mole fraction of 0·004 are upper limits and may be significantly reduced if the activity coefficient of water in these solutions differs from unity by more than a few parts in a thousand. Information on the solubility of silica gels, with which to compare these figures, is conflicting. Direct measurements of the solubility usually lead to values corresponding to a mole fraction in the region of 2×10^{-5} (ref. 13); but the molybdate method usually used to estimate silica detects only fairly low oligomers. On the other hand, early workers[14] claimed to have prepared metastable SiO_2 sols containing up to 140 g l.$^{-1}$, while sols containing 10 g l.$^{-1}$ were claimed to be stable indefinitely. If we assume a molecular weight of about 100, then the concentrations calculated on the basis of our experiments would fall roughly in the range 150 to 20 g l.$^{-1}$.

(c) Is our hypothesis consistent with the claims that anomalous water can be distilled[1,4] ? If the polymer is of relatively low molecular weight, then arguments based on the properties of known silica sols cannot be applied. Moreover, it is known that low molecular weight silicic acid polymers can be distilled with water from a silicic acid sol[15,16]; and it is well known by engineers that steam turbine blades become coated with siliceous material carried over in the steam.

(d) Are the analytical data of Lippincott et al. reliable ? The laser probe technique, claimed to be sensitive to 10^{-11} g, gave only a "trace" of silicon, whereas our measurements suggest that in a typical preparation (assuming, say, a molecular weight of only 100) there would be some 3×10^{-8} g. The evidence here needs confirmation for, at the very least, the normal solubility of quartz in water should be detectable.

(e) Is the high viscosity attributed to anomalous water, and its reported reduction by a shear-degradation process, compatible with known properties of silica sols ? While, qualitatively, it would appear to be so, it must be remembered that the method of measurement, necessitated by the small quantities of material available, renders equally acceptable an explanation in terms of hysteresis of the contact angle at the menisci at each end of the liquid column.

(f) Is an explanation avoiding the postulation of hitherto unknown polymeric species equally acceptable in the cases reported[17] of anomalous behaviour in other liquids ? The properties of non-aqueous colloidal systems have been

little studied; we regard, however, the confirmation of the existence of anomalous methanol, acetone, acetic acid, and so on as being of prime importance, and have such work in progress now.

(g) Is there any reason to doubt that similar anomalies are to be expected in the presence of other solids ? If the explanation in terms of a sol-gel transformation is correct, then it is not an effect necessarily specific to silica and should be sought in other oxide/water systems in which gel formation is known to occur.

We conclude that it is still premature to reach final conclusions as to the origin of the phenomenon of anomalous water, and that theoretical calculations of possible structures of water polymers are largely irrelevant until the need for a description in terms of "polywater" is called for. An equally, if not more, important theoretical problem will be that of explaining why such polywater should exist in "frozen equilibrium" with ordinary water. A more profitable approach, we believe, is to seek to establish whether there are any properties of anomalous water which are incompatible with our assumptions. Only if and when such incompatibility is proved will it become important to seek an explanation in terms of hitherto unknown and unsuspected chemical species.

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The Runaway Greenhouse and the Accumulation of CO_2 in the Venus Atmosphere

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Conditions on Earth would be as hostile as on Venus if the Earth were closer to the Sun by only 6–10 million miles.

ALTHOUGH Venus and the Earth are similar in size and mass, are adjacent in the solar system and were probably formed out of the same homogenous mix of gas and dust about 4·5 billion years ago, their atmospheres and surface conditions differ markedly[1] (Table 1). For example, the atmosphere of Venus is ~75 times more massive than that of the Earth and is largely composed of carbon dioxide, a gas which constitutes only 0·03 per cent of the Earth's atmosphere. The Venus atmosphere seems to be

deficient in water, with respect to Earth, by as much as a factor of 10^4. The surface temperature of Venus is 700 K.

We believe that the chief differences can be explained by the single circumstance that Venus was formed 30 per cent closer to the Sun. If the Earth had formed only 6 to 10 million km nearer to the Sun, it may also have become a hot and sterile planet. As for Mars, it seems that it is the relative smallness of its size and mass—

a weaker internal activity—which has slowed its progress towards accumulating an Earth-type atmosphere and oceans.

