

VENUS METHANE AND WATER

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Abstract. The Pioneer Venus Large Probe Neutral Mass Spectrometer collected data that apparently, but almost surely misleadingly, indicate the presence of a large amount of methane (1000 - 6000 ppm) in the atmosphere of Venus from 60 km to the surface. The measured ratio of CH₃D to CH₄ was about 5×10^{-3} . The ratio for Venus methane equilibrated with water would have been 9×10^{-2} and for terrestrial methane 6×10^{-4} . Transfer of deuterium from atmospheric HDO to poorly deuterated methane can account for the strange gradient in the water vapor mixing ratio below 10 km previously reported. Similar deuterium transfer within the mass spectrometer causes reduction in the apparent ratio of HDO to H₂O. A full accounting for the deuterium atoms increases the ratio from 100 to 157 times terrestrial. This, in turn, leads to a revised value of 28 ppm, constant with altitude below 25 km, for the mixing ratio of water vapor. Terrestrial methane mixed with ¹³⁶Xe was introduced into the instrument for technical reasons and is the logical candidate for the source. But the methane detected, unlike ¹³⁶Xe, closely mimics the behavior of an atmospheric gas. Despite this and the strange D/H ratio, the arguments against this methane being purely atmospheric are overwhelming. A preferable, but not provable, explanation is that it was generated by a reaction between an unidentified highly deuterated atmospheric constituent and a poorly deuterated instrumental contaminant.

The Observations

The Pioneer Venus Large Probe Neutral Mass Spectrometer (LNMS) sampled 236 discrete mass settings between 1 and 208 amu instead of scanning continuously through the spectrum. In the device CO₂ and other active gases were pumped by a chemical getter, while inert gases like Ar and CH₄ follow a different flow path to a sputter ion pump. The instrument was designed to operate at constant ion source pressure by control of the pumping speed of CO₂ and sequencing of the inlet leaks. Consequently, the instrumental response is not proportional to the external pressure, and the altitude profiles for CO₂ and well mixed gases like Ar are very different. These instrumental issues are fully addressed by Hoffman et al. [1980a, 1980b]. The procedure for controlling precisely the setting of the discrete mass channels involved releasing methane and ¹³⁶Xe inside the instrument. These gases were transported from Earth in the same container and flowed out from it through the same

plumbing into the LNMS. In the forms of ¹³⁶Xe⁺, ¹³⁶Xe⁺⁺, CH₄⁺, CH₃⁺, H⁺, H₂⁺, and H₃⁺, products of these marker gases were monitored at a large number of mass settings. Because of this deliberate contamination of the LNMS with terrestrial CH₄ and its products, we refrained for a long time from attempting to extract information about methane and hydrogen as constituents of the atmosphere of Venus from the data. Eventually, however, in the hope of explaining the mysterious hydrogen deficit in the water vapor profile below 10 km found by the LNMS [Donahue and Hodges, 1992], we decided to examine carefully the 15, 16, 17, 2 and 3 amu data. When we did so we found (Figure 1) that, although the ¹³⁶Xe count rate remained stable within the expected range of variation throughout the descent, as it always had during pre-flight and post-flight laboratory simulations, the count rates for CH₄ and all its progeny jumped by about 30 percent as soon as the two entrance leaks to the LNMS were opened. They then increased steadily as the probe descended, except for a sharp drop at the time the inlet leaks were plugged by sulfuric acid droplets at 51 km. The counting rates for CH₄ and related species remained at a level of about 35 times that of the well mixed gas ³⁶Ar down to 50 km. The higher conductance microleak was valved off at 47 km. The rates increased after the remaining leak opened at 26 km to about 210 times mass 36 near 12 km and then decreased to about 100 times ³⁶Ar at 0.9 km, where the last full data set was acquired. The mixing ratio of ³⁶Ar measured by the LNMS was $30 \pm \frac{20}{10}$ ppm. On the basis of a relative instrument sensitivity of 0.93 ± 0.1 for methane and

