



Fig. 1 A Landsat image of the Cerro Galan caldera. The snow-capped, 6,100 m resurgent centre is conspicuous at the centre. Laguna Diamante is a relic of a much larger lake which may have filled caldera before resurgence. Extensive apron of Cerro Galan ignimbrite is discernible in pale-grey tones, deeply gullied terrain, best developed in north and west flanks. Cerro Colorado and Cerro Beltran are pre-caldera andesite volcanoes. Dark areas west of Cerro Colorado are basaltic andesite scoria cones and lava flows broadly contemporaneous with caldera forming events.

it of both pumice and lithic clasts suggest that the Cerro Galan ignimbrite was the result of a rather different eruption mechanism than that proposed for other well-described ignimbrites such as the Bandelier and Bishop Tuffs^{11,12}. The eruption rate may have been unusually rapid.

The fact that the Cerro Galan ignimbrites were able to travel horizontal distances in excess of 70 km indicates that they acquired much of their kinetic energy by collapse from a vertical eruption column, probably at least 10 km high⁷. A sustained, convecting vertical eruption column, however, would have led to the deposition of a recognizable plinian air fall deposit. This could suggest that the radius of the erupting vent widened almost instantaneously to the radius at which a convecting column would be unstable¹³. Alternatively, differences in magma volatile content may have been involved. Large volume silicic eruptions are now conceived as beginning with the eruption of a volatile-rich cap of the magma chamber, which leads to the formation of a crystal poor plinian deposit, followed by ignimbrite units and ultimately by extrusion of lavas¹⁴.

Previously models for resurgent calderas suggest that eruption commenced along inward dipping ring fractures¹⁵. Although there is no direct field evidence one way or the other, in the case of Cerro Galan, we suggest that it is more likely that the ring fractures were outward dipping, allowing for the catastrophic foundering of the caldera floor, much as originally suggested by Bailey *et al.* for the Glen Coe cauldron¹⁶. Such a triggering mechanism requires the magma chamber to be under-

pressured and the outward dipping shear fractures to be generated when the lithostatic pressure on the roof of the magma chamber exceeds the chamber pressure by the compressive strength of the rock¹⁷. Very large eruption rates (10^8 – 10^9 m³ s⁻¹) can be generated as the dense caldera floor block sinks into the lower density silicic magma, provided the ring fractures are outward dipping (T. H. Druitt and R.S.J.S. in preparation). Inward dips would inhibit such rapid eruption rates. The mechanism triggering the subsidence of the caldera floor into the underlying magma chamber, however, remains speculative.

We emphasize the preliminary nature of the conclusions presented here. Petrological studies are in progress and will be published elsewhere, but many years work will be required to document fully this large structure.

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Effects of increased CO₂ concentrations on surface temperature of the early Earth

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One of the major riddles of terrestrial evolution concerns the history of the Earth's surface temperature. Present models of solar evolution indicate that the luminosity was about 25% smaller at the time of formation of the Solar System¹. This factor alone would have caused the Earth's surface temperature to be below freezing, yet the geological record indicates that water has flowed on the surface since at least 3,800 Myr ago². Enhanced levels of CO₂ in the atmosphere could have provided the necessary warming to maintain the temperature above freezing. Increased tectonic activity, and a decrease in solubility of CO₂ in the oceans, rock weathering, and sediment deposition are processes that have been suggested for these larger amounts of CO₂. We show here that large CO₂ concentrations are necessary to maintain the early Earth's surface temperature at approximately today's level. If there were a thousand times the present atmospheric level (PAL) of CO₂ in the atmosphere, the temperature would be 292K, while a 100-fold increase in CO₂ concentration yields 284K. The surface warming is highly dependent on the amount of water vapour and clouds, both of which we have little knowledge of for this very early time in the Earth's history.

A likely mechanism for warming the early Earth was the presence of one or more greenhouse gases in the atmosphere in addition to water vapour. Sagan and Mullen³ suggested that ammonia could have provided the necessary heating if present in concentrations of a few parts per million. However, even this small mixing ratio would have been hard to support due to the photochemical instability of NH_3 with respect to conversion to N_2 (refs 4, 5). Carbon dioxide, which should have been one of the major constituents of Archaean volcanic emissions, is more likely^{6,7}. The ability of CO_2 to provide an effective greenhouse has been tested by Owen *et al.*⁸. Drawing on the evolutionary sequence proposed by Hart⁹, in which solar luminosity has increased by 25% and the partial pressure of CO_2 has decreased exponentially with time from an initial value of 0.31 bar, Owen *et al.*⁸ predict that surface temperatures during the Earth's early history could have been 10–20 K higher than at present.