Accumulation of CO_2 on Venus

Table 1 shows that the amount of CO_2 in the atmosphere of Venus is approximately equal to the amount buried in the crust of the Earth in the form of carbonates[2,3]. Nitrogen, the chief constituent of the Earth's atmosphere at present, is only 1–5 per cent of the amount of CO_2, not only on Earth but also on Mars and Venus. The large quantities of water which make up the oceans of the Earth are practically absent on Venus but may be present in a frozen state below or on the surface of Mars[4]. The amount of free oxygen in the atmosphere of the Earth is small compared with the total amount of oxygen in the crust, but is even less abundant in the atmospheres of Venus and Mars. When the abundances of the four gases in the atmosphere of Mars are compared with those on Venus and Earth, they suggest that if the origin of these gases is the same (outgassing from the interior), volcanic activity on Mars has been $\sim 1,000$ times less effective than that on either the Earth or Venus[4].

In our attempt to trace the evolutionary history of Venus, we make three basic assumptions. (a) At some time in the early history of the solar system, the terrestrial planets Mercury, Venus, the Earth and Mars completely lost their primordial atmospheres[5,6]. (b) The present atmospheres of these planets have developed chiefly from the degassing of the planetary interiors[2,7] —excepting free oxygen in the Earth's atmosphere which is related to the presence of life. (c) The chief constituents of the outgassing from the interior for all three planets are essentially the same—water vapour and carbon dioxide with $H_2O/CO_2 = 4$, and nitrogen accounting for < 1 per cent.

Before outgassing when the planets are more or less devoid of an atmosphere, their ground temperatures, T_G, are essentially determined by the amount of solar radiation absorbed by the surface, and are equal to the effective temperatures of the planet, T_e. For a rapidly rotating planet and for a given planetary albedo, A_p, we have

$$T_G = T_e = \sqrt[4]{\frac{S_p}{4\sigma}(1 - A_p)}$$

where S_p is the solar constant.

As the atmosphere accumulates, the ground temperature begins to exceed the effective temperature because of the additional heating of the surface by the atmospheric greenhouse effect. The magnitude of the greenhouse effect can be calculated by solving the equation of radiative transfer for a given atmosphere, but the problem is complicated by the strong frequency dependence of the infrared molecular absorption coefficient, especially for water vapour. To a first approximation we assume a grey atmosphere and use the Eddington approximation for the solution of the radiative transfer equation[8,9].

Table 1. SURFACE PARAMETERS AND THE ABUNDANCES OF MAJOR VOLATILES ON VENUS, EARTH AND MARS

		Venus	Earth	Mars
Temperature		700 K	300 K	230 K
Pressure		75 atm.	1 atm.	0·01 atm.
Composition				
CO_2	Atm.	70,000 g/cm²	~ 1 g/cm²	~ 70 g/cm²
	Crust	?	70,000	?
N_2	Atm.	< 3,000	800	< 1
	Crust	?	$\sim 2,000$?	?
H_2O	Atm.	~ 100	~ 1	~ 0.01
	Oceans	0	300,000	?
O_2	Atm.	< 10	200	~ 0.01
	Crust	?	8×10^6 Total	?

The amount of CO_2 shown for Mars includes ~ 50 g cm⁻² believed to be present as solid CO_2 over the polar caps.

