suppressed. The diurnal temperature ranges (beginning at local midnight) from 17 through 21 May were 18°, 17°, 9°, 13°, and 20°C, respectively.

Boise, which was never exposed to the dust, exhibited a gradual warming trend. The temperature ranges (beginning at local midnight), for 17 through 20 May, were 16°, 15°, 14°, and 19°C, respectively.

The dust cloud from the Mount St. Helens volcanic eruption produced cooling of surface air temperatures during the daytime and warming at night. Warming at the surface at night is produced by enhanced downward longwave emission; when the sun is shining, this effect is overwhelmed by albedo enhancement, causing net cooling at the surface.

Similar processes have been discussed on climatic time scales, but there are crucial differences between the two cases in the particle size distribution and the vertical distribution of the volcanic aerosol. During the first day the troposphere was full of large particles (*5*); in contrast, very small particle sulfate aerosols form as a result of gas-to-particle conversions in the stratosphere months after large eruptions. According to the calculations of Pollack *et al.* (*2*), large particles characteristic of the early period of a volcanic plume would produce warming strong enough to cancel or even overwhelm the cooling due to scattering and reflection of the visible radiation. Later, as the large tropospheric particles precipitate out, leaving the far smaller stratospheric aerosols, the cooling effects would dominate.

The cooling effects of the volcanic cloud lasted for only 1 day, while the nighttime warming persisted for at least 2 days, as low-level particles remained in the atmosphere (Fig. 3). Although large warming and cooling were produced by the eruption cloud, the net effect of this volcanic eruption was warming for the first few days, in contrast to cooling which might be expected on climatic time scales.

ALAN ROBOCK
CLIFFORD MASS*
Department of Meteorology,
University of Maryland,
College Park 20742

References and Notes

1. J. M. Mitchell, *Ann. N.Y. Acad. Sci.* **95**, 235 (1961); S. H. Schneider and C. Mass, *Science* **190**, 741 (1975); C. Mass and S. H. Schneider, *J. Atmos. Sci.* **34**, 1995 (1977); J. E. Hansen, W.-C. Wang, A. A. Lacis, *Science* **199**,1065 (1978); A. Robock, *J. Atmos. Sci.* **35**, 1111 (1978); *Science* **206**, 1402 (1979); *J. Volcanol. Geotherm. Res.* **11**, 67 (1981). A. Robock [*Science* **212**, 1383 (1981)] showed that the climatic effects of the Mount St. Helens eruption of 18 May 1980 are expected to be very small.
2. J. B. Pollack, O. B. Toon, C. Sagan, A. Summers, B. Baldwin, W. Van Camp, *J. Geophys. Res.* **81**, 1071 (1976).
3. C. Mass and A. Robock, *Mon. Weather Rev.*, in press.
4. H. R. Glahn and D. A. Lowry, *J. Appl. Meteorol.* **11**, 1203 (1972); W. H. Klein and H. R. Glahn, *Bull. Am. Meteorol. Soc.* **55**, 1217 (1974).
5. P. V. Hobbs, L. F. Radke, M. W. Eltgroth, D. A. Hegg, *Science* **211**, 816 (1981).
6. We thank K. Hebenstreidt and J. P. Dallavalle of the National Oceanic and Atmospheric Administration Techniques Development Laboratory for providing surface observations, MOS forecasts, and monthly average errors; we thank W. Klein and K. Dewey for informative discussions concerning MOS. C. Pearson, P. Ruchkin, and J. Terry helped plot the maps, and C. Villanti drafted the figures. We also acknowledge the use of the SCRIPT text editor on the Amdahl computer of the Goddard Laboratory for Atmospheric Sciences. This research was supported by National Oceanic and Atmospheric Administration grant ATM-80-24881 and National Science Foundation grant ATM-7918215.

* Present address: Department of Atmospheric Sciences, AK-40, University of Washington, Seattle 98195.

