The Mn 539.4-nm line strength fails to track well at solar minimum (b in Fig. 1). We hypothesize that beginning in the spring of 1985 seedlings of new cycle flux emerged which weakened the strength of the Mn 539.4-nm line but did not reach high enough to affect the CN band head and cause faculae. Possibly for this reason, the CN band head appears to report more accurately on the solar minimum facular layers. Our best surrogate for the entire cycle is a combination of Mn 539.4- and CN 388.3-nm line strengths.

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Deuterium on Mars: The Abundance of HDO and the Value of D/H

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Deuterium on Mars has been detected by the resolution of several Doppler-shifted lines of HDO near 3.7 micrometers in the planet's spectrum. The ratio of deuterium to hydrogen is (9 ± 4) × 10^{-4}; the abundance of H_2O was derived from lines near 1.1 micrometers. This ratio is enriched on Mars over the telluric value by a factor of 6 ± 3. The enrichment implies that hydrogen escaped more rapidly from Mars in the past than it does now, consistent with a dense and warm ancient atmosphere on the planet.

THE GEOMORPHOLOGY OF THE MARTIAN surface indicates that running water was present in the distant past, but the total amount of water and the periods of its activity are still uncertain (*1*–*3*). Estimates of the total quantity of volatiles that have been outgassed by the planet are consistent with the formation of the dense, warm, ancient atmosphere that would have been required for the presence of slow-moving water (*4*), but nongeological evidence for an early warm and wet climate on Mars has been lacking. The present ratio of deuterium to hydrogen, D/H, in the martian atmosphere can help constrain models for the near-surface reservoir of water and the loss of H_2O by photodissociation and escape. Accordingly, we decided to search for HDO on Mars and compare the resulting abundance with that of H_2O to determine D/H.

Using the Fourier transform spectrometer with the Canada-France-Hawaii 3.6-m telescope at Mauna Kea, we detected many lines of the *P*- and *Q*-branches of the ν_1 fundamental of HDO near 3.7 μm (Fig. 1). The observations were made on 10 January 1987 UT, when the Doppler shift for martian lines relative to their broader telluric counterparts was 0.125 cm^{-1}. At our unapodized resolution of 0.030 cm^{-1}, the two sets of lines were unambiguously separated. Eight separate scans of 16 min each were recorded with 5-arc-s apertures in a beam-switched mode, for a total integration time in excess of 2 hours. The co-added and apodized spectra yielded a final spectrum with a signal-to-noise ratio of approximately 200 in the continuum and a spectral resolution of 0.036 cm^{-1}. Our ability to detect the martian lines was aided by the low amount of precipitable water in Earth's atmosphere above Mauna Kea (about 0.3 mm) at the time of our observations.

We have analyzed these data using room-temperature line strengths (*5*) that we adjusted to an average atmospheric temperature of 200 K (*6*, *7*). We derived the total, integrated line-of-sight column density of HDO on Mars by first taking the ratio of the apodized martian spectrum to a lunar spectrum that was recorded during the same night, and then fitting this ratioed spectrum with a synthetic spectrum of Mars in which we could vary the amount of HDO. For the calculation of the synthetic spectrum, we assumed that the spectrum followed a simple reflecting-layer model. Jakosky and Farmer (*7*) showed that the water-vapor abundances they derived were unaffected by dust, except during global dust storms, as long as their viewing angle was less than 60°. In the 3 months before our observations, a period that normally corresponds to the dust-storm season on Mars, no global dust storms were observed (*8*). Furthermore, we easily observed albedo contrasts on the disk of Mars during the nights of our observation, which supports the clear atmosphere assumption to the extent that we require it.

The contribution of thermal radiation from Mars was estimated in the computation of the synthetic spectrum by the following method. We adopted a geometric albedo of 0.17 with an infrared phase function of 0.5 (*9*), which corresponds to the 40° phase angle of our observations. Assuming an average ground temperature of 245 K (*10*), we estimated that the thermal flux contributed about 12% of the total martian flux that was recorded near 2720 cm^{-1}. As an additional check, we compared several solar lines that were also observed in our martian spectrum in this region with the same lines in a solar spectrum that was recorded with the ATMOS spectrometer on the Shuttle-based Space Lab (*11*). The solar lines in the martian spectrum were generally weaker than in the direct solar spectrum. The difference can be accounted for by a martian thermal flux that is, on the average, about 11% of the total flux, which is in good agreement with our first estimate. Correction for this thermal flux changed the calculated abundance of HDO by only 5%.