While these results do suggest that CO_2 could have provided the required warming, it is unwise to interpret them literally as a time history of the Earth's surface temperature. Hart's evolutionary model provides at best only a crude parameterization of the factors controlling the atmospheric CO_2 partial pressure. Hart's basic assumption that the rate of CO_2 outgassing is balanced by the consumption of CO_2 due to weathering of silicate minerals and subsequent deposition of carbonate sediments is in accord with present theories concerning the carbon cycle^{7,10}. He assumes that the degassing rates for juvenile CO_2 and other constituents have declined exponentially with a time constant of 800 Myr, similar to the time constant of 862 Myr estimated by Li¹¹ for juvenile degassing processes. Recycling of CO_2 was not included. The latter process, which accounts for almost all the CO_2 outgassed today, occurs at an estimated global rate of $10^{14} \text{ g yr}^{-1}$ (ref. 7). The rate of recycling should have been higher in the past due to increased tectonic activity on a younger, hotter Earth, but probably did not exceed the present rate by more than a factor of several. The rate of juvenile degassing of CO_2 could not have been significantly higher than this for more than a few hundred million years, without exceeding the known carbonate inventory in the Earth's crust.

High CO_2 levels could also have occurred if the rate of CO_2 removal by silicate weathering was smaller than it is today. Walker *et al.*¹² have suggested that the atmospheric CO_2 level should rise if the Earth's surface temperature were to fall, due to the temperature dependence of the rainfall rate and the chemical weathering rates of various silicate minerals. According to this model, decreased solar luminosity during the Earth's early history would have resulted in lower average surface temperatures, and hence, higher CO_2 levels (up to ≈ 100 PAL). The increased greenhouse effect due to CO_2 would, in turn, have tended to moderate the temperature drop due to the lower solar luminosity. CO_2 levels could have been further enhanced if outgassing rates were higher than today or if less continental area were exposed to weathering, as suggested by Hargraves¹³.

We have not attempted to develop a self-consistent evolutionary model of CO_2 partial pressure, solar luminosity, and surface temperature. Our purpose here is to calculate the radiative heating due to increased CO_2 levels and compare our results with those of previous studies. As the most detailed treatment has been that of Owen *et al.*⁸, we have adopted the same time history for the changes in solar luminosity and CO_2 partial pressure although this does not imply that we endorse the particular evolutionary sequence proposed by Hart⁹.

The calculation by Owen *et al.*⁸ used a non-grey model and included weak bands of CO_2 which become important for large CO_2 mass paths such as may have existed on the early Earth. A constant relative humidity distribution and a single effective cloud at 6.25 km were specified, consistent with present conditions. Yet one might well expect that the appreciable surface temperature changes brought about by large amounts of CO_2 could alter the distribution of water vapour as well as the cloud height and thickness, all of which affect surface temperature.

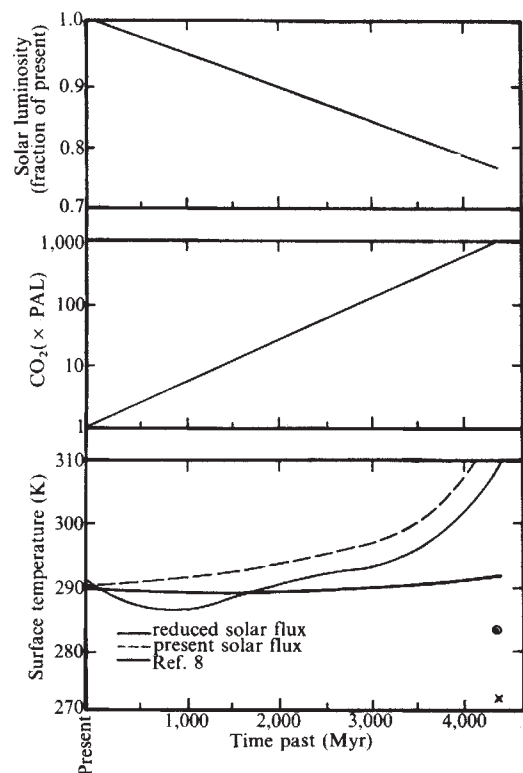


Fig. 1 Mean surface temperature of the primitive Earth for different atmospheric CO_2 concentrations. The temporal variations in solar luminosity and carbon dioxide are from ref. 9. \circ and \times refer to reduced solar flux with CO_2 concentrations of 100 and 1 PAL respectively.

