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Planetary Probe: Origin of Atmosphere of Venus

Abstract. *The high temperatures and chemical composition, as determined by space probe and terrestrial observation, suggest that the present atmosphere of Venus has formed by chemical interaction with the lithosphere. Although the precise reactions have not been identified, good theoretical approximations to the molecular abundance may be obtained from reactions applicable to terrestial rocks. The high temperatures and chemical reactivity create conditions on Venus which are fundamentally different from those on the cooler terrestrial planets where the attainment of equilibrium is prevented by kinetic barriers.*

One model for the origin of the atmosphere of Venus is based on pervasive chemical reactions between gases in the basal atmosphere and minerals of the lithosphere (*1, 2*). This interaction model adequately accounts for the composition of the atmosphere if the unconfirmed high surface temperatures are accepted (*3, 4*). This report considers how this model fits the observational data obtained from recent planetary probes, in particular data from Venera 4.

Venera 4 descended into the atmosphere of Venus at a position within 10° of the equator and approximately 20° from the terminator on the dark side (*5*). The measurements, which were obtained at three atmospheric levels, indicate that the atmosphere of Venus is characterized by high temperatures and an abundance of CO_2. The data are also in essential agreement with the more indirect measurements of the Mariner V probe, which executed a simultaneous flyby of the planet (*6*). The only discrepancy involves the altitudes of the probes as compared with the planetary radius deduced from radar measurements made on Earth. Thus far no satisfactory explanation has been offered for this discrepancy, but the Mariner V data would lead to somewhat higher temperatures and pressures than those recorded by Venera 4 (*7*).

The high CO_2 pressure (20 atm or greater) must be explained by any comprehensive model of the planet. Urey (*8*) suggested that the CO_2 pressures in the atmospheres of the terrestrial planets might be governed by reactions of the following types

$$\overset{\text{calcite}}{CaCO_3} + \overset{\text{quartz}}{SiO_2} \rightleftarrows \overset{\text{wollastonite}}{CaSiO_3} + \overset{\text{gas}}{CO_2} \qquad (1a)$$

$$\overset{\text{orthopyroxene}}{MgSiO_3} + \overset{\text{calcite}}{CaCO_3} + \overset{\text{quartz}}{SiO_2} \rightleftarrows \overset{\text{diopside}}{CaMgSi_2O_6} + \overset{\text{gas}}{CO_2} \qquad (1b)$$

Reaction 1a was proposed to account for the CO_2 content of Earth's atmosphere, and 1b is applicable to certain terrestrial metamorphic terrains (*9*).

Urey explained the high CO_2 content in the atmosphere of Venus by proposing that kinetic barriers prevent equilibrium reactions such as 1a from shifting to the left; he believed that these kinetic barriers developed as a result of the dry conditions on the planet. Thus the CO_2 concentration might build up far above the equilibrium value. However, at the high temperatures now accepted for the lower atmosphere and surface of Venus, these reactions should not only equilibrate but should also yield CO_2 pressures very close to those observed (*1, 2*). Actually equilibrium is required only on a geologic time scale; however, direct experiment (*10*) indicates that equilibrium is approached even on a laboratory time scale (~ 500 hours) at temperatures as low as 850°K.

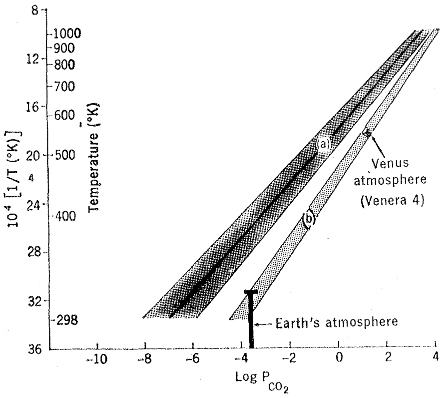

Fig. 1. Comparison of observational data for CO_2 abundance in the atmosphere of Venus and Earth with several reactions (1a and 1b) based on thermochemical data. The Venera 4 observational point corresponds to $T = 543$°K and a CO_2 pressure of 20 atm, whereas the bandwidths indicate uncertainties in the thermochemical data.

If it is assumed that all the solid phases are of constant composition, the equation of equilibrium for reactions 1a and 1b may be written as

$$K_{1a} = P_{CO_2} \qquad (2a)$$

$$K_{1b} = P_{CO_2} \qquad (2b)$$

where P represents the fugacity of CO_2. At the surface temperatures and pressures which exist on Venus, these fugacities correspond essentially to partial pressures and are equal to the total pressure (*11*).