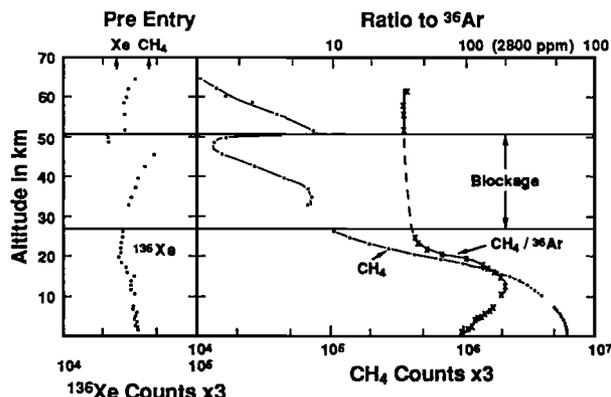


Fig. 1 CH₄ and ¹³⁶Xe counts per data frame multiplied by 3. The preentry CH₄ count rate, corrected for the variation in calibration gas background exhibited by ¹³⁶Xe, has been subtracted. A ratio of 100 to ³⁶Ar translates to a CH₄ mixing ratio of 2800 ppm/v. The increase in ¹³⁶Xe counts near 47 km is related to the discharge of an isotope enrichment cell.

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Paper Number 93GL00513
0094-8534/93/93GL-00513\$03.00

argon the maximum mixing ratio of methane, if it is atmospheric, turns out to be $5900 \pm \frac{400}{200}$ ppm. Above 50 km the mixing ratio was 980 ppm and near the surface 2800 ppm. The excess CH₄ detected by the LNMS behaved like other atmospheric gases, such as CO₂, the noble gases, H₂S, C₂H₂, and C₂H₆, in that their counting rates all abruptly increased when the leaks were opened at 64 km, then increased steadily as the probe descended until the leaks closed at 51 km, whereupon they dropped sharply for several data frames, slowly recovered below 45 km, and recommenced a rapid increase after the leak opened at 26 km (Figure 2).

There were LNMS channels at 17.002 and 17.026 amu. The first of these was sensitive, mainly, to OH, and the signal in it tracked water vapor closely. The second was affected by both ¹³CH₄ (17.032 amu) and CH₃D (17.037 amu). The ratio of the counts in the 17.026 channel to those in the 16.031 (mainly CH₄) channel (Figure 3) was not constant with altitude. Before entry, the ratio was consistent with that expected for a mixture of isotopic species with terrestrial ratios of ¹³C/¹²C and D/H. We have decomposed the signal in the 17.026 channel into the contributions of ¹³CH₄ and ¹²CH₃D, using the ¹³C/¹²C measurement of 1.10×10^{-2} obtained from CO₂ data to determine the ¹³CH₄ portion of the 17.026 amu data; the method is similar to that described by Donahue and Hodges [1992]. This analysis yielded the CH₃D/CH₄ values plotted in Figure 4. The average value of the ratio from the surface to 20 km is $(4.9 \pm 1.5) \times 10^{-3}$, where the uncertainty is almost all due to the procedure of subtracting the ¹³CH₄ contribution to the 17 amu data. Above 20 km the ratio appears to increase to about 8×10^{-3} at 26 km, the altitude at which the sulfuric acid stoppage of the inlet leak was terminated. The terrestrial ratio would be 5.8×10^{-4} ($0.9 \times 2 \times 3.23 \times 10^{-4}$), where 0.9 is a fractionation factor [Fegley and Treiman, 1992] and 3.2×10^{-4} is the ratio of HDO to H₂O. On the basis of a Venus ratio of 5×10^{-2} for HDO and H₂O, as deduced in the next section, the ratio expected for Cytherean methane would be 9×10^{-2} . The measured ratio is neither terrestrial nor Cytherean. Because of low count rates and inaccuracies in the subtraction process the statistics of the ratios obtained above 50 km are very

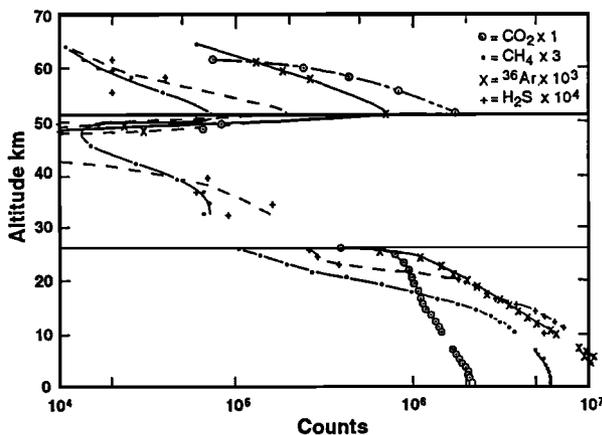


Fig. 2 Counts versus altitude for CH₄ and a number of atmospheric species. One of the two microleaks was closed at about 45 km. This accounts for the apparent discontinuity between count rates before and just after leak blockage.

