displacement of range boundaries by >300 km. A temperature rise of this amount by 2050 gives a rate of movement of 5 km yr^{-1}. This must be regarded as a minimum rate, not only because few range limits are determined by absolute temperature alone—more often it is temperature sums that are important, and these are likely to show larger proportional increases—but also because Europe is likely to experience a greater degree of warming than the global average (*20*). Nonetheless, even this minimum rate is about 20 times faster than the post-glacial rate of expansion of many European trees (*3*).
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Deuterium on Venus: Observations From Earth

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Absorption lines of HDO and H_2O have been detected in a 0.23–wave number resolution spectrum of the dark side of Venus in the interval 2.34 to 2.43 micrometers, where the atmosphere is sounded in the altitude range from 32 to 42 kilometers (8 to 3 bars). The resulting value of the deuterium-to-hydrogen ratio (D/H) is 120 ± 40 times the telluric ratio, providing unequivocal confirmation of in situ Pioneer Venus mass spectrometer measurements that were in apparent conflict with an upper limit set from International Ultraviolet Explorer spectra. The 100-fold enrichment of the D/H ratio on Venus compared to Earth is thus a fundamental constraint on models for its atmospheric evolution.

THE DRYNESS OF THE ATMOSPHERE of Venus has been an intriguing puzzle for theorists and observers alike. Although the abundances of CO_2 and N_2 in the planet's atmosphere are similar to those outgassed over geologic time on Earth, water is deficient by four to five orders of magnitude. The two extreme explanations of this apparent anomaly are (i) that desiccation occurred before formation of the planet, as Venus formed from the high-temperature region of the solar nebula (*1*) and (ii) that formation with abundant water was followed by desiccation through atmospheric evolution, as H_2O was photodissociated and hydrogen escaped (*2*). The assumption in the latter hypothesis is that Venus received most of its volatiles during accretion from late bombardment by comets and meteorites that formed in a cooler part of the nebula where water could condense (*3*). Because escape of hydrogen leads to relative enhancement of deuterium, the D/H ratio is an important constraint that must be accommodated by any theory for the history of water on Venus. The value of this ratio has been the subject of some dispute, however.

McElroy *et al.* (*4*) were the first to suggest that the D/H ratio in Venus' atmosphere is much larger than on Earth. They proposed that the mass-2 ion detected by the ion mass spectrometer on the Pioneer Venus Orbiter was D^+, rather than H_2^+, as originally suggested by Taylor *et al.* (*5*). The corresponding D/H ratio is about 10^{-2}, compared with the terrestrial value of 1.6×10^{-4} (*6*). This interpretation was subsequently supported by more detailed analyses (*7*). Meanwhile, Donahue *et al.* (*8*) had published their investigation of a remarkable set of observations by the neutral mass spectrometer on the Pioneer Venus large entry probe. As the probe descended through the atmosphere, the inlets to the mass spectrometer became temporarily clogged, presumably by droplets of H_2SO_4 from the clouds on Venus. Mass spectra of the increased flux of H_2O produced during this event revealed a value of the D/H ratio of $(1.6 \pm 0.2) \times 10^{-2}$. McElroy *et al.* (*4*) and Donahue *et al.* (*8*) interpreted their results to indicate that Venus once contained at least as much H_2O as the equivalent of 0.3% of Earth's contemporary oceans.

In contrast to the good agreement between these two spacecraft measurements, Bertaux and Clarke (*9*) recently reported an upper limit of $(3.6 \pm 1.5) \times 10^{-3}$ for the D/H ratio from the absence of the D Lyα line in International Ultraviolet Explorer spectra of Venus. However, this upper limit is dependent on a model for the vertical distribution of molecular and atomic hydrogen in the planet's upper atmosphere, and difficulties in the analysis have led to the suggestion that more observations are needed (*10*).

In view of the significance of the D/H ratio and these discrepant results, a new measurement that is not affected by the complexities that plague the interpretation of upper atmosphere observations was clearly needed. We therefore decided to measure the D/H ratio in H_2O, the most abundant hydrogen-containing compound on Venus, far below the homopause using the same general approach that was successful on Mars (*11*). We used the Fourier Transform Spectrometer with the 3.6-m Canada-France-Hawaii Telescope on Mauna Kea to detect and measure lines of HDO and H_2O in the spectrum of Venus.

