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ANALYSIS OF DATA FROM THE PIONEER VENUS SOUNDER PROBE MASS SPECTROMETER

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On December 9, 1978, the Pioneer Venus Sounder Probe carried to Venus a neutral gas mass spectrometer that measured the composition of the lower atmosphere of the planet from 62 km to the surface. Fifty one mass spectra were obtained with an average altitude resolution of approximately 1 km. The instrument measured the composition of the gases relative to CO_2, the dominant gas, that it sampled from the Venus atmosphere through a special leak. The mass range extended from 1 to 208 amu with a sensitivity of the order of 1 ppm relative to CO_2, but for the noble gases nearly 100 times better. A description of the instrument can be found in Hoffman, et al. (1979a, 1980a).

Initial results have been published in Hoffman, et al. (1979b, c). These were brief papers in Science that represented a first look at the data. A more detailed paper was prepared for the Journal of Geophysical Research as part of an extensive Venus issue published in December 1980 (Hoffman, et al. 1980b).

The data confirm that the major constituents of the lower atmosphere of Venus are CO_2 and N_2, with the latter having a mass abundance of about 3%. The data allow the order of up to 1000 ppm of water vapor, and 500 ppm of SO_2 and COS below the clouds, but lower bounds for the abundances of these compounds cannot be established because they appeared in large amounts as lingering products of the reaction of cloud droplets deposited on the gas inlet leak to the mass spectrometer. The presence of several minor constituents on Venus is more certain. Of particular significance is the discovery that there is a hundred-fold excess of nonradiogenic argon and neon on Venus over terrestrial abundances in addition to a small deficit of radiogenic ^{40}Ar.

The isotopic ratios of carbon, oxygen, and nonradiogenic argon are similar to those on earth. Other minor constituents detected on Venus include helium and ethane, and there is strong, but presently inconclusive, evidence for H_2S. Through laboratory simulation it has been shown that the measured pattern of volatile release during the evaporation of cloud materials blocking the inlet leak correspond to the volatiles produced when a leak is coated with an 85% concentration solution of H_2SO_4 and immersed in a Venus atmosphere simulator.

Another paper in the Journal of Geophysical Research special Venus issue dealt with comparisons of composition results from the 5 direct measurements instruments on the Pioneer Venus Sounder Probe, bus and the Venera 11 and 12 landers. Two gas chromatograph and three mass spectrometer results are compared along with data on SO_2 from the Pioneer Venus UV spectrometer and the Venera spectrophotometer. Data on the chemical composition of the Venus atmosphere from about 700 km to the surface were obtained. In general, reasonable consistency can be found among the results from the seven gas analyzers that encountered Venus in December, 1978. One of the more significant findings is the large excess abundance of primordial gases on Venus. The O_2 abundances below 30 km must be very small since none of the instruments detected O_2 there. In and near the clouds the O_2 mixing ratio may be as much as a few tens of ppm. CO is 20 to 30 ppm. The existence of COS, originally reported to be a major sulfur compound in the lowest part of the atmosphere is doubtful there and its mixing ratio at higher altitudes does not exceed a few ppm. On the other hand, SO_2 may exist below the clouds at a mixing ratio of the order of 100 ppm. In the clouds it is less than 10 ppm. A serious discrepancy in the data still exists for the case of the water vapor abundance. As a result of the cross checks provided by the number and types of instruments flown to Venus, confidence in the validity of these results on its atmospheric composition has progressed to a reasonable degree of certitude.

In the laboratory, tests were run on various gas mixtures with the flight spare mass spectrometer and the Venus atmosphere simulator (VAS), a high pressure-high temperature chamber in which conditions of temperature and pressure representing the Venus atmosphere over the range of altitudes sampled by the flight mass spectrometer can be duplicated. Studies of the instrument sensitivity to the noble gases have been undertaken to verify pre-flight calibrations. In particular, the sensitivity to Kr and Xe was studied. It was found that the flight data on Kr and Xe represent mixing ratios of the order of 47 ppb for Kr and a probable upper limit of 40 ppb for Xe. The isotopic composition of both gases are given in Table I.

