preferential survival of the diamond-bearing eclogite would be expected if the oxidation state of the mantle beneath Roberts Victor was defined by the EMOD or EMFDD reactions in the dominant peridotite. Carbonate- and diamond-bearing peridotite would coexist with diamond-bearing eclogite. Upon incorporation into the ascending kimberlite magma, the peridotite would undergo decarbonation reactions such as reactions 1 or 3. These reactions would liberate CO_2 and disaggregate the xenolith. In contrast, the carbon-bearing eclogitic rocks would contain diamond rather than carbonate and therefore would not experience decarbonation; hence, they would be more likely to survive the trip to the surface intact. In this scenario, differential carbon contents in peridotite versus eclogite need not be invoked to explain the observations, merely that the diamond-carbonate equilibria be dictated by reactions involving olivine and orthopyroxene in the lherzolite or harzburgite and by reactions involving clinopyroxene and coesite in the eclogite.

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4. This reaction and the subsequent ones are written with the high-temperature side on the right, as is conventional. Abbreviations under the formulas refer to the phase containing the component referenced: coes, coesite; cpx, clinopyroxene; dia, diamond; dol, dolomite; mag, magnesite; ol, olivine; opx, orthopyroxene; V, vapor. Components are abbreviated: Fo, forsterite, Mg_2SiO_4; Cc, calcite, $CaCO_3$; En, enstatite, $MgSiO_3$; and Di, diopside, $CaMgSi_2O_6$.
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8. Composition (in weight %): SiO_2, 46.51; TiO_2, 0.53; Al_2O_3, 14.85; MgO, 13.66; CaO, 12.04; Na_2O, 1.73; and CO_2, 10.68. These values were derived, by isomolar substitution of Mg for Fe and addition of CO_2, from a composition used by T. Irifune, T Sekine, A. E Ringwood, and W. O. Hibberson [*Earth Planet. Sci. Lett.* **77**, 245 (1986)], who studied the phase relations of CO_2-free eclogites to 15 GPa.
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$$\begin{aligned}\Delta\log f_{O_2}(\mathrm{DCDD}) &= -0.71734 + 0.13175\,P \\ &\quad + (143.2743 - 59.1790\,P)/T \\ &\quad - 0.5\log a(\mathrm{Di}) + 0.5\log a(\mathrm{Dol})\end{aligned}$$

$$\begin{aligned}\Delta\log f_{O_2}(\mathrm{EMOD}) &= -0.68258 + 0.13320\,P \\ &\quad - (329.5898 + 258.0536\,P)/T \\ &\quad - \log a(\mathrm{Fo}) + 0.5\log a(\mathrm{En}) + \log a(\mathrm{Mag})\end{aligned}$$

$$\begin{aligned}\Delta\log f_{O_2}(\mathrm{EMFDD}) &= -0.51839 + 0.08335\,P \\ &\quad + T(-4.7750 \times 10^{-4} + 7.64169 \times 10^{-6}\,P) \\ &\quad - \log a(\mathrm{Fo}) - \log a(\mathrm{Di}) \\ &\quad + 1.5\log a(\mathrm{En}) + \log a(\mathrm{Cc})\end{aligned}$$

(pressure *P* in gigapascals and *T* in kelvins). The standard state for all solids is the pure solid at pressure and temperature. Both coesite and diamond are presumed to be pure phases; hence, *a*(Coes) and *a*(Dia) do not appear in these equations. These equations reproduce the values calculated with the rigorous equations and the data (*11*) to less than ±0.1 unit of $\Delta\log f_{O_2}$ in the range 4 to 7 GPa and 600° to 1300°C.
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Paleozoic Atmospheric CO_2: Importance of Solar Radiation and Plant Evolution

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Changes in solar radiation, as it affects the rate of weathering of silicates on the continents, and other changes involving weathering and the degassing of carbon dioxide (CO_2) have been included in a long-term carbon-cycle model. These additions to the model show that the major controls on CO_2 concentrations during the Paleozoic era were solar and biological, and not tectonic, in origin. The model predictions agree with independent estimates of a large mid-Paleozoic (400 to 320 million years ago) drop in CO_2 concentrations, which led to large-scale glaciation. This agreement indicates that variations in the atmospheric greenhouse effect were important in global climate change during the distant geologic past.