We first tried to utilize the 3- to 4-μm region in spectra of the bright side of Venus, but this attempt was not fully satisfactory (*12*). We found that the detection of thermal emission from below the clouds on the dark side of Venus at 2.3 μm (*13*) provided a better opportunity to study both HDO and H_2O. We recorded the spectrum of the dark side of Venus in this region on 10 November 1989 at an unapodized resolution of 0.23 cm^{-1} (*14, 15*). The Doppler shift of Venusian lines was +0.19 cm^{-1}. The nightside spectrum was divided by a spectrum of the dayside recorded at a similar zenith angle to correct for telluric absorption and the filter response (Fig. 1).

A first analysis of this data set (*15*) has shown that a large number of molecular lines can be identified, including many absorptions of HDO and H_2O between 4120 and 4275 cm^{-1}. In this region, CO is the dominant absorber; a few lines of HF are also present. Unlike the Venus H_2O lines, which are difficult to distinguish in the raw spectra because they are blended with their telluric counterparts, most of the Venus HDO lines are easily discernible (Fig. 1). This difference alone indicates that the D/H ratio on Venus must be highly enriched compared to the terrestrial value (*15*).

To measure the H_2O and HDO mixing ratios, we generated synthetic spectra of Venus from a radiative transfer program (*16*). In the spectral region where the H_2O and HDO lines are present, thermal emission originates from altitude levels between 32 and 42 km, below the sulfuric acid cloud

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deck (*17*). To account properly for CO absorption in this region, we adjusted the CO mixing ratio through a comparison between synthetic and observed spectra over the entire range from 4120 to 4350 cm^{-1} using the altitude variation for CO deduced from probe data (*15, 18*). The best fit was obtained for a vertical profile of CO corresponding to a mixing ratio of 45 ppm near an altitude of 42 km, where our determination is most precise (*19*).

The resolution of our Venus spectrum is not sufficient to provide a good constraint on the H_2O vertical distribution. We assumed that the H_2O mixing ratio was constant below the cloud deck at 48 km and that it decreased linearly with altitude above 48 km to a value of 2 ppm at 55 km, a value compatible with ground-based measurements above the clouds (*18*). The value of the H_2O mixing ratio below 48 km was adjusted to provide the best agreement with the observed line-to-continuum ratios in selected spectral intervals where H_2O absorption dominates (Fig. 2). The resulting mixing ratio (34 ± 10 ppm) is lower than the average values below the cloud deck recommended by Von Zahn *et al.* (*18*) and more recently by Hunten *et al.* (*20*) on the basis of their studies of all available measurements, but it is consistent with data in the 1.13-μm band of water vapor obtained by the spectrophotometer on board the Venera 11 and 12 landers (*18*). Horizontal variations in the mixing ratio that have been proposed (*21*) could also account for the low amounts of water we detected.

Using the same best fit approach, we derived a mixing ratio for HDO equal to 1.3 ± 0.2 ppm (Fig. 3). The errors for both H_2O and HDO were determined from noise level, uncertainties in the location of the continuum level, and blending with terrestrial lines, but do not include uncertainties in the atmospheric model. Because we are working with absorption lines of H_2O and HDO that have comparable strengths in the same region of the spectrum, the retrieval of the [HDO]/[H_2O] ratio is much less sensitive to uncertainties in the atmospheric model than the individual determinations of the HDO and H_2O column abundances. The resulting value of the D/H ratio (equal to 1/2 × [HDO]/[H_2O]), in consideration of all sources of uncertainty, is $(1.9 \pm 0.6) \times 10^{-2}$ or 120 ± 40 times the telluric ratio. The 100-fold enrichment of the D/H ratio deduced from the two Pioneer Venus mass spectrometer measurements is thus confirmed.