TABLE I

ISOTOPIC COMPOSITION OF Kr AND Xe

Isotopic Composition in ppb		Upper Limits in ppb	
$^{80}\mathrm{Kr}$	3.5	$^{128}\mathrm{Xe}$	0.6
$^{82}\mathrm{Kr}$	15	$^{129}\mathrm{Xe}$	8
$^{83}\mathrm{Kr}$	8.7	$^{130}\mathrm{Xe}$	4
$^{84}\mathrm{Kr}$	32	$^{131}\mathrm{Xe}$	14
$^{86}\mathrm{Kr}$	4.2	$^{132}\mathrm{Xe}$	8

$^{134}\mathrm{Xe}$ and $^{136}\mathrm{Xe}$ were used as calibration gases

Counting rates are exceedingly small, in the range of 20/sec for the sum of the Kr isotopes and 10 to 50/sec for the sum of the Xe isotopes. Thus statistical errors are very large, but not so large as to preclude a measurement of the mixing ratio of Kr by a curve fitting process involving the removal of a contaminant related to the mass 78 amu peak (unknown composition, but probably C_6H_6) from the noble gas peaks. Since normal earth atmospheric Xe had been introduced in the instrument prior to flight, a small residual at all of the Xe isotope peak positions could be residual Xe in the instrument's ion pumps. The isotopic pattern follows that of terrestrial Xe. Therefore, the most logical conclusion is that no atmospheric Xe has been detected on Venus and only an upper limit has been determined.

For Kr actual values of the mixing ratios for the isotopes were obtained. These correspond roughly with terrestrial values in that ^{84}Kr is the most abundant.

Istomin, et al. (1980) have reported that the mixing ratio of ^{84}Kr in the atmosphere of Venus is 600 ± 200 ppb by volume. The isotope ratios appear to be terrestrial. It is not possible to reconcile such a result with ours. There is no evidence that the LNMS became insensitive to heavy gases by the time it reached Venus. Its response to the xenon marker gas is evidence to the contrary. It is possible that the krypton detected by the Venera NMS was terrestrial, since the spectrometer had been exposed to krypton and utilized ion sputter pumps. The absence of a high altitude check in the Venera measurements leaves this possibility open and inviting.

Fig. 1 shows the concentration of inert gases in the atmospheres of the terrestrial planets and a C3V chondritic meteorite in units of cc at STP per gram of planetary matter. The small excesses in abundance of Kr and Xe in the atmosphere of Venus compared with that of earth are in striking contrast with the large increases in Ne and Ar. The ratios are 3.5 and less than 30 for Kr and Xe, 43 and 74 for ^{20}Ne and ^{36}Ar. Careful study has further reinforced our conviction (Hoffman, et al., 1979b) that the constituent detected at 36 amu is argon and not some compound such as HCl. These results appear