Twenty-two lines of HDO were analyzed, eleven in each of the *P*- and *Q*-branches. Additional lines of HDO were detected, but they were either too weak to be useful or blended with lines of CO_2 isotopes in the martian atmosphere. Our best fit was obtained for a total, integrated line-of-sight column density of 3.6 × 10^{-2} precipitable micrometers of HDO (Fig. 2). The uncertainty in this column density is derived from three major sources. First, the random error associated with a signal-to-noise ratio of 200 in the continuum of the HDO spectrum

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propagates to a 3σ relative uncertainty of 6% in the abundance, for the simultaneous fit of all 22 lines considered. Second, the relative uncertainty due to possible systematic errors in the line intensities is about 10%. Third, the temperature, the placement of the continuum level, possible blending of the martian lines with terrestrial or solar features, and the possible effects of any undetected dust in the atmosphere are collectively estimated to be about 20%. Thus we estimate that the total uncertainty in the measured abundance is $\pm 0.8 \times 10^{-2}$ precipitable micrometers which corresponds to the extreme range of values that can be satisfied by the observations.

Because seasonal variations in the water vapor abundance on Mars occur, we must know the amount of H_2O that was present near the time of the HDO observations to derive a value for D/H. Because no strong features of normal water vapor occur in the region that was covered by our HDO spectrum, we recorded a spectrum of Mars near 1.1 μm, which contains several H_2O lines, two and four nights later. The same instrumental configuration was used, but the spectrum was recorded with an apodized resolution of 0.064 cm^{-1} and a signal-to-noise ratio of approximately 250 in a total of 3 hours, 15 minutes. On these nights, the precipitable water in the earth's atmosphere above Mauna Kea was approximately 0.6 mm.

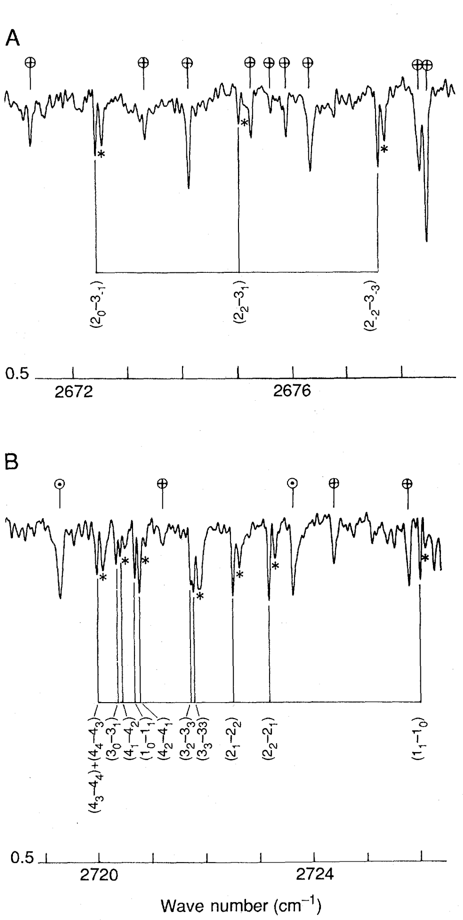

Fig. 1. Final apodized spectrum of Mars near 3.6 μm that shows both martian and telluric HDO lines. The martian lines are indicated by their rotational (J, K) assignments; the corresponding telluric lines (*) are shifted 0.125 cm^{-1} toward higher wave numbers. Other telluric absorptions (⊕) are mainly CH_4; solar lines are labeled (⊙). Direct comparisons of the intensities of martian and telluric HDO lines are hindered by blends with solar and other telluric lines and by the temperature difference between the two planetary atmospheres. (**A**) The region 2672 to 2678 cm^{-1}. (**B**) The region 2719 to 2726 cm^{-1}.

We were able to discern weak, red-shifted martian lines that belong to the $\nu_1 + \nu_2 + \nu_3$ and $\nu_2 + 2\nu_3$ combination bands of H_2O in these spectra. We confirmed that these features could not be Doppler-shifted solar lines and derived from a synthetic spectral analysis an integrated, line-of-sight column density of 20 ± 8 precipitable micrometers of H_2O. For comparison with other observations during the same martian season (summer in the southern hemisphere), we must use an air-mass factor appropriate to the geometry of the observations. With a 5-arc-s circular aperture, which accepted about 75% of the apparent disk of Mars, this factor is close to 4 (*12*), which yields 5 ± 2 precipitable micrometers of H_2O on Mars for the single column abundance at the time of our observations. The uncertainty was derived in the same way as the uncertainty for the HDO abundance: 12% (3σ) systematic error due to the signal-to-noise level in the H_2O spectrum for the simultaneous fit of all four observed lines; 30% from uncertainties in the line intensities; and about 30% from uncertainties in the assumed average temperature, continuum placement, blending with terrestrial or solar lines, and uncertainties due to the possible presence of any undetected dust.

