

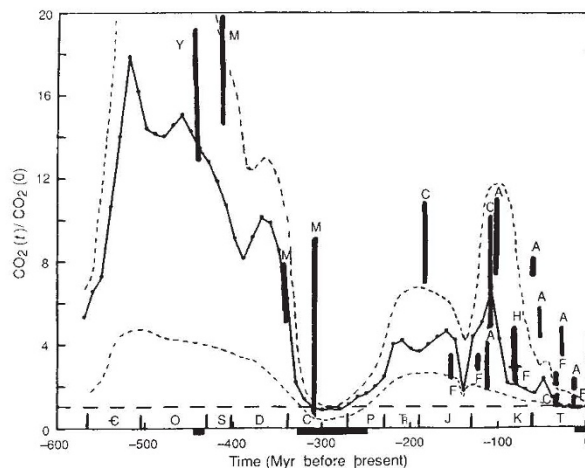
## Palaeo-CO<sub>2</sub> and climate

SIR — As recognized by Kasting in his News and Views article<sup>1</sup>, there is a problem in reconciling high estimated atmospheric CO<sub>2</sub> levels<sup>2,3</sup> for the late Ordovician period (about 440 million years (Myr) ago) with the occurrence of continental glaciation at that time. Nevertheless, other estimates of palaeolevels of CO<sub>2</sub> are in general agreement with independent estimates of palaeoclimate for the remaining portion of Phanerozoic time (the past 570 Myr). The two most thoroughly studied Phanerozoic glaciations are those of the Permo-Carboniferous and late Cenozoic which occur at times of minimum CO<sub>2</sub> (see figure). Also, well-documented warm periods, such as the Cretaceous (symbol K, 135–65 Myr ago), correspond to high estimated levels of atmospheric CO<sub>2</sub>. Taken together, these results all point to the importance of the atmospheric greenhouse effect as a major control on very long-term climate.

The methods used in constructing the figure are quite different. The curve is the best estimate obtained from a computer model of the long-term carbon cycle<sup>3,4</sup>. This model considers the effect on atmospheric CO<sub>2</sub> of the large and dominant carbon fluxes over millions of years between rocks and the atmosphere/hydrosphere/biosphere system. This includes: (1) weathering of Ca and Mg silicates and carbonates and sedimentary organic matter on the continents; (2) the burial of carbonates and organic matter in sediments; and (3) the thermal breakdown of carbonates and organic matter at depth with resultant CO<sub>2</sub> degassing to the atmosphere. The area, mean elevation and position of the continents, the rise and evolution of vascular land plants, and the feedback effect of CO<sub>2</sub> on both greenhouse global warming and plant growth are considered as important factors affecting weathering rates. The carbon isotope composition and abundance of carbonates and organic matter in sedimentary rocks are used to calculate burial rates (see also ref. 5). Rates of seafloor creation and subduction, as revealed by plate-tectonic theory and changes in sea level, are assumed to be a direct measure of degassing rate. Many of these parameters are not well known and variation of their values between reasonable limits gives rise to the range of CO<sub>2</sub> values enclosed by the dashed lines in the figure. Also, this type of modelling is subject to constant revision as better methods of estimating the various parameters arise.

Another method for calculating palaeo-CO<sub>2</sub> is the measurement of the

Carbon dioxide against time based on a theoretical model of the long-term carbon cycle<sup>3,4</sup>. The parameter CO<sub>2</sub>(t)/CO<sub>2</sub>(0) is the ratio of mass of CO<sub>2</sub> in the atmosphere at some time in the past to that at present. Dashed lines enclose the approximate range of error of the model based on sensitivity analysis<sup>4</sup>. Horizontal bars along the abscissa, major glaciations; vertical bars, independent palaeo-CO<sub>2</sub> estimates based on: (1) carbon isotope analyses of CaCO<sub>3</sub> in palaeosols (C, ref. 6; M, ref. 7); (2) carbon content and isotope composition of the FeCO<sub>3</sub> component of goethite in palaeosols (Y, ref. 2); (3) the difference in carbon isotope composition between organic matter and CaCO<sub>3</sub> in marine sedimentary rocks (A, ref. 8; H, ref. 10); and (4) the difference in carbon isotope composition between specific biomarker compounds and CaCO<sub>3</sub> in marine sedimentary rocks (F, ref. 9). Lengths of vertical bars represent each published estimate of range in error. (The 320 Myr value is corrected for change in the carbon isotope composition of the ocean and atmosphere and the probably arid character of the sample<sup>7</sup>.)



<sup>13</sup>C content of CaCO<sub>3</sub> (refs 6,7) and the FeCO<sub>3</sub> component of goethite<sup>2</sup> in ancient palaeosols. Both methods assume that the <sup>13</sup>C content of pedogenic carbonate represents a mixture of <sup>13</sup>C-enriched atmospheric CO<sub>2</sub> and <sup>13</sup>C-depleted CO<sub>2</sub> generated from the decomposition of soil organic debris. The palaeolevel of CO<sub>2</sub> at depth in the soil is assumed constant in the CaCO<sub>3</sub> method, whereas in the other method it is calculated from the FeCO<sub>3</sub> content of the goethite. There are many assumptions in these methods and the range of error stated in each study referenced is shown in the figure.

A third method of palaeo-CO<sub>2</sub> estimation is based on the fractionation of <sup>13</sup>C between carbonates and organic matter in marine sedimentary rocks<sup>8–10</sup>. The isotope composition of carbonate carbon reflects ancient seawater composition and the difference between this and the isotope composition of organic carbon reflects the degree of carbon isotope fractionation during photosynthesis. This fractionation has been shown to be a function of the CO<sub>2</sub> content of sea water<sup>10–12</sup>, so that assuming equilibrium with the atmosphere, one can calculate levels of palaeo-CO<sub>2</sub>. Lack of ocean-atmosphere equilibration, vital effects on carbon-isotope fractionation, differences in temperature, and diagenetic processing of organic matter can all give rise to errors in this method. (To avoid the last problem the <sup>13</sup>C content of unaltered biomarker compounds only are analysed in ref. 9.) This helps explain the length of each vertical bar and the disagreement between studies shown in the figure.

Regardless of the numerous errors mentioned above, there is an amazing semi-quantitative agreement between the results of the various methods for

estimating palaeo-CO<sub>2</sub>. In other words, the times of high versus low CO<sub>2</sub> are similar and actual calculated values agree within a factor of about three. Kasting's hope<sup>1</sup> for methods of deducing ancient CO<sub>2</sub> levels as accurate as those based on the study of trapped air bubbles in glacial ice is probably overly optimistic because of various inherent errors in the carbon isotope methods, as well as large ones in the model calculations. Nevertheless, the isotope methods do hold promise for making semi-quantitative estimates of ancient CO<sub>2</sub> levels, and modelling calculations at least point to important processes affecting CO<sub>2</sub> and the need for a better understanding of them.

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