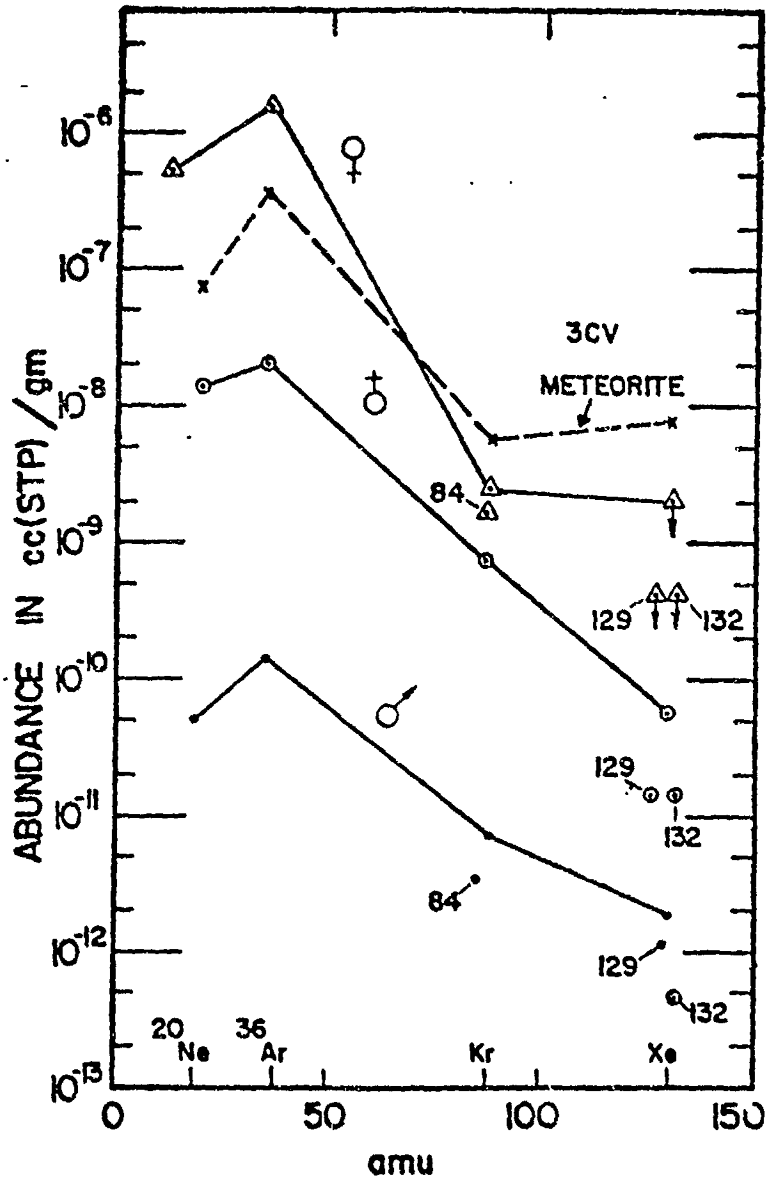

Fig. 1. Abundances of rare gas isotopes on three terrestrial planets and C3V meteorites.

to be fatal for simple models of the acquisition of volatiles by the terrestrial planets. The ratio of ^{36}Ar to ^{84}Kr is 1000 on Venus. Compared to a solar ratio between 2500 and 3710, a terrestrial ratio of 48, a Martian ratio of 32 and a meteorite ratio of about 75, this could be taken to suggest a much larger "solar" component of inert gases in the Venusian atmosphere than on the other planetary bodies of the inner solar system. We might assume that Venus is a planet with the earth's endowment of volatiles to which some process contributed an extra dose of volatiles with abundances in solar proportions and containing 75 times as much ^{36}Ar as in the earth's atmosphere. The ^{36}Ar ratios would perforce be correct if the added inert gases were atmophile. The extra component of any other inert gas on Venus would be equal to 75 times the solar abundance ratio of that gas relative to ^{36}Ar divided by the terrestrial abundance relative to ^{36}Ar. This is between 1 and 1.5 for ^{84}Kr and 1.5-4 for ^{132}Xe. Thus, there could be about 2.5 times as much atmophile ^{84}Kr on Venus as on earth. There may be 5 to 10 times as much xenon in terrestrial shales as there is in the atmosphere. Since the corresponding "planetary" xenon would presumably be atmophile on Venus where the surface temperature is 700K we could expect the atmosphere of Venus to contain 10 to 15 times as much ^{132}Xe as that of the earth.

There is a conspicuous problem in accounting for the behavior of neon. Since the solar ratio of neon to ^{36}Ar is between 20 and 40 and the terrestrial ratio is 0.57, there should be not 43 but almost 5300 times as much neon on Venus as on the earth. In the case of the planetary component of rare gases in meteorites, on the moon and on the terrestrial planets a mass dependent depletion process is supposed to have favored retention of the heavier gases and to account for the neon deficiency. Another mechanism equally effective for neon but less so for the heavier noble gases should be involved in the process that adds the extra "solar" component to Venus. The other volatiles accompanying the rare gases would present no problem. The solar ratios of O, C, and N to ^{36}Ar are about 240, 140 and 35 while the terrestrial ratios are about 2.7×10^6, 1.3×10^6 and 8.6×10^4 where the oxygen is only that associated with outgassed CO_2. Hence, the extra source of volatiles would bring to Venus only a tiny increment of oxygen, carbon and nitrogen. Whatever the final explanation it seems clear that the results presented here constitute a fresh challenge to our understanding of the processes that were involved in the formation and evolution of the terrestrial planets and their atmospheres.

This work has been submitted to Geophysical Research Letters for publication. (Donahue, Hoffman and Hodges, 1981).

A global Monte Carlo model of the exosphere of Venus, simulating the normal exospheric processes as well as the production of a 'hot' hydrogen component by charge exchange of H^+ with H and O, has been made. The resulting altitude profiles of atomic hydrogen concentration over both the day and night hemispheres are in reasonable agreement with Mariner 5 and Mariner 10 observations of Lyman α, showing that the ionospheric charge exchange reactions are a sufficient source of 'hot' hydrogen to be an explanation of the long standing problem of the two-temperature exosphere on Venus.

This work has been submitted to the Journal of Geophysical Research (Hodges and Tinsley, 1981).

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