23 October 1981; revised 20 January 1982

Venus Was Wet: A Measurement of the Ratio of Deuterium to Hydrogen

Abstract. *The deuterium-hydrogen abundance ratio in the Venus atmosphere was measured while the inlets to the Pioneer Venus large probe mass spectrometer were coated with sulfuric acid from Venus' clouds. The ratio is* $(1.6 \pm 0.2) \times 10^{-2}$. *The hundredfold enrichment of deuterium means that at least 0.3 percent of a terrestrial ocean was outgassed on Venus, but is consistent with a much greater production.*

One of the most significant problems related to the origin and evolution of Venus is that of its "missing" water. There certainly is no liquid water on the surface of Venus today and the water vapor content in the atmosphere is probably not more than 200 ppm by volume (*1, 2*). Either Venus was formed of material very poor in water (*3*) or whatever water was originally present has since disappeared, the hydrogen into space and the oxygen into the interior (*4*). It has long been recognized that measurement of the ratio of deuterium to hydrogen in the atmosphere of Venus today would discriminate between these alternatives. There are various ways in which gases escape from a planet's atmosphere, ranging from classical Jeans escape to hydrodynamic outflow at a supersonic velocity. Most mechanisms identified as potentially important for escape of hydrogen from Venus discriminate strongly against loss of deuterium and heavier gases with one conspicuous exception. Hydrodynamic flow would have carried HD away along with H_2. This mode of escape would have prevailed in an atmosphere in which hydrogen was a dominant constituent. The velocity of the flowing H_2 would have become too low to sweep HD along when the mixing ratio of H_2 dropped below about 2 percent by volume (*5*). Subsequent escape of hydrogen should have resulted in an enrichment of deuterium in the hydrogen compounds residing in the atmosphere. The atmosphere of Venus now contains two orders of magnitude less hydrogen (in the form of H_2O) than that corresponding to the critical mixing ratio of 2 percent. Thus a hundredfold enrichment of deuterium is the most that can be expected even if Venus outgassed an appreciable fraction of the equivalent of a terrestrial ocean of water. If the initial ratio of D to H on Venus was about 1.5×10^{-4}, as it is on the earth, the present ratio could be at most about 1.5×10^{-2}. In this report evidence will be presented that the ratio of D to H on Venus is $(1.6 \pm 0.2) \times 10^{-2}$.

Data obtained by the Pioneer Venus large probe neutral mass spectrometer (LNMS) were scrutinized in the hope of using them to deduce the ratio of D to H on Venus. This mass spectrometer and its mode of operation during its descent to the surface of Venus have been described fully (*6*). The instrument was a magnetic sector device that scanned the mass spectrum in 236 discrete steps from 1 to 208 atomic mass units once every 64 seconds. Gas from the atmosphere was admitted to the ionization chamber of the LNMS through two microleaks and pumped internally by chemical getter and ion sputter pumps. The leaks were opened at about 63 km in the upper cloud layer of Venus and data obtained in 51 mass spectra between this altitude and the surface. Just as the probe entered the lower cloud layer at about 50 km the inlet leaks became clogged with a substance that was almost surely sulfuric acid from cloud droplets. Evidence for this event was a dramatic drop in CO_2 and noble gas counting rates and similarly striking increase in counting rates in channels appropriate to H_2O and SO_2. One inlet leak was closed off by a valve at 47 km; the other was cleared between 29 and 26 km.

Attempts to measure the D/H ratio from the mass spectrometer data were hampered by the problem of distinguishing Cytherean hydrogen from terrestrial hydrogen transported to Venus in the spectrometer. A mass peak found at 18.010 amu was surely caused by H_2O, and there was also a channel at 19.010 amu appropriate for the detection of HDO (*7*). The inlet tubes were heated to inhibit condensation and this led to the production of some degassed water vapor during the time the probe was descending. While the probe was in the middle cloud layer between 62 and 50 km above the surface of Venus (and before the leaks were blocked) the mass 18 signal increased rapidly (Fig. 1A). There were very few counts in the mass 19 channel. After the leaks were clogged the amount of water detected increased noticeably (Fig. 1). When they reopened the counting rate remained high, although initially not as high as it had been when the leaks were stopped. The mass 18 and mass 19 count rates increased between 25 and about 7 km and thereafter decreased again, although they continued to remain large. The ratio of mass 19 to mass 18 counts in the lowest 10 km was between 3×10^{-3} and 5×10^{-3} (Fig. 2). This result suggests that there are two components in the data, one ascribable to outgassed terrestrial water with an HDO/H_2O ratio of about 3×10^{-4} (*8*) and the other to Cytherean water, either outgassed or collected directly from the atmosphere but with a D to H ratio higher than terrestrial. Clearly, the low-altitude data, which do not maintain anything like a constant counting rate ratio to CO_2 or the noble gases, result partly from outgassed water. A guide to decomposing them into a terrestrial and a Venus component is needed.