In their review of martian H_2O measurements from 1964 to 1983, Jakosky and Barker (*13*) reported that the average value for the global atmospheric water vapor during the period that corresponded to our observations was 13 ± 8 precipitable micrometers for the single column abundance. In this average, the 1969 values, which ranged from 20 to 30 μm, were excluded because such high abundances have not been measured at any other time. The Viking orbiter observations (*6, 7*) for the martian season corresponding to our measurements give a global average value of 6 μm. We conclude that our determination is consistent with previous observations of H_2O on Mars during summer in the planet's southern hemisphere.

In that the geometry of our observations was the same for both HDO and H_2O, the D/H ratio that is derived from their abundances is independent of the air-mass factor and its uncertainty. It is directly obtained from the ratio of the integrated, line-of-sight column densities derived from the two sets of lines, 1/2 [HDO]/[H_2O], which yields a value of D/H = $(9 \pm 4) \times 10^{-4}$. The value of D/H on Mars is thus enhanced by a factor of 6 ± 3 over the terrestrial ratio of 1.5×10^{-4} for standard mean ocean water (SMOW).

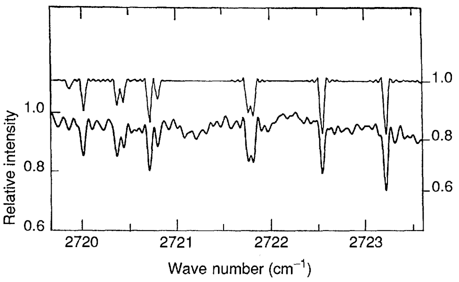

Fig. 2. Comparison of a section of the martian spectrum (corresponding to part of Fig. 1B) divided by the lunar spectrum (below) with a synthetic spectrum of martian HDO absorptions as described in the text (above). The scale for the upper spectrum has been shifted as indicated by the tick marks at the right (upper spectrum) and left (lower spectrum) margins of the figure.

No theoretical predictions for the value of D/H on Mars have been published. The simplest interpretation of the enhancement of D/H that we have derived over the telluric value is that a large fraction of the water on Mars that has been accessible to the atmosphere over geologic time has been photodissociated, with differential escape of H and retention of D. To see whether this effect could have produced the observed D/H value, we need to determine the extent that D/H changes in the upper atmosphere. Following Hunten (*14*), we can define a fractionation factor $1 + x = \exp(\Delta z/Hd)$ where Hd is a scale height for the isotopic mass difference $Hd = kT/(m_D - m_H)g$ (k is Boltzmann's constant, T is temperature, m_D and m_H are the masses of D and H, and g is the gravitational constant), and Δz is the height of the base of the atmospheric region from which escape takes place (the exobase) above the upper boundary of the mixed region (the homopause). For H and D on Mars, $x = 0.2$.

This same diffusive separation should have occurred for other isotopes that differ by 1 atomic mass unit and was indeed predicted and the effect observed for nonthermal escape of ^{15}N and ^{14}N on Mars (*15–17*). McElroy (*15*) showed that oxygen also escapes from Mars and that the nonthermal escape of oxygen and the thermal or Jeans escape of hydrogen are linked. Diffusive separation of ^{16}O and ^{18}O in the martian upper atmosphere should then also have led to preferential loss of ^{16}O and an increase in $^{18}O/^{16}O$, which was not observed (*17*). McElroy *et al.* (*18*) therefore proposed that atmospheric oxygen exchanged with a contemporary global reservoir that corresponded to the equivalent of at least a 13.5-m layer of liquid water averaged over the martian surface. If water were the only source of both escaping hydrogen and oxygen, however, we would not expect the observed sixfold enhancement of D/H over SMOW in the absence of any enrichment of ^{18}O. Thus the coupling between H and O escape did not always obtain, and the exchangeable reservoir of oxygen was most likely some form of CO_2 (*18*, *19*), that corresponded to an atmospheric surface pressure of >0.6 bars.

Independent estimates of the original abundance of water on Mars are required to test the implications of the observed enhancement of D/H. Anders and Owen (*20*) used a carbonaceous chondrite model to predict abundances of volatiles on Mars; they derived a value of 10 m cm^{-2} for the equivalent water layer. This estimate is suspect, however, in view of subsequent tests of their model (*21*). Estimating only the amount of water that was released by volcanic activity on Mars, Greeley (*3*) suggested an abundance of 46 m cm^{-2}, whereas Carr (*2*) deduced an equivalent depth of approximately 500 to 1000 m cm^{-2}, on the basis of his evaluation of total fluvial erosion.

