking about the early atmosphere of the Earth is shifting away from the traditional view that called for a highly reduced mixture of methane, ammonia and hydrogen, for reasons summarised by Walker<sup>6</sup>. More recent data have simply added strength to Walker's conclusions. As the noble gases on Mars show the same pattern of relative abundances as they do on Earth and in the 'planetary component' of the meteoritic gases, whatever fractionation process caused this pattern must have occurred before planet formation<sup>7</sup>. This being the case, the cosmic abundance ratio of 1.6 × 10<sup>4</sup> for H/Ne<sup>8</sup> gives the maximum amount of hydrogen available for a 'captured' primitive atmosphere. Using the present atmospheric partial pressure of Ne (12.7 × 10<sup>-6</sup> bar), the maximum hydrogen partial pressure on the primitive Earth from this source was 10 mbar. As Walker<sup>6</sup> has pointed out, such an atmosphere would have dissipated in <10<sup>4</sup> yr. The partial pressure of ammonia in this atmosphere would have been comparable to that of neon, but its lifetime against photodissociation would have been short and it would have been out of equilibrium with crustal rocks.

Photochemical calculations by Kuhn and Atreya<sup>9</sup> indicate that ammonia would be irreversibly converted to N<sub>2</sub> on the primitive Earth in <40 yr if the mixing ratio were ≤10<sup>-4</sup>. Eugster<sup>10</sup> has investigated the stability of ammonia on the primitive Earth and concluded that a mixture of N<sub>2</sub> and H<sub>2</sub> will predominate over ammonia in a normal crustal environment. Outgassing of ammonia after the last phase of accretion (or after differentiation, choosing either an inhomogeneous or homogeneous model for planet formation) seems precluded by the lack of free iron in the upper mantle<sup>6</sup>. As life must have begun after this phase in the planet's history, it seems reasonable to agree with Eugster<sup>10</sup> that any initial ammonia in the atmosphere "was oxidised to nitrogen long before the origin of life". Small amounts of methane and ammonia may have been transiently

present in later times as a result of meteoritic and cometary impact, but lunar evidence indicates that bombardment rates must have been close to their present low values ~3,600 Myr ago<sup>11</sup>.

In fact, the idea that the chemistry preceding the origin of life must have occurred in highly reducing conditions supported the traditional view of the composition of the early atmosphere<sup>12</sup>. But there have been sufficient demonstrations that pathways towards the formation of essential pre-life compounds can occur only in weakly reducing conditions for this argument to have lost its original force. For example, Abelson<sup>13</sup> was able to produce amino acids from the UV irradiation of a mixture of CO<sub>2</sub>, CO, N<sub>2</sub>, H<sub>2</sub>O and just 1-10% H<sub>2</sub>. This seems a much more reasonable composition for the post-accretion (or post-differentiation) atmosphere of the primitive Earth<sup>6,10</sup>. It is especially unlikely that the ammonia-containing mixture invoked by Sagan and Mullen<sup>4</sup> (or ammonia plus methane suggested by Hart<sup>5</sup>) would last for 2,000-3,000 Myr after formation of the planet. But can this weakly reducing atmosphere provide the required greenhouse effect? The answer depends on carbon dioxide and water vapour, as the other gases are ineffective absorbers of IR radiation.

We have tested this possibility by assuming that the concentration of CO<sub>2</sub> in the early atmosphere was much higher than the present value. We have coupled the evolutionary model for the CO<sub>2</sub> abundance used by Hart<sup>5</sup> with a radiative-convective CO<sub>2</sub>-climate model. (We used the model as in Augustsson and Ramanathan<sup>14</sup> except that we do not include the 7.6 μm pressure-induced band of CO<sub>2</sub> in the present analysis, because of the lack of band absorption data for the large amounts of CO<sub>2</sub> considered here.) Hart's model comprises a numerical simulation of the evolution of the Earth's atmosphere over its 4,500 Myr history, accounting for time-dependent outgassing, the Urey equilibrium, the onset of photosynthesis, and crude atmospheric chemistry to develop the time-history of the CO<sub>2</sub> concentration. Hart also presents NH<sub>3</sub> and CH<sub>4</sub> concentrations but we do not believe that these gases would persist within the early atmosphere. Moreover, even if CH<sub>4</sub> were present in the early atmosphere, this constitutes a very inefficient greenhouse gas. Quite obviously Hart's attempt contains many modelling uncertainties, but at least it produces a first estimate for the variability of atmospheric CO<sub>2</sub> over geological time.

Although Hart<sup>5</sup> has considered the greenhouse effect from enhanced CO<sub>2</sub>, as well as other gases, he uses grey gas radiation modelling. But the realities of accounting for enhanced CO<sub>2</sub> require a more detailed radiation model<sup>14,15</sup>. Moreover, Hart has used a cloud radiation model which produces strong negative climate feedback, contrary to the findings of recent cloud-climate modelling studies<sup>16,17</sup>. This occurs as Hart relates global cloud amount to atmospheric water-vapour content, such that his cloud amount increases with increasing planetary surface

Table 1 Predicted global surface temperature,  $T_s$ , throughout the evolution of the Earth's atmosphere