There was a time when the hydrogen being sampled by the mass spectrometer surely contained a very large contribution from Venus. This was while the leaks were clogged with cloud droplets of H_2SO_4 and large signals at 18 and 19 amu were detected. In effect, the entire mass spectrometer was behaving like a large hydrogen enrichment chamber during this time. Figure 1, A and B, shows a great increase in count rates at 18 and 19 amu between frames 51 and 80—from 50.3 to 26 km. Although the CO_2 count rate decreased abruptly between frames 49 and 51, little of the water vapor detected in frame 51 seems to be from the H_2SO_4 sealing the inlets. The ratio of mass 19 to mass 18 count rates was 1×10^{-3}. After frame 51 the mass 19 signal rapidly increased so that the 19/18 ratio rose quickly to values above 10^{-2}. The 19/18 ratios are plotted in Fig. 2 with 1σ error bars. The contrast between conditions when the leaks were plugged and when they were open is great. The average ratio when the signals were greatest—frames 63 through 73—was $(2.68 \pm 0.20) \times 10^{-2}$, indicating that the water detected when the leaks were coated had a different composition than at other times. Since the largest ratio measured—in frame 63—was (3.2 ±

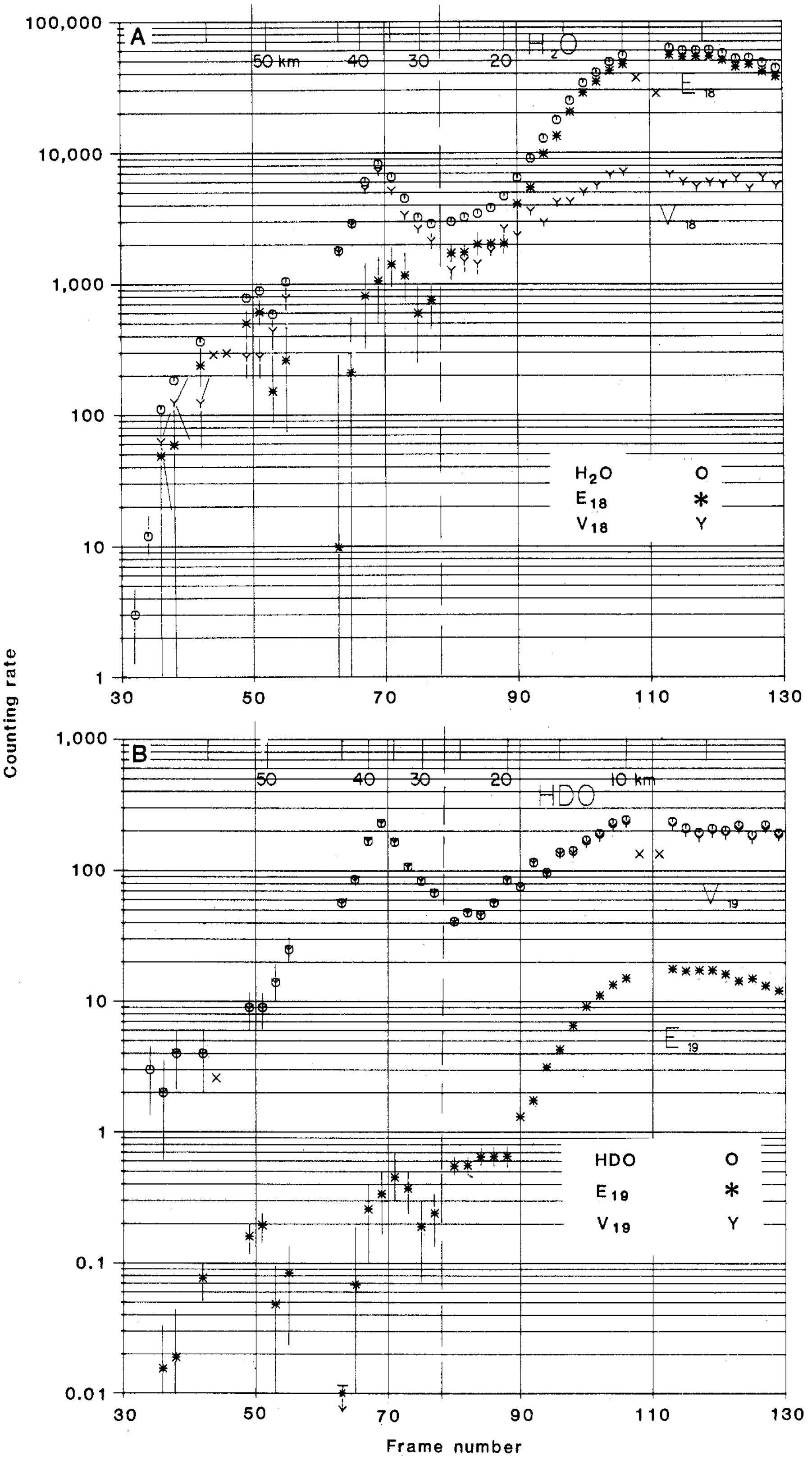

Fig. 1. (A) Counts per data frame in H_2O channel, E_{18}, and V_{18}, the terrestrial outgassed and Venus components for $R = 3.2 \times 10^{-2}$. Error bars are 1σ. During the period between frames 55 and 63 an isotope ratio measurement was being made. (B) Similar plots for the HDO channel. Time of leak opening is indicated by the broken vertical line.

$0.4) \times 10^{-2}$, the abundance ratio of HDO to H_2O on Venus is at least 2.8×10^{-2}. It could be larger if not all the water detected in frame 63 was Venus water.

Further refinement of this analysis is possible. The mass 18 peak, which will be called S_{18}, has two components, E_{18} and V_{18}, from terrestrial and Cytherean sources, respectively. Whether these are caused by outgassed or freshly sampled water does not matter. Similarly, at S_{19} mass 19 is composed of E_{19} and V_{19}. For the terrestrial component (*8*)

$$E_{19}/E_{18} = 3.2 \times 10^{-4}$$

For the Cytherean component

$$V_{19}/V_{18} = R$$