If we assume that the initial value for D/H on Mars was equal to or less than the SMOW value on Earth (*22*), we must conclude that at least 83% of the water that circulated through the Martian atmosphere since the last giant impact has been photolyzed with escape of H and retention of D to produce the observed value of D/H. Following Hunten (*14*) and setting $x = 0.2$, we can expect that more than 99% of the water has been lost. If the present rate of escape of hydrogen from Mars has remained constant for the last 4.5 billion years, however, the equivalent of only a 2.5-m layer of water would have been destroyed by photodissociation (*18*). This implies that the initial abundance of water was no more than 3 m cm^{-2}, which is significantly less than any of the above estimates. Given the evidence that volatiles were initially abundant on Mars (*4*, *20*, *23*), we must assume that the escape of hydrogen was more rapid in the past than it is today to achieve the observed sixfold enrichment in D/H. However, the escape rate must also have been slow enough to maintain a large volume of running water on the surface for a long enough period to produce the observed erosion features. Approximately 200 times the present flux of escaping hydrogen during the first billion years of Martian history would suffice.

Several mechanisms could have increased the rate of hydrogen escape from Mars in the past. Hunten *et al.* (*24*) estimated that the high flux of extreme ultraviolet radiation from the young sun would have increased the amount of hydrogen escaping from Mars by a factor of four to eight times the current rate if the present coupling between nonthermal escape of oxygen and Jeans escape of hydrogen was maintained. To increase this factor further (and another factor of 25 to 50 is needed), a large upward flux of hydrogen to the exobase, is required. If Walker's (*25*) calculation for the oxidation of the surface of Venus is used as a limiting case, the equivalent of a 27-m layer of water could fully oxidize a 1-km regolith of basalt on Mars, but this is still not enough.

Even to get this much hydrogen from oxidation, however, liquid water is probably required (*26*), and the thick, warm atmosphere that is necessary for liquid water to exist on Mars could have itself provided the additional source of hydrogen. Currently, most of the photochemistry leading to the destruction of water vapor on Mars occurs far below the tropopause, which therefore does not function as a bottleneck for hydrogen escape (*27*). Increasing the temperature of the lower atmosphere increases its carrying capacity for water vapor, which was most likely the dominant hydrogen-carrying compound during the first billion years of martian history. Krasnopolsky (*28*) has shown that an increase of 10 K in the mean temperature of the troposphere leads to an increase of a factor of 10 in the water-vapor photolysis rate. Because models for the early atmosphere predict that changes in mean temperature of several tens of degrees occurred (*4*), this mechanism offers the best possibility for producing a large flux of hydrogen. Indeed, if the atmosphere were sufficiently warm and wet, the flux of escaping hydrogen might reach the blowoff condition, which would provide another opportunity for D/H fractionation (*29*).

This speculation illustrates the intricacies of the problem. In a thick, dense atmosphere, the solar ultraviolet light required for photolysis will not penetrate deeply. The limitation on the upward flux of water vapor established by the tropopause temperature then becomes an important constraint. Thus a rigorous analysis of hydrogen escape from Mars will require the use of time-dependent models that take into account the detailed photochemistry (*30*), the effects of changing atmospheric composition, density, and structure, variations in solar luminosity, and the changing composition of evolved gases, and their interactions with the crust. These processes have the potential to destroy enough water vapor to allow both the early, wet period required to produce the observed fluvial erosion and the enhancement in D/H above the terrestrial value.

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31. We thank C. Camy-Peyret for providing appropriate line strengths from (*5*), R. Kurucz for furnishing new line lists of atomic and molecular transitions that could contribute to the 1 μm spectral region, N. Grevesse and E. Biemont for useful discussion on

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Anomalous Upstream Retroflection in the Agulhas Current

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The Agulhas current, the major western boundary current of the Southern Hemisphere, plays a crucial role in the water mass balance of the world oceans by controlling the transfer of thermocline water from the Indian to the Atlantic ocean systems. The main mechanism for such transfer is through the shedding of large rings of warm water at the Agulhas retroflection south of Africa. On the basis of satellite imagery and drifter tracks, anomalous reversals of the current are observed to occur far upstream of its characteristic retroflection location. The observations agree with results of an inertial jet model of the current. These anomalous reversals probably cause abrupt and major changes in the fluxes south of Africa and thus in the rate of ring shedding. This unusual flow bimodality in a major component of the global ocean heat transport system could have important climatic implications.