Here we determine the surface temperature for amounts of CO_2 that may have existed in the prebiological atmosphere by including the corresponding changes in water vapour amount and cloud height and thickness.

The model used has been described previously¹⁴ and will only be outlined here. A radiative-convective model is coupled to the water vapour transport. As the temperature profile changes in response to radiative heating or cooling, and latent heating, the distribution of water vapour changes in response to changes in the large scale vertical velocity field and eddy diffusion. Clouds are formed whenever the atmosphere is saturated and the associated latent heat is released to the atmosphere. The number of cloud layers, their altitudes and thicknesses are computed. The total cloud cover is assumed to be 50% for a random cloud distribution.

Figure 1 shows the resultant surface temperature. In addition to showing the results for reduced solar flux, we include calculations with solar flux fixed at the present level as well as the results of Owen *et al.*⁸. The present calculations indicate that, for Hart's CO_2 evolutionary sequence, surface temperature would have varied little over geological time (due to decreased solar flux compensating for larger CO_2 amounts) in contrast to the similar study of Owen *et al.* which indicates a temperature decrease of some 20K over a 4,250-Myr period. The difference between the two calculations is due primarily to the processes associated with water, that is, the amount of water vapour in the atmosphere, the location of clouds, and the rate at which temperature changes with height. We used a moist adiabatic lapse rate rather than 6.5 K km^{-1} as used by Owen *et al.* which, as shown by Hummel and Kuhn¹⁴ produces a smaller change in surface temperature than does a 6.5 K km^{-1} lapse rate. The cloud top in the present model is calculated to be near 500 mbar while Owen *et al.* fix the cloud top at 6.25 km. This causes their cloud top pressure to be less than in the present study, varying from ~ 453 mbar at a 290K surface temperature to 478 mbar at 310K, and substantially decreasing the cloud contribution

to the outward radiation, which necessitates a higher surface temperature. Finally, we calculate an increase in atmospheric water vapour of ~30% for 1,000 PAL CO₂ while Owen *et al.*, who assumed constant relative humidity, used four times the present-day water vapour amount. Water vapour does contribute significantly to the greenhouse effect; for example Hansen *et al.*¹⁵ have shown that for a doubling of CO₂, water vapour contributes about as much to the temperature increase as does CO₂.

We conclude that there is still much uncertainty as to the 'greenhouse effect' that could have been produced from increased CO₂ aside from the uncertainty in the CO₂ concentrations. Much of the difficulty concerns water both in the vapour and condensed (cloud) phase. Although our model does represent an improvement in the treatment of atmospheric water vapour, there are still major difficulties. We do fix the surface relative humidity and although the water vapour is calculated when clouds are present, a constant relative humidity assumption is used for clear sky. Yet, one might question whether a constant relative humidity assumption would be valid for atmospheric conditions much different from today, which certainly would have been the case if surface temperatures were even 5K higher than at present. Finally, it is unknown whether the global cloud cover would remain at 50% for different climatological conditions.

While a 'greenhouse effect' is a very plausible mechanism for maintaining the temperature of the early Earth above freezing, the concentrations of CO₂ and water vapour remain very much an uncertainty and the early surface temperature is therefore still unknown. Indeed there is some question concerning the oxidation state of the early atmosphere. Arculus and Delano¹⁶ suggest that the mantle has become progressively more oxidized throughout the Earth's history and that the gases evolved from the original mantle could have been much more reduced than present day volcanic emissions. If CH₄ and CO were present in significant concentrations, they might also have contributed to the greenhouse effect.