where R must be constant. The problem is to find R. There is no unique solution, but R cannot be less than 2.8×10^{-2}. Larger values of R are implied if in fact E_{18}, the outgassed terrestrial contribution to the counting rate during leak blockage, was not negligible even at frame 63; V_{18} is thereby reduced and R increased. The small ratio of E_{19} to E_{18} means that E_{19} is a very small part of S_{19} even if R is as large as 10×10^{-2} (1.6 counts out of 165). Larger R comes about by decreasing V_{18} rather than increasing V_{19}.

The four simultaneous equations for V_{18}, V_{19}, E_{18}, and E_{19} have been solved for various values of R. Figure 1, A and B, shows S_{18}, V_{18}, E_{18}, S_{19}, V_{19}, and E_{19} for $R = 3.2 \times 10^{-2}$ (*9*). In principle, E_{18} could have any value less than S_{18} and R could be very large. For $R = 2.8 \times 10^{-2}$ positive values of E_{18} for frames 63 through 69 are obtained only if the extreme limits allowed by the 1σ error bars on S_{18} and S_{19} are assumed. If R is 3.6×10^{-2}, E_{18} at frame 71 is 2000 and at frame 80 it is 1850. It is difficult to imagine how the outgassed terrestrial component could have been much larger at frame 71 than it was at frames 80 and 82 just after the leak opened. For this reason R appears to be constrained to the range 2.8×10^{-2} to 3.6×10^{-2}.

In fact, E_{18} and E_{19} should have been considerably smaller at frames 69 and 71 than at frame 80, because one microleak was closed off from the ion source by a valve just after frame 55 at 47 km. Thus the source of outgassed water (the heated inlet tube walls) was cut approximately in half at that time. The fact that S_{18} and S_{19} extrapolate backward from their values at frame 63 to levels far below those at frames 49 and 51 shows the effect of this reduction. A cap can be placed on E_{18} and E_{19} during the time the leaks were blocked by connecting the points after frame 80 with about half the value measured at frame 49. This would exclude values of E_{18} and E_{19} that allow R to be greater than 3.2×10^{-2}—allowing for 1σ deviations in E_{18} and E_{19}. Connecting the actual count rates before and after closure would permit R to be 3.4×10^{-2}. Imposition of the condition that no value of E_{18} while the leak was blocked could be larger than those attained just after it cleared would allow R to be as large as 3.6×10^{-2}. If confidence limits are relaxed to 3σ the same procedure expands the range of R from 2.2×10^{-2} to 4.0×10^{-2} (*10*).