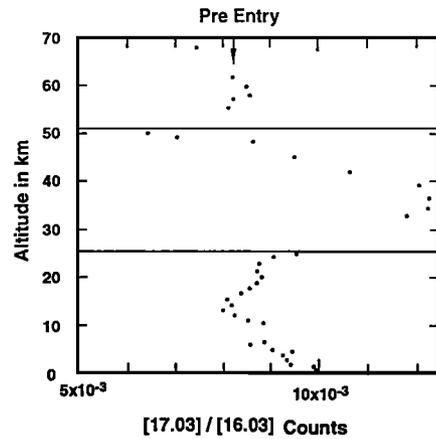


Fig. 3 Ratio of counts in the 17.03 to the counts in the 16.03 amu channel. 17.03 counts are due mainly to CH₃D and ¹³CH₄.

poor. The difference between the measured ratio before entry and the value for terrestrial methane is not statistically significant.

Transfer of D from HDO to CH₄: D/H Revisited

While the microleaks were covered with sulphuric acid droplets between 50.3 km and 26 km the counting rate for CH₄ and CH₃D dropped at first and slowly recovered in the fashion of other atmospheric species. The ratio of CH₃D to CH₄ did not remain constant during this period but rose from about 7×10^{-3} to almost 10^{-2} before dropping again to about 8×10^{-3} just before the leak reopened. The CH₃D counting rate and the CH₄ counting rate multiplied by 7×10^{-3} , are plotted in Figure 5, together with the difference between them. We believe that the "excess" CH₃D counts near 37 km were probably produced by transfer of deuterium atoms to CH₄ from the HDO in the LNMS. These transfer reactions could not have occurred in the gas phase. The partial pressures were too low. If our proposal is correct, the reactions must have occurred on instrumental surfaces, particularly in the getters. The suggestion of a hysteresis effect in the decay of the CH₃D to CH₄ ratio between 25 km

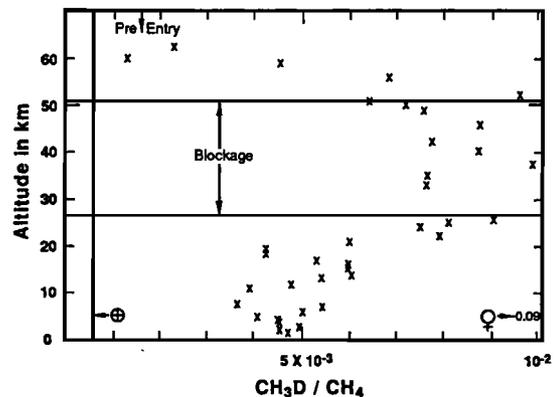


Fig. 4 Data in Fig. 3 with ¹³CH₄ contribution removed and corrected for offset of CH₃D mass from the LNMS 16.03 mass setting. Terrestrial and equilibrium Venus ratios are indicated.

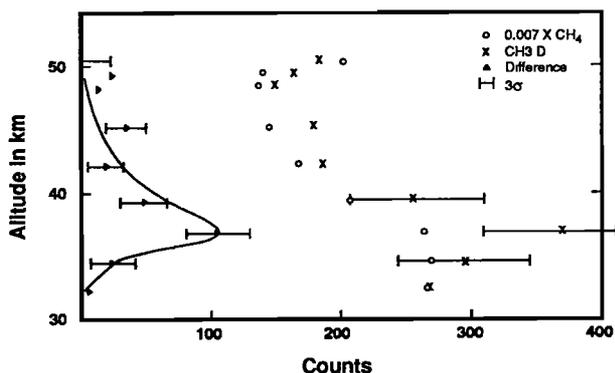


Fig. 5 CH_3D counts and CH_4 counts multiplied by 0.007 during leak blockage. Rates are not corrected for preentry levels, thus represent total methane. The difference is attributed to enrichment of CH_3D by HDO in the LNMS.

and 20 km is evidence in favor of this mechanism. If the excess deuterium in CH_3D was derived from HDO , our previous inventory of HDO [Donahue et al., 1982], made while the leak was closed, amounting to 225 ± 30 counts at its maximum, must be increased by 117 ± 70 counts to allow for the deuterium atoms lost by HDO molecules. Since the H_2O count rate was 6800 at that time, our HDO to H_2O ratio for Venus water in sulfuric acid droplets needs to be increased to $(5.0 \pm 1.0) \times 10^{-2}$, 157 times terrestrial, which does not disagree with $(3.8 \pm 1.2) \times 10^{-2}$ obtained by de Bergh et al. [1991].