With these approximations,

$$T_G^4 = T_e^4 (1 + 3/4 \, \tau_0)$$

where τ_0 is the total optical thickness of the atmosphere and is defined as $\int_0^\infty \bar{\varkappa} \rho dz$, where $\bar{\varkappa}$ is the average absorption coefficient, ρ the density of the absorbing gas and z is the vertical coordinate. The values of τ_0 for various amounts of H_2O and CO_2 can be calculated from tables of transmission functions (refs. 10–12 and unpublished work of Wyatt et al.). A weighted average over the Planck spectrum is used to determine $\bar{\varkappa}$. The values of τ_0 follow.
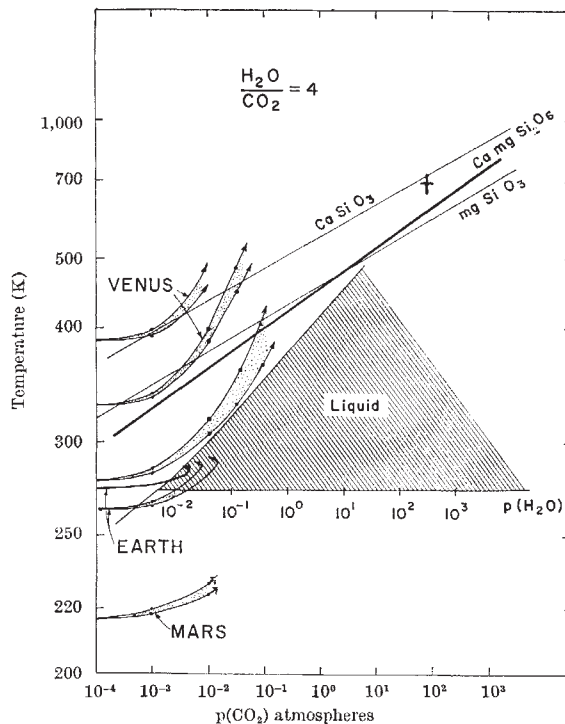

Fig. 1. Plot of increase in surface temperatures on Venus, Earth and Mars by the greenhouse effect of an H_2O–CO_2 atmosphere during the evolution of the three planets. The initial temperatures on these planets equal the effective temperature for a planetary albedo of 7 per cent, and two different rates of rotation in the case of Venus. In the case of the Earth, two values of the planetary albedo have been chosen (7 and 20 per cent). The phase diagram for water is shown and the region in which water can exist as liquid is represented by the hatched area. Also plotted are the equilibrium values for the partial pressures of CO_2 as a function of temperature for three different silicate reactions.

We start the greenhouse calculations for Venus at time zero, when the outgassing has just begun and the total amount of atmosphere is $< 10^{-3}$ mbar. At this point we assume the planetary albedo to be 7 per cent by analogy with the Moon and Mercury. The ground temperature at this time is T_e and for an albedo of 7 per cent it will be 330 K for the fast rotation and 390 K for slow rotation. As the atmosphere accumulates, the greenhouse effect increases the ground temperature provided the albedo remains constant. (This was probably the case until the total atmospheric pressure on Venus reached $\sim 10^{-1}$ atmosphere and condensation in the atmosphere and cloud formation began. At lower pressures the atmosphere was too thin to sustain clouds thick enough to modify the albedo, as is the case in the stratosphere of the Earth and the atmosphere of Mars.) Because the initial surface temperature (T_e) is already quite high, H_2O remains in the atmosphere as vapour and accelerates the greenhouse effect. The increase in ground temperature as a function of the build-up of H_2O–CO_2 pressure is

shown in Fig. 1. Each set of curves indicates the range of possible temperatures, considering the uncertainties in the greenhouse calculations and the effect of convection. When the Venus atmosphere has a total pressure of 10^{-1} atmospheres the ground temperature has already risen to 430 K for $T_e = 330$ K and > 500 K for $T_e = 390$ K. Thus the surface temperature of Venus was always above the boiling point of water at the pressures involved. The temperature curves for Venus miss the liquid phase of water by a wide margin (Fig. 1). The calculated Venus temperatures are so much higher than the boiling point of water that even if the albedo of the planet were 30–40 per cent instead of 7 per cent, water would not condense at the surface.

These initial high temperatures and the complete absence of liquid water from the surface had a significant bearing on the accumulation of CO_2. As the CO_2 is degassed from the interior into the atmosphere, its partial pressure should be buffered by reactions with the crust such as[2,7,13]

$$CaMgSi_2O_6 + CO_2 \rightleftharpoons MgSiO_3 + CaCO_3 + SiO_2$$

These reactions are, however, temperature-dependent, and at high temperatures large quantities of CO_2 can accumulate in equilibrium with the silicates. Fig. 1 also shows the plots of CO_2 partial pressures as a function of temperature for reactions with $CaSiO_3$, $CaMgSi_2O_6$ and $MgSiO_3$ (refs. 13 and 14). If at any time the amount of CO_2 in the atmosphere is higher than the equilibrium value at that temperature, then the situation is unstable and CO_2 should be removed from the atmosphere and deposited into the crust as carbonates. But the atmosphere–crust reaction will proceed rapidly only if liquid water is present at the surface to facilitate the contact. Both these conditions should be satisfied in order to remove CO_2 from the atmosphere effectively. In the case of Venus the temperature was always high enough so that the amount of CO_2 in the atmosphere never substantially exceeded the equilibrium pressure at that temperature. The only exception is for the case of $T_e = 330$ K and the reaction with $CaSiO_3$. The absence of liquid water, however, would have impeded the reaction and the temperature should have built up soon to a value at which the atmospheric CO_2 would be in equilibrium with the crust. In this way the CO_2 continued to accumulate in the atmosphere to the present value of ~ 75 atmospheres at a temperature of 700 K.