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Selenium pollution of lakes near the smelters at Sudbury, Ontario

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Mining and smelting of Cu-Ni ores at Sudbury, Ontario, release about 2 tonnes of Se to the environment per day. We show here that within a 30-km radius of Sudbury, the Se concentrations in the lake waters range from 0.1 to 0.4 µg l⁻¹; the Se contents of the suspended particulates in the lakes vary from ~2 to 6 µg per g. The Se profiles in the lake sediments generally parallel the history of Cu-Ni production in the district. The present-day rates of Se accumulation in the sediments are found to be 0.3-12 mg m⁻² yr⁻¹. These current deposition rates exceed those of precolonial times by factors of 3-18, and are among the highest recorded anywhere in North America.

Table 1 Se contents of Cu-Ni ores around Sudbury

Mine	Sample no.	Level (ft)	Ore type*	Se concentration (µg per g)
Murray	1	1,650	MS	64
	2	1,650	GPIS	82
	3	1,650	MS	32
Creighton	Cr-1	4,200	IS	26
	Cr-2	3,200	RDS	20
	Cr-3	5,000	GPIS	42
	Cr-4	3,600	MS	65
Garson	Ga-10	2,000	CS	22
Levack	Lev-12	3,000	ISSN	25
Frood	Fr-5	1,000	DSQD	28
	Fr-8	1,000	IS	36
	Fr-9	2,200	RDS	20

Detailed descriptions of the ores, sample locations, relative ore production rates, and so on are given in ref. 11.

* MS, massive sulphide; GPIS, gabbro periodotite inclusion sulphide; IS, interstitial sulphide; RDS, ragged disseminated sulphide; CS, contorted schist inclusion sulphide in sub-layer norite; DSQD, disseminated sulphide in quartz norite. Details of these ore types are given in ref. 11.

Selenium is an unusual element in terms of its biological function. At low levels, it is an essential nutrient but at slightly higher concentrations it becomes quite toxic^{1,2}. Furthermore, Se typically has an antagonistic effect on the heavy metal (particularly mercury) toxicity, but in certain circumstances can mobilize heavy metals from some of the organs^{3,4}. Little is known about the distribution and possible role of Se in lakes which are highly contaminated with heavy metals.

Selenium replaces sulphur diadochically in sulphides with the result that commercial production of Se is a by-product of the copper (and to a much lesser extent, lead, zinc and iron) industry⁵. The Se contents of representative Cu-Ni ores at Sudbury range from 20 to 80 µg per g (Table 1). During the pyrometallurgical processing, some of the Se is converted to the gaseous phases, but being less volatile and less readily oxidized than the sulphur, it tends to accumulate in the matte, slags and especially the precipitator dusts of the roasting and smelting plants^{6,7}. The awkward chemistry and relatively high volatility of Se and its compounds usually ensure a low overall recovery rate of the Se in the ores of just 5-10% (refs 6, 7).

In 1977, about 17 × 10⁶ tonnes of the Cu-Ni ores were produced in Sudbury⁵. Using the average Se concentration of 40 µg per g, the quantity of Se produced with the ores is estimated to be 680,000 kg. During the same year, the Inco Metals Company plant at Copper Cliff recovered 53,000 kg of Se from the tankhouse slimes⁵. This implies that roughly 630,000 kg (equivalent to 1.7 tonnes day⁻¹), or over 90% of the Se in the ores produced, was lost to the ambient environment. Of these 630 tonnes or so of Se wasted annually in the environment, about 50 tonnes is dispersed through the atmosphere, probably in the form of selenium dioxide⁸. The plumes from the smelter stack at Sudbury (sampled using airborne instruments in both 1979 and 1980 at distances of 1-3 km from the source) indeed show high Se concentrations of 0.1-6.0 µg m⁻³ (W. Chan, personal communication). The rest of the pollutant selenium (580 tonnes) has to be associated with mine tailings, wastewaters and scoria and would constitute a very local source of lake pollution exemplified, for instance, in Kelly Lake (see below).

The lakes sampled are located within a radius of 30 km from the 381-m super stack at Copper Cliff, near Sudbury, Ontario. The water samples were obtained by means of a peristaltic pump with all-plastic tubing. The suspended particulates were recovered from ~1,200 l of water using a Westfalia four-bowl continuous flow centrifuge. At the flow rate of 6 l min⁻¹ used during the study, the centrifuge has a recovery efficiency of 90-95% for particles having diameters > 0.25 µm (ref. 9). The particulate samples were kept frozen until freeze-dried.