From thermochemical data (*12*), we may obtain K_{1a} and consequently P_{CO_2} as a function of the temperature (curve *a*, Fig. 1). The hatched bandwidth of this curve corresponds to the maximum and minimum values of the enthalpy and entropy contributions at 298°K and gives an indication of the uncertainty in the thermochemical data. The analogous data for K_{1b} for reaction 1b has a somewhat different meaning. The low-pressure limit of the hatched area (curve *b*, Fig. 1) was determined in the same way, but the high-pressure limit was determined by considering the geologic conditions of the occurrence of the mineral assemblage under terrestrial conditions (*9*). The values of P_{CO_2} for both reactions 1a and 1b will also be influenced by deviations from stoichiometry of the solid phases, with probably the greatest effect on reaction 1b. An estimate of this effect, which takes into account the presence of such components as $FeSiO_3$ and $CaFeSi_2O_6$, shows that the curve *b* will be shifted toward lower pressures by a maximum of only a factor of 2 (*9*).

Also shown in Fig. 1 is the value of P_{CO_2} for Earth's atmosphere (*8*). Although the vertical height of the bar in this case includes the range of surface temperatures, coincidence with curve *b* may be fortuitous. However, Urey (*8*) believed that the value represents an approach to equilibrium for reactions of this general type.

It also seems likely that the precise coincidence of curve *b* and the Venera 4 observation point (at 543°K and $P_{CO_2} = 20$ atm) is, in part, coincidental. It has been suggested (*13*) that each reaction, such as 1a and 1b, is characterized by an effective temperature which is in part kinetically determined and which corresponds to some ambient temperature of the surface or subsurface. Thus it is possible that the P_{CO_2} value for Venus actually reflects a somewhat higher temperature than that recorded by Venera 4 and that this temperature may correspond to curve *a*. It is also possible that the probe may not have reached the actual surface of the planet (*7*) so that the actual temperatures and CO_2 pressures are somewhat higher than 543°K and 20 atm, respectively. The important point here is not a precise coincidence of observation and any specific theoretical curve but rather the general correlation of CO_2 pressures and temperatures within the range of those characteristic of common decarbonation reactions. Such a correlation implies that the atmosphere is approximately buffered with respect to CO_2 content by this mechanism. However, the high CO_2 pressure thus accounted for does not necessarily mean that the carbon content of Venus is higher than that of Earth. What it probably implies is that on Venus a larger proportion of carbon, which on Earth occurs largely in rocks, has been released into the atmosphere because of higher temperatures.

Venera 4 recorded concentrations of water from 0.1 to 1 percent (by volume) or $10^{-1.70}$ to $10^{-0.70}$ atm near the surface. This range of values corresponds to pressures required to stabilize certain hydrous silicates (*2*). It is likely that hydrogen, derived from the photochemical decomposition of water, escapes at geologically significant rates from the upper atmosphere so that the quantity of water in the lithosphere may be subject to decline over a long period. However, if the time scale of reaction of the hydrous silicates is short as compared to the time scale of atmospheric loss, the atmosphere may still be approximately buffered with respect to water in much the same way as it is for CO_2.

The state of oxidation of the atmosphere and the temperature and water content should be critical in determining the stabilities of a variety of molecules within the atmosphere and mineral phases within the lithosphere (*2–4*). According to the Venera 4 measurements, free oxygen is present in about the same concentration as water. Although this is very low by terrestrial standards, it conflicts with the upper limit in the mixing ratio of about 10^{-4}, as determined spectrographically by Spinrad and Richardson (*14*). Furthermore, the quenched equilibrium demands compatibility with the reaction

$$\overset{\text{gas}}{CO_2} \rightleftarrows \overset{\text{gas}}{CO} + \overset{\text{gas}}{1/2\,O_2} \qquad (3)$$

so that P_{O_2} (the fugacity of oxygen) is directly proportional to $(P_{CO_2}/P_{CO})^2$ at any temperature. According to Moroz (*15*), the observed value of the P_{CO_2}/P_{CO} ratio is approximately 10^6. In the range of ambient surface temperatures, this corresponds to an equilibrium oxygen fugacity of only about 10^{-30} atm. The interaction between atmospheric oxygen and the rock-forming oxides FeO and Fe_2O_3 would appear to favor oxygen fugacities of this order (*3*). Thus it seems possible that the oxygen abundance measured by Venera 4 may be spurious, resulting from some kind of instrument failure. If we disregard the measured value of P_{CO_2}/P_{CO}, it is still possible that the O_2 abundance recorded by Venera 4 is valid and corresponds to equilibrium. However, in this case the measurement implies that the upward transport of oxidizable iron (FeO) in the lithosphere is inadequate to react with the O_2 deposited in the atmosphere by other processes such as the photochemical decomposition of H_2O (*3*).