H_2O Mixing Ratio Revised

In turn this means that the analysis we presented of the H_2O mixing ratio in the Venus atmosphere [Donahue and Hodges, 1992] must be revised downward by a factor of at least 1.5. We have also determined that the relative efficiency for production of H_2O^+ and Ar^+ ions should be corrected from 3.1 [Lampe et al., 1957] to 1.6 [Rapp and Golden, 1965; Orient and Srivastava, 1987]. This reduces the mixing ratio of water vapor measured by the LNMS from 67 ppm to 28 ± 5 ppm/v. This result agrees with the recent analysis of a near IR spectrum [Pollack et al., 1992] which yields a mixing ratio of 30 ppm below the clouds.

The transfer of deuterium atoms from HDO to CH_4 that apparently occurred in the LNMS while the leaks were closed suggests that the same phenomenon could account for the deficiency in deuterated water detected by the mass spectrometer that we have interpreted as a decrease in H_2O mixing ratio between 10 km and the surface [Donahue and Hodges, 1992]. This finding was based on the assumption that the D/H ratio in HDO and H_2O detected by the LNMS remained constant with altitude and equal to the ratio in the ambient atmosphere. If 425 HDO molecules out of a total of 705 had exchanged deuterium for hydrogen with methane molecules at 0.9 km and a progressively smaller fraction up to 10 km, the gradient in HDO would be accounted for. This requires an increase in the counting rate of CH_3D near the surface of only 365 counts in 10000, too small to be detectable. We suggest that this is what happened. The transfer could have occurred within the LNMS as well as outside it in the atmosphere -- given the evidence of transfer

inside the LNMS that took place near 40 km. Hence this proposed solution for the water vapor gradient problem does not depend on an actual encounter of the probe with deuterium-poor atmospheric methane.

We have found evidence for similar transfer of deuterium from deuterated hydrogen compounds in the case of hydrogen sulfide and ethane, both of which seem to be well mixed in the lowest 20 km of the atmosphere. In Figure 6, for example, the counting rate for H_2S is compared with that expected if its mixing ratio is 3 ppm. It appears that the mixing ratio is constant to about 20 km where the H_2S begins to disappear. Above 50 km its mixing ratio is only about 0.5 ppm. The counting rate for HDS is 5×10^{-2} that of H_2S down to about 15 km. Below 10 km it decreases to about 1.5×10^{-2} times the H_2S rate in a fashion quite like that of the decrease suggested for the $\text{HDO}/\text{H}_2\text{O}$ ratio. We note that these data confirm, not only the postulated transfer of deuterium to methane, but also the D/H ratio of 2.5×10^{-2} for Venus hydrogen, albeit with very poor statistics.

Discussion

The methane observations have presented us with a puzzle for which we can offer no convincing solution. Methane cannot be a stable atmospheric constituent with no exo-atmospheric source. Irreversible oxidation at high altitude with surely occur. Gas phase reactions in the lower atmosphere will limit its lifetime to ten years if

$$kn \geq 2.5 \times 10^{-9} \text{ s}^{-1},$$

where k is a two body rate constant and n is the density of a reaction partner. This condition would be satisfied by $k \geq 2.5 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$ if the reactant mixing ratio is only 1 ppt/v. If k is $10^{-13} \text{ cm}^3 \text{ s}^{-1}$ the reactant mixing ratio can be as low as 3×10^{-17} . In our data we find evidence for ^{35}Cl and ^{37}Cl , with mixing ratios of 1.3×10^{-7} and 3.3×10^{-8} respectively, both well mixed below 25 km. Cl efficiently transforms CH_4 to CH_3 . Of course this chlorine may be produced in the ion source from HCl , for example. Unfortunately, HCl at 36 and 38 amu is hopelessly masked in the LNMS data by the argon isotopes.