But according to this model, the Venus atmosphere should contain ~ 300 atmospheres of H_2O, and only $\sim 10^{-1}$ atmospheres seems to be present today (Table 1). It has been suggested that this water vapour was dissociated by the solar ultraviolet into hydrogen and oxygen; hydrogen escaped and the oxygen was consumed in various oxidation processes at the surface[1,15–17]. This suggestion has been reinforced by a recent study which concludes that if H_2O were a major constituent of the Venus atmosphere, its exospheric temperature would have been high ($> 3,000$ K) and the escape of hydrogen rapid (Smith and Gross at the 130th meeting of the American Astronomical Society, Albany, 1969).

If the present amount of H_2O in the Venus atmosphere is the equilibrium value between the outgassing and loss of hydrogen to space, it implies that the escape of water from Venus began at $P_{H_2O} \sim 10^{-1}$ atmospheres. At this point, however, according to Fig. 1, the surface temperature is already > 430 K and CO_2 in the atmosphere is in equilibrium with the silicates. From this time to the present, if the partial pressure of water never exceeded 10^{-1} atmospheres, the increase in the surface temperature to the present value of 700 K would have been governed principally by the greenhouse effect of CO_2 alone. The temperature consequently would increase at a slower rate than shown by the arrows in Fig. 1 and would probably follow the CO_2 equilibrium curve for $CaSiO_3$.

Earth and Mars

A completely different evolution emerges for the Earth, explaining why the surface temperature remains a comfortable 300 K, and why almost all of the CO_2 is in the crust and H_2O is in the oceans. For the Earth, the initial value of T_e for an albedo of 7 per cent is 275 K. The ground temperature increases as the water vapour and CO_2 atmosphere begin to accumulate as on Venus, but soon the temperature and pressure conditions allow liquid water to condense at the surface (Fig. 1). From this point on, the evolutionary path of the Earth is completely different from that of Venus. The amount of water vapour remaining in the atmosphere is small and the increase in ground temperature is determined by the accumulation of CO_2 alone. The total amount of CO_2 soon becomes greater than the equilibrium value with the silicates, however. The reactions with crustal rocks proceed rapidly and are accelerated by the presence of liquid water on the surface. Erosion by liquid water brings fresh silicates into contact with the CO_2 in the atmosphere and in the oceans. The CO_2 therefore never accumulates in excess of the equilibrium value of $\sim 10^{-4}$ atmospheres at 300 K. Nitrogen, the inert gas which constitutes only ~ 1 per cent of the volcanic gases, accumulates to make up the bulk of the present atmosphere.

Fig. 1 clearly shows that the initial temperature of the planet is an extremely critical parameter in determining which evolutionary path the planetary atmosphere will follow. In fact, a calculation for an initial temperature of 280 K instead of 275 K indicates that the increase of surface temperature would have been rapid enough for the Earth to miss the liquid phase of water at its surface. A runaway greenhouse effect would have made the conditions on the Earth as hostile as on Venus. This could have occurred if the Earth were closer to the Sun by only 6–10 million km.

For a planet farther away from the Sun, like Mars, the chances that a runaway greenhouse would ever take place are slim. When the initial temperature is < 273 K the volcanic steam freezes at the surface and only CO_2 accumulates in the atmosphere (as is the case on Mars today). When large quantities of CO_2 have accumulated on the planet, the greenhouse effect due to CO_2 alone will raise the surface temperature above 273 K, melting the frozen water and thereby initiating the transfer of CO_2 from the atmosphere into the crust. When this evolutionary stage is reached on Mars, conditions on the surface may become very similar to those on the Earth today: water in a liquid state, CO_2 in the sediments, and an atmosphere consisting chiefly of N_2.

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