The interpretation of this enrichment depends critically on the amount of water currently in the atmosphere, a poorly defined quantity. The original conclusion that Venus lost an ocean of water (*4, 8*) has been challenged by Grinspoon (*22*), who suggested that a steady flux of impacting comets was necessary to supply the planet's current water reservoir and thus concluded that the observed D/H tells nothing about the original H_2O abundance. Grinspoon (*22*), using 20 ppm for the global mixing ratio of atmospheric water, derived a mean lifetime of only 10^8 years for water in the atmosphere. However, Hunten *et al.* (*20*) have recently reanalyzed data from the Pioneer Mission and concluded that the best current value for atmospheric water is 200 ± 100 ppm. Also, Rodriguez *et al.* (*23*) estimated an escape rate for hydrogen that is two to five times lower than Grinspoon's. These two revisions would yield a mean lifetime of at least 10^9

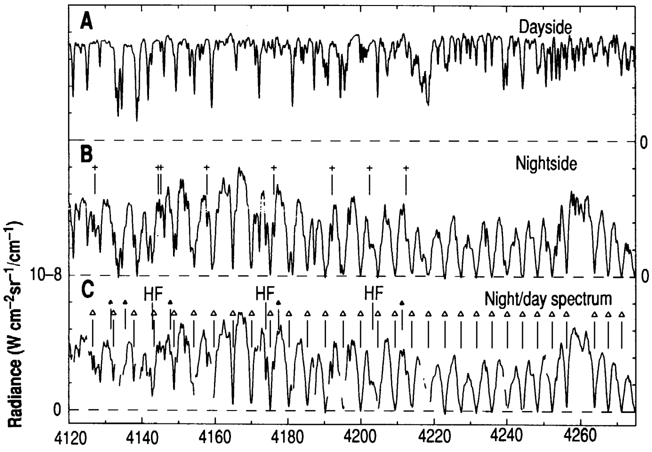

Fig. 1. Spectra of the dayside and nightside of Venus recorded at similar zenith angles at a resolution of 0.28 cm^{-1} (apodized). The dayside spectrum (**A**) exhibits H_2O and CH_4 lines of terrestrial origin. The nightside spectrum (**B**) has been corrected for contamination by reflected sunlight (*14*). The most easily discernible absorptions due to Venus HDO are marked as (+). Correction for telluric absorption and filter response was achieved by ratioing the nightside spectrum by the dayside spectrum (**C**). The calibrated spectrum (C) is in watts per centimeter squared per steradian per wave number. Missing data points in (C) correspond to spectral regions where the telluric absorption exceeded 40%. The strongest absorption features in this spectrum are due to Venus ^{12}CO lines (△). Some weak Venus ^{13}CO lines are also present (▲) along with a few HF lines. All the other absorptions are due to H_2O (ν_1 and ν_3 bands) and HDO ($\nu_1+\nu_2$ and ν_2 bands) in the atmosphere of Venus.

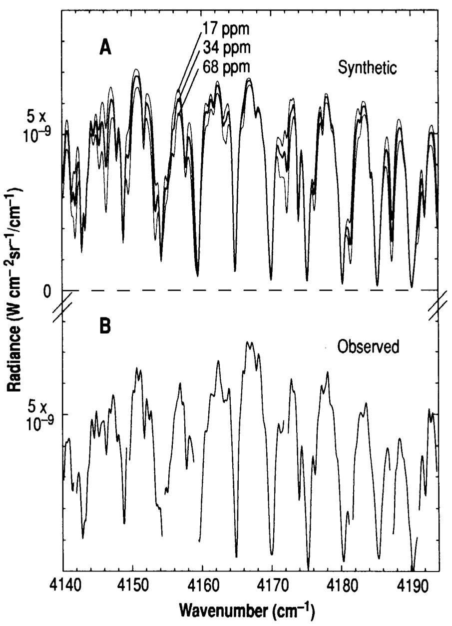

Fig. 2. Comparison of the observed spectrum (**B**) with three synthetic spectra (**A**) in which the subcloud (below 48 km) H_2O mixing ratio has been varied. The subcloud HDO mixing ratio is assumed to be equal to 1.3 ppm, the value that provides the best overall agreement with the observations (see Fig. 3). The thick curve in (A) corresponds to our nominal value for H_2O, the two thinner curves refer to excursions by a factor of 2 around this best fit value. The synthetic spectra in (A) have been computed for a mixing ratio of HF equal to 6×10^{-9} and the CO vertical profile described in the text.