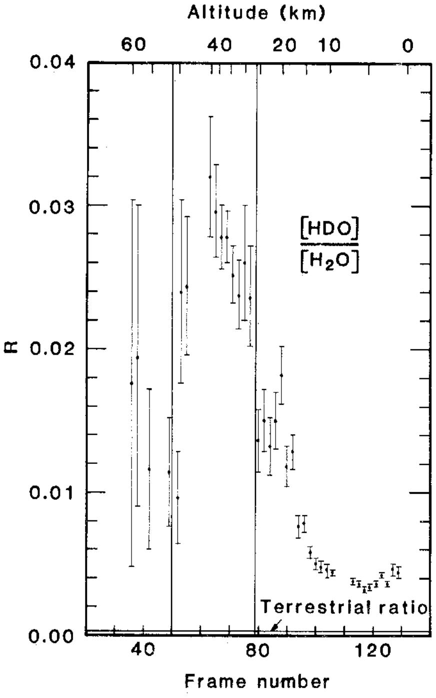

Fig. 2. Ratio of counting rates for HDO and H_2O as function of data frame (time). The period of leak blockage is set off by the vertical lines at frames 50 and 79.

In Fig. 1 it can be seen that the outgassed terrestrial components E_{18} and E_{19} increase rapidly after frame 63 in response to heating of the leak tubing and evaporation of the overcoat of sulfuric acid. The steady decrease in R (Fig. 2) shows that the amount of terrestrial water relative to Venus water was increasing during this time. The Venus components are maximal at frame 69 and then decrease until the leak opens between frames 77 and 80. Just after the entrance to the leak clears, as signaled by a great increase in CO_2 count rate, V_{18} and V_{19} drop sharply while E_{18} and E_{19} increase. The R value drops from 0.0236 to 0.0136. Immediately V_{18} and V_{19} begin to rise again, probably because water from the Venus atmosphere was being sampled. The outgassing terrestrial components remain relatively constant down to frame 90 at 19 km, where they begin to increase rapidly with decreasing altitude. This behavior is almost surely ascribable to an increase in temperature of the walls of the mass spectrometer. It is interesting that after the leak cleared V_{18} maintained a constant ratio of about 1.15 to the ^{36}Ar count rate between 25 and 10 km. This may mean that Venus water was being directly sampled and that the chemical getter was not pumping water. If so, the mixing ratio below 10 km decreased toward the surface by about 30 percent. This behavior is similar to that reported by Moroz *et al.* (*1*).

The hydrogen associated with the equivalent of a terrestrial ocean could have escaped from Venus in the form of H_2 if it left at an average rate of 7×10^{10} cm^{-2} sec^{-1} for 4.6 billion years. This is less than the largest flux that diffusion could have supported if the water vapor or H_2 mixing ratios were greater than about 0.35 percent (*5*). However, it does not seem likely that escape of that much hydrogen or even a large fraction of it would have occurred at such a slow pace over billions of years. Instead, it is very likely that after a large amount of water had outgassed from Venus, a runaway greenhouse ensued (*11*) and a copious amount of hydrogen produced from this water appeared in the atmosphere. Hydrogen would then have been the dominant gas in the upper atmosphere if, for example, the surface of Venus acted as an efficient sink for oxygen because of reactions such as

$$2FeO + H_2O \rightarrow Fe_2O_3 + H_2$$

Escape would have been powered by solar extreme-ultraviolet heating and a supersonic hydrodynamic outflow of H_2 would have resulted. There is a limit of about 10^{12} cm^{-2} sec^{-1} to the rate at which H_2 would have escaped in this way (*5*). Still, this flux is large enough to have exhausted the equivalent of an ocean in 280 million years. The H_2 flowing outward would have swept other gases along unless they were heavy enough to diffuse downward so fast that they remained in the atmosphere. On the other hand, there is a maximum flux of H_2 that could have been supported by diffusion if the background gas was CO_2. When the mixing ratio is small enough the diffusion-limited flow will no longer be rapid enough to allow a hydrodynamic flow of H_2 to sweep HD away. This occurs when the mixing ratio of H_2 becomes about 2×10^{-2} by volume (*5*). Thus, enrichment of deuterium begins only after the mixing ratio of H_2 drops below about 2 percent no matter how much water was originally present on the planet. The subsequent enrichment is then the ratio of 2 × 10^{-2} to the present equivalent H_2 mixing ratio. The enrichment given by the present HD/H_2 ratio of (3.2 ± 0.2) × 10^{-2} is 100 ± 12 referred to an initial ratio of 3.2 × 10^{-4}. It implies that the mixing ratio of H_2O is now 200 ± 25 ppm. This is in good agreement with the 100 to 200 ppm measured by the Venera spectrophotometer (*1*, *2*).