The weathering of Ca-Mg silicate rocks on the continents, followed by the precipitation of the Ca and Mg as carbonate minerals in the oceans, constitutes a major process whereby atmospheric CO_2 is regulated on a multimillion-year time scale. This process can be generalized in terms of the overall reactions (*1*)

$$CO_2 + CaSiO_3 \rightarrow CaCO_3 + SiO_2$$

$$CO_2 + MgSiO_3 \rightarrow MgCO_3 + SiO_2$$

Several major factors affect CO_2 uptake by Ca-Mg silicate weathering. The changes in intensity of solar radiation with time affect the surface temperature of the Earth and, thereby, the rate of rock weathering. The CO_2 greenhouse effect acts as a negative feedback mechanism to stabilize the Earth's surface temperature. The rise and evolution of vascular land plants have resulted in accelerated chemical weathering by their secretion of acids, providing ground litter for the microbial production of CO_2 and holding and recycling moisture in the soil. Finally, mountain uplift brings about the exposure of weatherable rock by erosion.

In this report, I show how solar radiation and the rise and spread of land plants were major factors affecting continental weathering, and consequently the concentrations of atmospheric CO_2, during the Paleozoic era [approximately 570 to 250 million years ago (Ma)]. Estimated CO_2 concentrations are high for this time (*2*, *3*), during which a transition from the extremely high CO_2

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values believed to have been present on the early Earth and the lower concentrations characteristic of the more recent geologic past took place (*4*).

To account for a number of important studies, I have revised the Phanerozoic (past 570 million years) carbon-cycle model (*5*). This new model, GEOCARB II (*6*), includes the following changes: (i) the increase in solar radiation with time in the feedback function for weathering, on the basis of general circulation model (GCM) calculations (*7, 8*); (ii) the separation of the feedback function for silicates from that for carbonates; (iii) the weaker dependence of prevascular plant weathering on atmospheric CO_2, which allows for a weathering system more open to the atmosphere; (iv) the Sr isotopic composition of ancient seawater as it defines the role of mountain uplift in the exposure of radiogenic silicates to enhanced weathering (*9, 10*); (v) recent estimates of the temperature coefficient of Ca-Mg silicate weathering (*11, 12*); (vi) the effect of changes in global river runoff on the concentration of dissolved bicarbonate that is derived from Ca and Mg silicate weathering (*13, 14*); (vii) new data on runoff as a function of geologic time (*15*); and (viii) additional data on sea-floor spreading and subduction rates, changes in land area underlain by carbonates, and the relative proportion of $CaCO_3$ deposition in shallow water to that in the deep sea.

The most significant effect on the amended model is the inclusion of solar evolution. Estimates (*4*) of changes in the solar constant with time show that it essentially increased linearly over the past 570 million years by 4.6%. This result, when combined with GCM results (*7, 8*), enables erivation of the simple expression

$$T(t) - T(0) = G \ln RCO_2(t) - W_s(t/570) \quad (1)$$

where $T(t)$ is the global mean air surface temperature at some time before the present, in millions of years; $T(0)$ is the global mean air surface temperature at present (15°C); $RCO_2(t)$ is the mass of CO_2 in the atmosphere at time t divided by that at present; and G and W_s are empirical constants derived from GCM modeling [$G = 6°C$; $W_s = 12.9°C$ (*7, 8*)]. [For the range of RCO_2 values I considered, Eq. 1 is in good agreement with the more complicated expressions of Caldeira and Kasting (*4*).] Equation 1 implies that the doubling of RCO_2 at present ($t = 0$) would result in a 4°C rise in temperature, whereas at the beginning of the Cambrian (570 Ma), because of lower solar radiation, the doubling of CO_2 over the present value would result in a temperature 9°C cooler than it is today. A frozen Earth seems unlikely during the early Paleozoic, a period during which warm shallow water organisms thrived (*16*). Therefore, the atmospheric CO_2 concentration should have been considerably higher during that time than at present.

I also improved the feedback expression for rock weathering before the rise of vascular land plants. The earlier model had a closed system linear feedback to prevent excessive atmospheric CO_2 levels in the model at that time. However, the new model has the geologically more reasonable formulation of a square root dependence between the weathering feedback function $f_B(CO_2)$ and RCO_2. This approach represents an intermediate between completely closed system, abiological weathering [$f_B(CO_2) = RCO_2$], in which all CO_2 entering the regolith from the atmosphere is consumed, and completely open system weathering [$f_B(CO_2) = RCO_2^{0.25}$], in which there is an exchange equilibrium between weathering solutions and the atmosphere (*17*). In addition, the use of weaker feedback takes into account the possible enhancement of weathering by primitive microbiota (*18*) over abiological weathering.