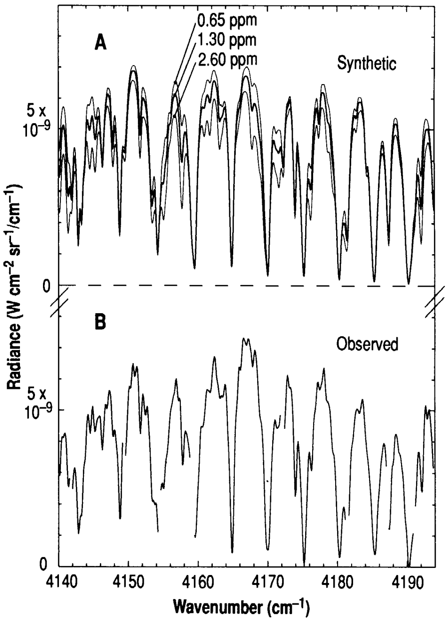

Fig. 3. Comparison of the observed spectrum (**B**) with three synthetic spectra (**A**) in which the subcloud (below 48 km) HDO mixing ratio has been varied. The subcloud H_2O mixing ratio is assumed to be equal to 34 ppm, which provides the best overall agreement with the observations (see Fig. 2). The thick curve in (A) corresponds to our nominal value for HDO, the two thinner curves to excursions by a factor of 2 around this best fit value. The HF and CO mixing ratios are the same as for Fig. 2.

years for water on Venus, significantly reducing the need for continuous replenishment. The effect of a single large cometary impact (*22*) would also be proportionally diminished. Using different arguments, both Chyba (*24*) and Ip and Fernandez (*25*) concluded that Earth's oceans could have been provided by an early flux of comets—possibly tied to the formation of Uranus and Neptune. It is hard to see how this bombardment could have missed Venus. Unfortunately, the massive early escape of hydrogen required to remove an ocean of water would leave no record of D-H fractionation (*8, 20*); therefore, we cannot evaluate the size of the original reservoir from this ratio alone. Removal of an original, large water reservoir through dissociation and hydrogen escape (*4, 8*) appears to be the simplest explanation of the available data, however, provided such escape can occur in a way that does not affect the noble gases.

Our observations can easily be repeated at higher spectral resolution and for several locations on the planet at future inferior conjunctions of Venus. Additional data will improve the accuracy of the determination of the D/H ratio and the measurement of water abundance above 32-km altitude. If, as seems likely, radiation that has been detected from the dark side at shorter wavelengths (*26*) comes from still deeper levels in the atmosphere, it should ultimately be possible to reevaluate the global abundance of water vapor on Venus from Earth. This is now the greatest obstacle for efforts to understand the significance of the high value of the D/H ratio. Galileo observations of Venus made in February 1990 will also help. The prospect of Magellan radar maps with a resolution capable of detecting traces of ancient fluvial erosion adds yet another approach to the study of the history of water on Venus.

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An Interplanetary Dust Particle Linked Directly to Type CM Meteorites and an Asteroidal Origin

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Tochilinite, an ordered mixed-layer mineral containing Mg, Al, Fe, Ni, S, and O, has been identified in an interplanetary dust particle (IDP). This mineral is found in only one other class of meteoritic materials, type CM carbonaceous chondrites. The presence of tochilinite in an IDP provides a direct petrogenetic link between a member of the layer-silicate subset of IDPs and a specific class of meteorites and thus establishes that some IDPs collected in the stratosphere have an asteroidal origin. The scarcity of this IDP type suggests that materials with CM mineralogy are not abundant among the dust-producing asteroids.

EXTRATERRESTRIAL MATERIALS CAPTURED by Earth include both conventional meteorites and micrometer-sized interplanetary dust particles (IDPs). Meteorites have been intensively studied because laboratory specimens have been available for many decades and most are large (>1 cm) objects that can be examined by multiple analytical techniques. The IDPs have been studied in less detail because most have been collected only during the past decade (*1*) and because techniques sensitive enough for analysis of nanogram quantities of material are required. Meteorites are believed to be derived primarily from asteroids (*2, 3*), but because only a few asteroids have spectral reflectances similar to those of the major meteorite classes (*4*), it appears that meteorites are a highly biased sampling. This bias is believed to result from two processes. First, for bodies larger than about 1 cm^3, only strong objects can survive atmospheric entry, and fragile objects, like cometary meteors and weaker asteroidal materials, fragment into dust (*5*). Second, the

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