Closely related to the state of oxidation and hydration of the atmosphere are the stability relations of the hydrogen compounds. If P_{H_2O} and P_{O_2} are known, the fugacity of hydrogen may be obtained from the reaction

$$\overset{\text{gas}}{H_2O} \rightleftarrows \overset{\text{gas}}{H_2} + \overset{\text{gas}}{1/2\,O_2} \qquad (4)$$

for any equilibrium temperature. For example, if we use the values $P_{H_2O} = 10^{-1.70}$ atm (corresponding to a water content of 0.1 percent), $(P_{CO_2}/P_{CO}) = 10^6$, and $T = 543$°K, then data from thermochemical tables (*16*) yield a value of $P_{H_2} \sim 10^{-6}$ atm at the surface.

If spectrographic observations made on Earth (*17*) of hydrogen compounds are combined with data from Venera 4, the interaction model gains additional support. Most interesting of these data, because of their quantitative nature, are the molecular abundance ratios HCl/CO_2 and HF/CO_2. If we set these ratios equal to the ratios of the fugacities, we obtain

$$P_{HCl}/P_{CO_2} = 10^{-6.22}$$
$$P_{HF}/P_{CO_2} = 10^{-8.30}$$

If we now assume that, like P_{CO_2}, P_{HCl} and P_{HF} are ultimately determined by the interaction between the lower atmosphere and the lithosphere, it should be possible, by selecting naturally occurring mineral phases of low free energy, to express these ratios in terms of certain heterogeneous reactions. The following reactions should meet this criterion, since they include only highly stable phases which are observed in terrestrial rocks

$$\overset{\text{halite}}{2NaCl} + \overset{\text{andalusite}}{Al_2SiO_5} + \overset{\text{quartz}}{5SiO_2} + \overset{\text{gas}}{H_2O} \rightleftarrows \overset{\text{plagioclase}}{2NaAlSi_3O_8} + \overset{\text{gas}}{2HCl} \qquad (5a)$$

$$\overset{\text{fluorite}}{CaF_2} + \overset{\text{quartz}}{SiO_2} + \overset{\text{gas}}{H_2O} \rightleftarrows \overset{\text{wollastonite}}{CaSiO_3} + \overset{\text{gas}}{2HF} \qquad (5b)$$

The corresponding equations of equilibrium are

$$P_{HCl} = (K_{5a}P_{H_2O})^{1/2} \qquad (6a)$$

$$P_{HF} = (K_{5b}P_{H_2O})^{1/2} \qquad (6b)$$

where K_{5a} and K_{5b} are the equilibrium constants. From thermochemical data (*12, 18*) for these constituents we may calculate P_{HCl}/P_{CO_2} and P_{HF}/P_{CO_2} for any given temperature (*19*). The results for $T = 543$°K, corresponding to the observed values of P_{H_2O} and P_{CO_2}, are

$$P_{HCl}/P_{CO_2} \simeq 10^{-5.7}$$
$$P_{HF}/P_{CO_2} \simeq 10^{-8.0}$$

This calculation is subject to several major uncertainties. One of these is related to errors in the thermochemical data expressed in K_{5a} and K_{5b}. These cannot be evaluated because of uncertainties in the data for Al_2SiO_5. Similarly, in any real case constituents, such as NaCl and $NaAlSi_3O_8$, are likely to occur in nonstoichiometric phases, which will tend to reduce their activities. However, this effect on the two constituents should tend to cancel to a certain extent. If all these uncertainties are taken into account, the correspondence with the observed values is quite good.

The same observations which revealed

the presence of HCl and HF failed to show any sign of the species CH, CH_3Cl, CH_3F, C_2H_2, and HCN, although their spectra are favorable for observation if they are present in concentrations greater than one part per million (*17*). This confirms the observation of Kuiper (*20*) regarding molecular abundances of hydrocarbons. It is also consistent with the instabilities of these compounds in an anhydrous, oxidizing, hot environment (*4*).