The possibility that there is a large abundance of deuterium in the upper atmosphere of Venus was suggested by the Mariner 5 Lyman α observation (*12*). It was recently asserted again by McElroy *et al.* (*13*), who argue that a mass 2 ion detected by the ion mass spectrometer on the Pioneer Venus orbiter is D^+. The D/H ratio of about 1 × 10^{-2} for the bulk atmosphere implied by this interpretation is one that could have resulted from nonthermal loss of hydrogen resulting from collision of fast oxygen atoms produced in dissociative recombination of O_2^+ with hydrogen atoms. The ratio of (1.6 ± 0.2) × 10^{-2} obtained by the LNMS agrees with the value required by McElroy *et al.* The lifetime of 9 × 10^8 years for hydrogen deduced from their mechanism would allow the water vapor mixing ratio to grow from 200 ppm to 2 percent in about 4.2 × 10^9 years. There is time enough left for hydrodynamic escape to have exhausted the equivalent of a terrestrial ocean. Although the measurement reported here cannot reveal how much additional water may have been outgassed from the planet before the critical mixing ratio of 2 × 10^{-2} was reached, it would be astonishing if the quantity were not considerably larger than this lower limit (0.3 percent of a terrestrial ocean).

T. M. DONAHUE
Department of Atmospheric and
Oceanic Science, University of
Michigan, Ann Arbor 48109
J. H. HOFFMAN
R. R. HODGES, JR.
Department of Physics,
University of Texas at Dallas,
Richardson 75080
A. J. WATSON
Marine Biological Association of the
United Kingdom, Plymouth,
Devon, England

References and Notes

1. V. I. Moroz, B. E. Moshkin, A. P. Ekonomov, N. F. San'ko, N. A. Parfent'ev, Y. U. Golovin, *Publ. 117 Space Res. Inst. USSR Acad. Sci. Moscow* (1979).
2. J. H. Hoffman, V. I. Oyama, U. von Zahn, *J. Geophys. Res.* **85**, 7871 (1980).
3. J. S. Lewis, *Earth Planet Sci. Lett.* **10**, 73 (1970).
4. J. C. G. Walker, K. K. Turekian, D. M. Hunten, *J. Geophys. Res.* **75**, 3558 (1970).
5. A. Watson, T. M. Donahue, J. C. G. Walker, *Icarus* **48**, 150 (1981); see also D. M. Hunten, *ibid.* **37**, 113 (1979); M. Sekiya, K. Nakazawa, C. Hayeshi, *Earth Planet. Sci. Lett.* **50**, 197 (1980). The transition from a flow in which HD is fully entrained in escaping H_2 to one in which it is essentially retained by the atmosphere is not abrupt. For Venus it probably would have begun when the mixing ratio of H_2 was considerably larger than 2 percent. Careful study of this transition is needed, as is a firm value for the present total hydrogen mixing ratio in the atmosphere of Venus. Until these are achieved the close agreement between model predictions and observations reported here must be regarded as perhaps fortuitous.
6. J. H. Hoffman, R. R. Hodges, T. M. Donahue, M. B. McElroy, *J. Geophys. Res.* **85**, 7882 (1980).
7. Correction was made for contributions from $^{18}O^+$, $^{36}Ar^{2+}$, $^{18}OH^+$, and $^{38}Ar^{2+}$. Interferences from other species such as HCl, F, and H_3O were found to be negligible.
8. The HDO/H_2O and HD/H_2 ratios are twice the D/H ratios. The D/H ratio for seawater is 1.56 × 10^{-4} [R. Hagemann, G. Nief, E. Roth, *Tellus* **22**, 712 (1970)].
9. The data for frames 75 and 77 have been corrected to allow for deliberate reduction of the ionization voltage from 70 V to 30 and 22 V, respectively, in these frames, as in frames 44, 46 and 108, 111.
10. If a 3σ error is allowed for in evaluating E_{18} and E_{19}, a ratio of 2.2 × 10^{-2} permits nonnegative values for frames 63 through 77. However, such a value of R calls for negative E_{18} and E_{19} for central values of S_{18} and S_{19} at all frames and for all 1σ extremes except at frames 73 and 77.
11. C. Sagan, *JPL Tech. Rep.* **2234** (1960); A. P. Ingersoll, *J. Atmos. Sci.* **26**, 1191 (1969). C. Sagan [in *International Dictionary of Geophysics*, S. Runcorn, Ed. (Pergamon, London, 1968), p. 2049] discussed the possibility that Venus lost the hydrogen associated with a terrestrial ocean.
12. C. A. Barth, *J. Atmos. Sci.* **25**, 564 (1968); T. M. Donahue, *ibid.*, p. 568; M. B. McElroy and D. M. Hunten, *J. Geophys. Res.* **74**, 1720 (1969).
13. M. B. McElroy, M. J. Prather, and J. M. Rodriguez [*Science* **215**, 1614 (1982)] show that the present escape modes on Venus would imply a lower limit of 800 g cm^{-2} of H_2O on Venus 4.5 billion years ago. Escape of deuterium is negligible, and it is taken to be so in this report as well.
14. We thank G. Carignan and K. C. Lohmann for useful comments. Supported by NASA grants NAS2-9126 and NAGW-64.