Equation 1 in the feedback expression for the weathering of silicates on the continents, along with the other changes listed above, has been examined insofar as it affects RCO_2. When changes in solar radiation are ignored, the RCO_2 values for each time are markedly less than those resulting from their inclusion (Fig. 1). To retain the present temperature [$T = T(0)$] at the Earth's surface requires CO_2 values during the Paleozoic several times higher than those of today.

Much of the excess CO_2 during the early Paleozoic, above the value calculated to balance a lower solar constant (Fig. 1), results from the effect of land-plant evolution on the rate of continental weathering, which is expressed by the parameter $f_E(t)$ (*5, 17*). Calculated concentrations of CO_2 before the rise of vascular plants are highly sensitive to the values chosen for $f_E(t)$ at that time (Fig. 2). Although the effect of plants on the weathering rate is not clear (*17*), the value chosen as a standard [$f_E(t) = 0.15$] agrees with the results of Drever and Zobrist (*19*) and of Cochran and Berner (*20*). Drever and Zobrist found that present rates of silicate weathering in the southern Swiss Alps, deduced from a study of water chemistry, were increased sevenfold in the presence of trees and other higher plants at lower elevations from weathering rates in their absence at the

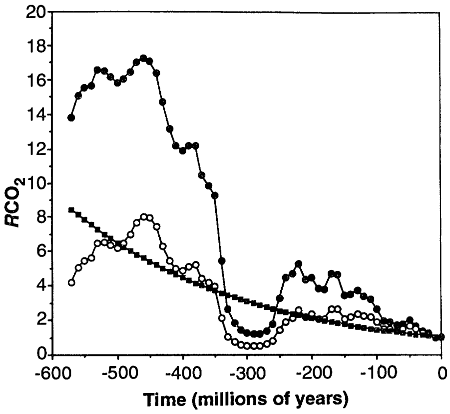

Fig. 1. Plots of RCO_2 versus time calculated with the GEOCARB II model. The RCO_2 value is the ratio of the mass of atmospheric CO_2 at a past time to that at present (300 ppmv). The standard RCO_2 formulation of the model where best estimates of all parameters were made is shown by filled circles; the standard RCO_2 formulation with solar radiation held at the present value for all time is shown by hollow circles; and the RCO_2 for constant Earth surface temperature for all time [derived from Eq. 1 by the solution for $T = T(0)$] is shown by filled squares.

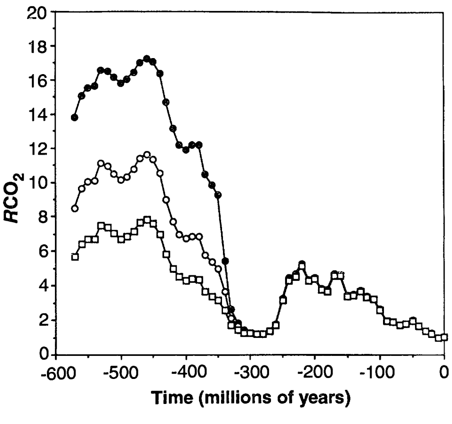

Fig. 2. Plots of RCO_2 versus time for the situation of varying $f_E(t)$ values before the rise of vascular land plants: filled circles, $f_E(t) = 0.15$; open circles, $f_E(t) = 0.30$; open squares, $f_E(t) = 0.50$. The parameter $f_E(t)$ expresses the effect of plants on the rate of CO_2 uptake by weathering [$f_E(t) = 1$ at present by definition].

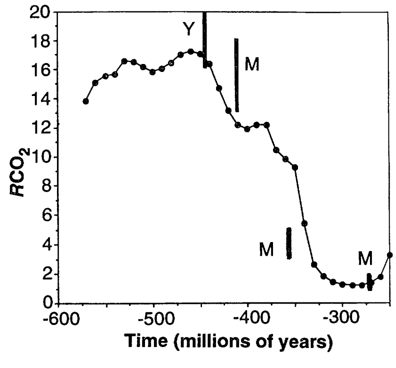

Fig. 3. Comparison of paleolevels of atmospheric CO_2 during the Paleozoic, between the theoretical calculations of the present study and the paleosol results of others. Abbreviations: M, Mora (*2*); Y, Yapp (*3*). The paleosol values fall well within the error limits of the model calculations (*5, 6*).

highest elevations. (The value of seven was calculated from the total effect of a factor of 20 by the removal of an approximately threefold difference in the weathering rate due to differences in mean annual temperature at the two elevations.)