The Agulhas current dominates the circulation pattern of the southwest Indian Ocean. It derives most of its water from the Mozambique channel (*1*), from east of Madagascar (*2, 3*) and from recirculation in a southwest Indian Ocean subgyre (*1, 2*). It reaches its full stature at about the latitude of Durban (Fig. 1) and closely follows the shelf edge of the southern African continent for most of its subsequent downstream path (*4*). On overshooting the southern tip of the continent, it retroflects in a reversal (*5*) that carries most of its warm, saline water back to the south Indian Ocean. The retroflection loop is an unstable configuration (*6*) that causes a large Agulhas ring to occasionally pinch off (*7*). These rings, described as the most intense observed anywhere (*8*), drift into the South Atlantic Ocean. Ring shedding occurs, on average, about nine times per year (*9*), which leads to a substantial transfer of energy and water from the Indian to the Atlantic ocean systems. This exchange of water has important climatic implications (*10, 11*).

The total flux of warm Indian Ocean water into the Atlantic by way of ring shedding is most likely a function of the volume flux of the Agulhas current (*12*). Various models of the current (*12*) suggest that perturbations in the flow may precipitate ring formation or influence the rate of ring shedding. The Agulhas current upstream of Port Elizabeth (Fig. 1), however, has a remarkably stable path configuration (*4*), flow rate (*13*), and mass transport (*14*) for a western boundary current.

We have scrutinized 11 years of thermal infrared satellite images of the southwest Indian Ocean to test the hypothesis (*15*) that the configuration of the southwest Indian Ocean subgyre might lead to an occasional eastward leakage of water from the Agulhas current location at a position far upstream of its usual retroflection location (*16*). This circulation system lends itself particularly well to investigations by thermal infrared remote sensing because sea-surface temperature contrasts are high in this area and the surface thermal expression of the Agulhas current is strongly coherent with its deeper flow (*7*).

This investigation revealed that significant leakage or virtually total retroflection of Agulhas current water occurred at about the longitude of Port Elizabeth (25°E) two to three times per year, on average (Fig. 1). These events had a typical duration of 3 to 6 weeks. The event that is partly shown in Fig. 2 lasted for more than 2 months. These periods are long enough for a significant part of the total flow to be diverted. The occurrence of persistent cloudiness over the area for long periods during which the sea surface was either partially or totally obscured implies that this assessment of the incidence of upstream reversals on the basis of satellite images is probably an underestimate.

A few drift tracks of free-drifting buoys describe such instances of upstream reversal (Fig. 2). The track of buoy 74625 south of Port Elizabeth simulates the disposition of the eastward warm water outflow from the Agulhas current which commenced a few days before the buoy reached the area. Sea-surface temperatures measured by the buoy were consistently higher than 20°C, which indicates that the buoy was continuously in surface water of the Agulhas current. The drift track for a buoy that was placed a number of years previously describes a similar current configuration (Fig. 2) somewhat farther to the west. These drift patterns present circumstantial evidence for the existence of upstream retroflections.

In two instances the area was sufficiently cloud-free over an extended period to ob-

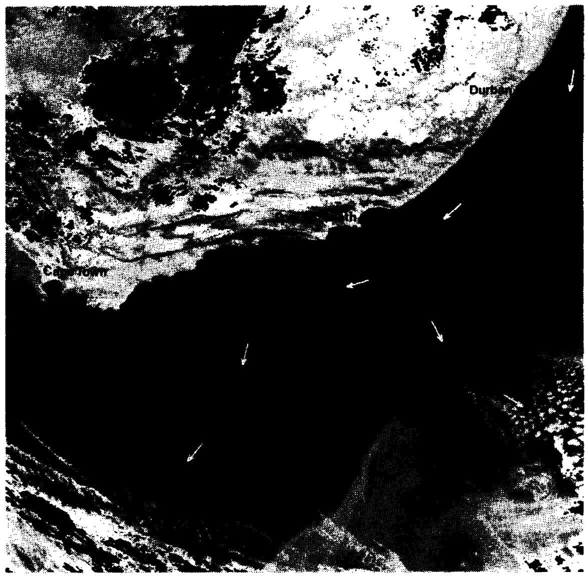

Fig. 1. Portrayal of an upstream retroflection of part of the Agulhas current in the vicinity of Port Elizabeth. This thermal infrared image is from the advanced very high resolution radiometer on board the NOAA (National Oceanic and Atmospheric Administration) satellite for 13 May 1983. Warm water is in darker hues. South of Port Elizabeth the Agulhas current is located seaward of its normal track and a clear bifurcation of warm water flow is apparent. The distance between Port Elizabeth and Cape Town is about 700 km.

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