Time (10 <sup>9</sup> yr BP)	S (W m <sup>-2</sup> )	P <sub>CO<sub>2</sub></sub> (bar)	T <sub>s</sub> (K)	
4.25	1,039	0.31	310	(284)
3.5	1,096	0.070	296	(284)
3.0	1,133	0.033	293	(284)
2.5	1,171	0.018	292	(286)
2.0	1,209	0.0086	290	(286)
1.5	1,247	0.0029	288	(286)
1.0	1,284	0.00065	286	(285)
0.5	1,322	0.00032	287	(287)
0	1,360	0.00032	290	(290)

The solar constant,  $S$ , is taken to be  $S = 1,020 \text{ W m}^{-2}$  4,500 Myr ago and is assumed to increase linearly with time. The CO<sub>2</sub> surface pressure,  $P_{\text{CO}_2}$ , is from Hart<sup>5</sup>. Temperatures listed in parentheses refer to deletion, within the model, of weak CO<sub>2</sub> bands at 9-10, 12 and 18 μm.

temperature. But recent model predictions suggest that the reverse occurs (see ref. 16). Hart has additionally neglected the IR opacity of clouds. Thus, in his model, a warmer planet produces an enhanced planetary albedo due to increased cloudiness, but with no compensatory IR modification, and for this reason his model gives negative cloud feedback.

In the present study, we ignore climate-induced changes in cloud-cover fraction, following the suggestion that the cloud albedo and IR modifications are compensatory<sup>17</sup>. Moreover, we do not attempt to incorporate ice-albedo feedback, as the extent of the polar caps seems to depend on ocean advection and, in turn, the positions of the continents which have changed considerably over geological time<sup>18</sup>. Even without this effect, there are substantial uncertainties in modelling ice-albedo feedback<sup>19</sup>. Our model mostly predicts global temperatures greater than those at present; neglect of positive ice-albedo feedback will simply produce an underestimate of these temperatures. We further assume that the Earth's surface albedo is constant and equal to its present value, ignoring changes caused by mountain building and surface vegetation.

The results of our modelling are summarised in Table 1. We have simply assumed a total atmospheric pressure of 1 bar; the predicted global temperatures are not particularly sensitive to this assumption. The solar constant was taken to be  $1,020 \text{ W m}^{-2}$  (75% of the present value), 4,500 Myr ago.

The predicted global temperatures of Table 1 suggest that enhanced  $\text{CO}_2$  concentrations could have been the sole mechanism for preventing glaciation of the Earth when there was reduced solar luminosity. Past global glaciation would be implied by climate models in the absence of an increased atmospheric greenhouse<sup>20</sup>. Within the confines of our model calculations, the Earth was never more than 4 K colder than at present. This, of course, does not account for glacial-interglacial oscillations which, on our time scales, comprise short-term climatic variability.

A detailed analysis of our model results revealed that some weak bands of  $\text{CO}_2$ , which have been neglected in previous studies of this problem<sup>4,5</sup>, contribute significantly to the surface warming. These comprise two bands at  $12 \mu\text{m}$ , two bands at  $18 \mu\text{m}$ , and two bands in the  $9\text{--}10 \mu\text{m}$  region. Predicted global surface temperatures, deleting these weak bands within the model calculation, are included in parentheses in Table 1. Clearly, these weak bands are important for large  $\text{CO}_2$  concentrations. In this context, the neglect of the  $7.6 \mu\text{m}$  band in the present model would produce an underestimate of the computed surface temperatures by about 5–10 K for  $\text{CO}_2$  surface pressures of the order of 0.1–0.3 bar.

Our results are quite insensitive to events occurring from 4,500 to 4,250 Myr ago. For example, if there were an initial global glaciation during this time period, due possibly to limited outgassed  $\text{CO}_2$ , the  $\text{CO}_2$  greenhouse effect at 4,250 Myr ago would be sufficient to melt the surface ice. To show this, taking the surface albedo for an ice-covered Earth to be 0.7, we estimate the corresponding global temperature 4,250 Myr ago to be 285 K, far too high for global glaciation to persist.

We conclude that there is no need for ammonia to be present in the early atmosphere to maintain moderate temperatures when the Sun's luminosity was low. Carbon dioxide alone is sufficient, provided the partial pressure of this gas approaches the values suggested by the evolutionary model of Hart<sup>4</sup>. In view of the huge amount of  $\text{CO}_2$  that has been produced over geological time and our lack of knowledge about rates at which

release and deposition occurred in primitive times, this does not seem an unwarranted assumption. In fact, more detailed calculations may permit us to place a limit on the amount of  $\text{CO}_2$  that could ever have been present in the atmosphere at one time, as the full complement (some 70 bar) would have caused excessive warming of the Earth's surface. We are also pursuing applications to the atmosphere of Mars, where larger  $\text{CO}_2$  abundances in primitive times might have provided a sufficient greenhouse effect to permit the flow of liquid water apparently required by the evidence for fluvial erosion on that planet's surface.

The transition to an oxidising atmosphere on Earth between 2,000 and 2,500 Myr ago, brought about by green-plant photosynthesis, is then not accompanied by a transition from an  $\text{NH}_3\text{--H}_2\text{O}$  to a  $\text{CO}_2\text{--H}_2\text{O}$  greenhouse, but rather represents a simple increase in free molecular oxygen with the concomitant disappearance of CO. The composition of the intermediate atmosphere, spanning  $\sim 2,000$  Myr from the early escape of hydrogen to the onset of oxygen-producing photosynthesis, was probably very similar to the present atmospheres of Mars and Venus, two planets on which any living organisms (if present) apparently have not been able to influence atmospheric composition as they have on Earth<sup>21,22</sup>.

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