Furthermore, there is a disabling constraint imposed by the requirement that the high D/H ratio of Venus water be stable

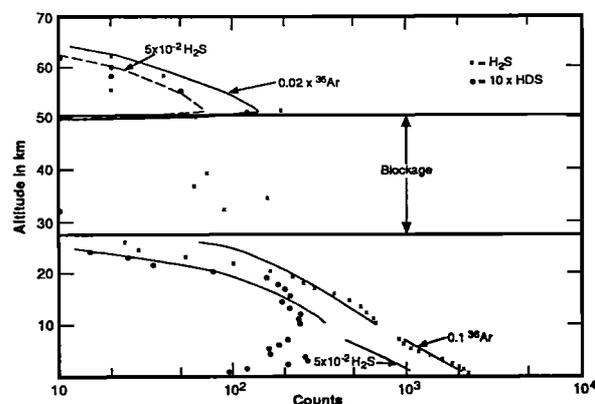


Fig. 6 Rates for H_2S and HDS compared to 0.1 times the ^{36}Ar rate and 5×10^{-2} H_2S rate respectively.

in the presence of such a large amount of deuterium poor methane. We know that the D/H ratio did not change in the decade after the entry of the PV probe [de Bergh et al., 1991]. If the methane detected was atmospheric, its contributions to the atomic hydrogen inventory would have been 2.4×10^{25} atoms cm^{-2} . There are only 8.3×10^{22} H atoms cm^{-2} in Venus water, if the mixing ratio of water is 30 ppm. Only if the methane had been confined to a region covering less than 3.8×10^{-4} of the surface of Venus ($4^\circ \times 4^\circ$) would transfer of deuterium from HDO to CH_4 have reduced the D/H ratio in Venus water less than 10%. Even though winds would transform such a methane plume into a continuous zonal band at high altitude in a short time, hitting such a plume and keeping the probe inside it from 60 km to the surface would be stunningly fortuitous. Furthermore, given that hydrogen escapes from the atmosphere with a flux of the order of $10^7 \text{ cm}^{-2} \text{ s}^{-1}$, 30 million years would be required to rid the atmosphere of the hydrogen in one such injection.

Given that atmospheric methane cannot be the explanation the problem is to account for the strange D/H ratio, the sudden increase in signal when the inlet leaks were opened, the decrease when they were sealed by sulfuric acid, and the large increase below 25 km, all so very different from the behavior of the other marker gas ^{136}Xe . A suggestion more attractive than atmospheric methane is that we were observing methane generated by a reaction between a high D/H atmospheric constituent and a low D/H instrumental contaminant. Such a reaction could produce CH_4 with a deuterium-hydrogen ratio intermediate between the Venus and terrestrial value. Unfortunately, we have no good candidate for the atmospheric constituent. None turned up at the 236 mass settings of the mass spectrometer, but possibly we jumped over the appropriate mass channel. Methane generating reactions that are not anaerobic and biological are not in standard catalogues of reactions. This interpretation, has the feature that it, unlike the one involving atmospheric methane, cannot be so completely discounted at this time and could be tested. But Occam's razor requires that a purely instrumental explanation exist. In the hope that it will eventually emerge, we feel obliged to publish these observations.

In any event, the positive consequences of this study are several. We have been able to offer an explanation for the puzzling apparent gradient in the mixing ratio of water vapor below 10 km to revise upward the deuterium - hydrogen ratio of Venus water vapor from 100 to 157 times terrestrial and to reduce our value for the mixing ratio of water vapor to 28 ppm, constant with altitude from 25 km to the surface. A D/H ratio as large as reported here it can be attained in a steady state only if D/H in the source of hydrogen is also large, even if the dominant hydrogen escape mechanisms discriminate strongly against deuterium. On the other hand, the tendency for Rayleigh fractionation of an ancient water reservoir to result in too large a ratio of D to H [Kumar et al. 1981] becomes a less serious problem, particularly if the escape mechanisms are not strongly fractionating.

Acknowledgements. We thank Mike Mumma for asking a revealing question, Don Hunten for a rigorous critique of our drafts and John Barker for chemical insights. This research was supported in part by grants from NASA.

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(Received: November 10, 1992

Revised: January 13, 1993

Accepted: February 23, 1993)