For reasonable ranges of values, other factors affected atmospheric CO_2 concentrations during the Paleozoic much less than those that resulted from changes in solar radiation or from plant evolution. These factors include changes in CO_2 degassing that accompanied changes in seafloor spreading, changes in the mean relief of the continents as indicated by the oceanic $^{87}Sr/^{86}Sr$ ratio, changes in land area subject to weathering, and changes in global river runoff. Most of these factors are tectonic in origin, which suggests that tectonics was overshadowed by solar and plant evolution as a major control of atmospheric CO_2 concentration during the Paleozoic but not at later times.

The CO_2 values calculated for the Paleozoic era agree with independently derived results from the carbon isotopic study of paleosols (Fig. 3) (*2, 3*). There is little doubt that the atmospheric CO_2 concentration during the early Paleozoic was considerably higher than it is today and that it probably dropped as vascular plants arose and accelerated the rate of CO_2 uptake by weathering. These plants had a double effect. In addition to accelerating weathering, they provided a new source of bacterially resistant organic matter (for example, lignin) for burial in sediments. As a result, the removal of atmospheric CO_2 by the massive burial of sedimentary organic matter during the Carboniferous and Permian periods (*21, 22*), evidenced by the abundance of coal of this age, amplified the large mid-Paleozoic drop in CO_2 concentration. The consequently lowered greenhouse effect from this drop likely had a major influence in bringing about the Permo-Carboniferous glaciation, the most extensive and longest glaciation of the entire Phanerozoic (*23*). These results further support the idea that the atmospheric greenhouse effect has been a major factor affecting global climate change over geologic time.

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Detection of Interstellar Pick-Up Hydrogen in the Solar System

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Interstellar hydrogen ionized primarily by the solar wind has been detected by the SWICS instrument on the Ulysses spacecraft at a distance of 4.8 astronomical units from the sun. This "pick-up" hydrogen is identified by its distinct velocity distribution function, which drops abruptly at twice the local solar wind speed. From the measured fluxes of pick-up protons and singly charged helium, the number densities of neutral hydrogen and helium in the distant regions of the solar system are estimated to be 0.077 ± 0.015 and 0.013 ± 0.003 per cubic centimeter, respectively.

As the solar system moves through the local galactic cloud, some interstellar atoms can penetrate as far in as the orbit of Earth. These neutrals, approaching the sun, follow orbits determined by the combined force of gravitational attraction and solar radiation pressure before being ionized by the solar wind and energetic solar photons. The radial distance from the sun at which a substantial fraction of neutrals has been singly ionized is different for various interstellar atoms, depending on ionization cross sections that in turn scale roughly as the first ionization potential of the atom. Helium atoms, whose ionization potential is high, penetrate as far in as ~0.5 astronomical unit, whereas hydrogen gas, and to a lesser degree neutral oxygen, nitrogen, and neon, are excluded from regions closer than several astronomical units (AU) from the sun. Singly charged pick-up helium of interstellar origin was discovered in 1984 at the orbit of Earth by means of a time-of-flight (TOF) instrument on board an Earth-orbiting spacecraft (*1*).

From measurements of light scattered from neutral interstellar hydrogen and known ionization processes in the heliosphere, pick-up hydrogen has long been inferred to exist at distances beyond several AU from the sun (*2–4*). However, direct evidence for its existence has been elusive, in spite of its dynamical importance in the solar wind. The detection of interstellar pick-up hydrogen poses an experimental challenge, requiring access to distances beyond several AU as well as appropriate instrumentation, such as a TOF ion composition spectrometer (*5*) with low background. Even then the separation of pick-up H^+ from the far more abundant solar wind protons is only possible when fluxes of suprathermal solar wind are sufficiently low, and because the two species have markedly different velocity distribution functions.

We report here the discovery of interstellar pick-up hydrogen. Our measurements were made using the Solar Wind Ion Composition Spectrometer (SWICS) (*6*)

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