22 December 1981; revised 23 March 1982

Uptake of Dissolved Sulfide by *Spartina alterniflora*: Evidence from Natural Sulfur Isotope Abundance Ratios

Abstract. *The difference in the stable sulfur isotope ratios of sulfate and sulfide in marsh pore water was used to verify the uptake of hydrogen sulfide by the salt marsh cordgrass* Spartina alterniflora *in a North Carolina salt marsh. Most of the plant sulfur derived from pore-water sulfide was recovered as sulfate, an indication that the sulfide had been oxidized within the plant. The analysis of the sulfur isotope ratios of other coastal halophytes may be a useful technique for determining whether sulfide is taken up by plants in saline wetlands.*

Spartina alterniflora, the salt marsh cordgrass, is the dominant vascular macrophyte of the regularly flooded salt marshes along the east coast of the United States (*1*). The rapid rates of sulfate reduction measured in salt marsh sediments (*2*) suggest the presence of adaptive mechanisms that enable *Spartina* to persist in sediments where dissolved sulfide concentrations frequently exceed those that are toxic to rice (*3*). The diffusion of oxygen through aerenchyma (air spaces) from aerial portions of the plant to the roots combined with the leakage of oxygen from the roots to the surrounding sediments, which oxidize the pore-water sulfide, has been postulated as the mechanism that prevents sulfide toxicity in *Spartina* (*4*). The oxidation-reduction potentials in sediments of a New England salt marsh are higher in areas where *Spartina* is present than in unvegetated sediments, an indication that roots or rhizosphere bacteria possess limited oxidizing ability (*5*). However, in marshes where organic matter accumulates rapidly, the sulfate reduction rates greatly exceed the capacity of *Spartina* plants to supply oxygen to the sediments and substantial concentrations of dissolved sulfide accumulate in marsh pore waters (*6*).

Short-term hydroponic experiments have demonstrated that *Spartina* can take up ^{35}S-labeled dissolved sulfide without short-term toxicity effects (*6*). A technique was needed, however, to determine whether sulfide uptake also occurs in *Spartina* in the natural marsh environment. The isotopic fractionation effect associated with dissimilatory reduction of sulfide by bacteria seemed to present a way to determine the source of sulfur taken up and incorporated by *Spartina*. Reduction of ^{32}S-sulfate by bacteria in anaerobic marine sediments typically proceeds at a rate 1.02 to 1.03 times faster than reduction of ^{34}S-sulfate; as a result, the ^{34}S:^{32}S ratio in the product sulfide is 1.02 to 1.03 times lower than that of the initial sulfate (*7*). The difference between the isotopic composition of the sulfate and sulfide present in marine sediments is relatively easily resolved by mass spectrometry, and we felt that determination of the isotopic composition of plant sulfur would indicate the form of sulfur taken up by the plants from the sediments.

To determine whether sulfide was taken up and incorporated by *Spartina* in a natural marsh, the isotopic composition of plant sulfur [expressed as $\delta^{34}S$ (*8*)] was compared with the isotopic composition of sulfate and sulfide in marsh pore waters. *Spartina* plants were also grown

0036-8075/82/0507-0633$01.00/0 Copyright © 1982 AAAS