If the interaction model applies, the atmosphere of Venus differs fundamentally from those of Earth and Mars. For example, the most important constituents of Earth's atmosphere result from reactions of the type (*21*)

$$\begin{aligned} \text{organisms} &\rightleftarrows O_2\ (\text{gas}) \\ \text{organisms} &\rightleftarrows CO_2\ (\text{gas}) \\ H_2O\ (\text{liquid}) &\rightleftarrows H_2O\ (\text{gas}) \end{aligned}$$

Constituents in the atmosphere of Venus derive from more fundamental reactions (reactions 1, 3, and 4). Furthermore, the classical concept of degassing has less applicability on a hot planet, for, although the atmospheric constituents may well have originated within the interior (or from a trapped primordial atmosphere), their excess accumulation in the atmosphere would be prevented by back reactions. Thus absorption is as important as degassing. These deductions are totally incompatible with certain current models on atmospheric evolution. Thus Dayhoff *et al.* (*22*) attempted to trace the evolutionary history of the atmosphere of Venus from its primordial state by reference to the system C-H-O without consideration of the effects of heterogeneous reactions such as (1a) and (1b). However, if the atmosphere is derived by chemical interaction with a lithosphere composed largely of silicates and oxides, then any evolutionary scheme must take account of these compounds.

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Thorny-Headed Worm Infection in North American Prehistoric Man

Abstract. *Examination of ova and parasites from coprolites of probable human origin revealed eggs of the phylum Acanthocephala. Specimens were gathered from Danger Cave in Utah, an area heavily populated with definitive rodent hosts for the Acanthocephala species* Moniliformis clarki. *It is postulated that prehistoric man developed Acanthocephala infection by ingesting the arthropod intermediate host, or that he was a victim of false parasitism by ingesting the whole rodent.*

Analysis of ancient, dried feces (coprolites) provides a rich source of information regarding certain dietary habits of prehistoric man (*1–3*). Although parasitological examination of various mummies, coprolites, and latrine deposits from the Old World has revealed eggs from a variety of trematodes and cestodes, as well as protozoan cysts (*4*), such analyses have been generally unrewarding in the New World with a few exceptions. Eggs of the genus *Diphyllobothrium* were recovered from a Peruvian midden coprolite dated between 3000 and 1000 B.C. (*1*). A mummified Inca child approximately 450 years old contained eggs of *Trichuris trichiura* and cysts of the protozoan *Entamoeba* (*4*). Eggs of *Enterobius vermicularis* were recovered from a coprolite about 1000 years old from Mesa Verde, Colorado (*5*). In addition, remains of lice, mites, and ticks—all possible ectoparasites of man—have been described (*3, 5*). Recognition of this biological material is possible after immersion of the dried specimen in a 0.5 percent aqueous solution of trisodium phosphate for 72 hours, a method introduced by Van Cleave and Ross for reclaiming dried zoological specimens and applied to the examination of coprolites by Callen (*6*). Specimens thus reconstituted are remarkably identical in morphology to their living counterparts.

Danger Cave, in Utah, was a site of inhabitation by early man during the ten millennia from the time of regression of the Wisconsin glacier to the beginning of the Christian era. The cave was filled with cultural debris, including coprolites, to a depth of 11 feet (3.3 m). The debris was separated into five sequential segments: D–I (D, Danger Cave) to D–V, with D–I the oldest and D–V the youngest levels (*7*). Radiocarbon dating of samples of charred bat guano, rat dung, charred twigs, and uncharred sheep dung (D–I only) yielded the following dates: 9503 B.C. ± 600 years for D–I; 7839 B.C. ± 630 years for D–II; 1869 B.C. ± 160 years for D–IV; and A.D. 20 ± 240 years for D–V. The D–III level was not carbon dated. Coprolites were found in all levels, being most abundant in the more recent. They were ascribed to human origin on the basis of content, color, and form; the properties of turning the immersing fluid a dark brown color and, in some specimens, emitting a distinctly fecal odor after several days in 0.5 percent trisodium phosphate (*1, 3*) were also indicative of human origin. Human coprolites contain a mixture of diverse plant material, bone, and charcoal ingredients, a feature which distinguishes them from coprolites of other mammals (*3*).

Iodine and saline preparations of small samples of reconstituted coprolite specimens were made for microscopic ova and parasite examination, just as is done with fresh feces in the modern clinical laboratory. Twenty specimens from D–V, six from D–IV, nine from D–III, and five from D–II constituted the survey. No protozoan parasites were encountered. In three of twenty specimens from D–V and one of six speci-