RE-ANALYSIS OF PHOSPHORUS AND RELATED TRACE SPECIES IN THE LOWER VENUS ATMOSPHERE FROM PIONEER VENUS NEUTRAL MASS SPECTROMETER DATA. W. B. Brinckerhoff[1], X. Li[1], P. R. Mahaffy[1], S. K. Atreya[2]; [1]NASA Goddard Space Flight Center, 8800 Greenbelt Rd., Greenbelt, MD 20771 (william.b.brinckerhoff@nasa.gov), [2]Planetary Science Laboratory, University of Michigan, Ann Arbor, MI 48109 (atreya@umich.edu).

Introduction: Recent remote observations of Venus suggesting the presence of non-equilibrium gas PH_3 in its middle atmosphere [1] have invigorated new interest and debate over the possibility of microbial life in the cloud layers [2,3], and in the production and cycling of the planet's trace atmospheric species generally. Elemental phosphorus was detected *in situ* with the x-ray fluorescence spectrometer on Vega 2 [4] and was interpreted to arise primarily from phosphoric acid H_3PO_4 aerosol droplets in the clouds [5] sourced from surface-derived P and mixed to altitude as phosphate gas such as P_4O_6. Phosphorus has to our knowledge not been reported among the published results from probe missions prior to Vega 2, such as Pioneer Venus (PV) and Venera. We have re-analyzed PV Large Probe Neutral Mass Spectrometer (LNMS) data, only recently made widely available, for the presence of P and related trace species over the altitude range 64.2 km to the surface (final scan at 0.2 km). Within reported LNMS experimental uncertainties, we find evidence of P-bearing species over the altitude ranges from ~60 km to 45 km (potentially consistent with Vega 2) and from ~26 km to the surface. Given the intensities associated with P_xO_y fragments and the shape of their lower-atmosphere altitude profiles, the below-cloud detections are presently best explained by a combination of ambient phosphate gas and desorption of residual phosphoric acid from droplets that may have adhered to the LNMS inlet walls, similarly to the behavior of sulfuric acid [6]. We do not find distinct evidence of PH_3 in these data, although its presence cannot be ruled out based solely on LNMS results. It has been suggested that published data from the scan at 51.3 km [7] are consistent with the presence of PH_3 [8].

PV LNMS Data: LNMS data [7] were obtained in a PDF microfilm image file from the NASA Space Science Data Coordinated Archive (NSSDCA) [9]. Digitized values, extracted via optical character recognition, represented raw detector counts (integers from 0 to more than 10^6) for mass scans over a pre-assigned (hard-coded) set of floating-point mass-to-charge (m/z) values ranging from 1.00 u to 208.02 u, along with the associated scan altitude. Archived m/z values included two decimals (0.01 u precision) whereas the one published scan for the 51.3 km altitude [7,10] contained three-digit masses. The two lists are consistent except for some values that may contain rounding errors. A few scans, recorded at reduced electron ionization energy (22 eV or 30 eV), compared to the nominal 70 eV, were not included in our analyses.

Major Species Recap: To confirm data set integrity, and to normalize values for mixing ratios, we first re-plotted m/z channels associated with known major atmospheric species CO_2 and N_2, as well as the isotope ^{36}Ar which (along with ^{38}Ar) was significantly enhanced, relative to ^{40}Ar, when compared with Earth [6]. Figure 1 shows altitude profiles for corresponding m/z values as follows: {44} (43.99 u), {45} (44.99 u), and {46} (45.99 u) are associated with CO_2 and its main isotopes. The {22} (21.99 'u') and {22.5} (22.50 'u') channels are associated with the 2+ ionization state of {44} and {45}, respectively. Suppression of 2+ ionization which can lead to interferences (e.g., with ^{22}Ne) was achieved with the lower electron energy spectra. The {28} (28.01 u) and {36} (35.97 u and 35.98 u shown) channels are associated with N_2 and ^{36}Ar, respectively. Values are plotted as $\log_{10}$(1+Raw Counts) to show zero counts, with minimal departures from the true log profiles for qualitative behavioral comparison.

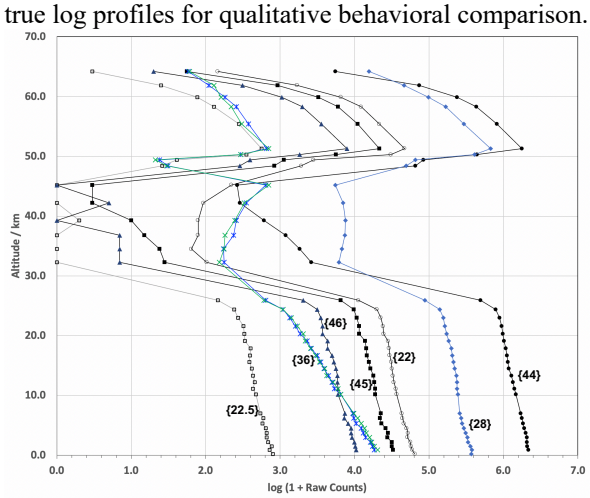

Fig. 1. LNMS raw count altitude profiles of selected m/z channels for CO_2, N_2, and Ar reproduce the reported behavior in the middle (> 50 km) and lowest (< 26 km) atmospheric regions as well as the reductions seen over ~50-26 km resulting from inlet clogging by H_2SO_4 cloud aerosol droplets.

As originally reported [6,10], the common features for these species are expected monotonic increases with decreasing altitude in the regions ~64 km to 50 km and ~26 km to the surface; and dramatic reductions over the range ~50-26 km. This behavior was attributed to the clogging of the two capillary inlets at ~51 km (the larger one was valved off at 47 km) by droplets of H_2SO_4, which is expected to be the dominant aerosol species

forming the low-level clouds. The significant transient increase of ^{36}Ar, and likely the smaller delayed increase of N_2, at 48.4 km to 45.2 km, correspond to pre-timed measurement of the content of the Isotope Ratio Measurement Cell [7] that was captured earlier, shortly after parachute jettison, for enriched noble gas analysis.

Mixing ratios such as N_2/CO_2 and Ar/CO_2 can be determined starting from raw counts, correcting for interfering fragment ($CO \sim N_2$) and background counts, and using the pumping speeds for each species [10]. Isotope ratios of CO_2 can however be estimated from raw counts alone. We find the $^{13}CO_2/^{12}CO_2$ ratio below 26 km of 0.013 ± 0.001 is very close to terrestrial (0.011) as expected, although this does not appear to have been reported as yet from LNMS data.

Phosphorus etc.: We interpret significant signal levels at m/z ~ 31 over much of the descent (Figure 2) as evidence of elemental P fragmented from one or more phosphorus-bearing parent compounds. LNMS recorded scans at two neighboring m/z channels – 30.97 u (corresponding to the 30.974 u exact mass of ^{31}P) and 31.01 u; both are plotted for reference. Assuming the LNMS m/z positions remained well-calibrated during the descent, the value 31.01 u, with its significantly higher signals compared to 30.97 u, then presents somewhat of a puzzle. The mass corresponds best with nitroxyl (HNO, 31.006 u), however as the LNMS data are fixed channel-based rates (not analog scans), at a nominal mass resolution of R = 500 (full-width at tenth maximum), counts at this value could also arise from isotopes of CO, NO, or C_2H_6. As a fragment of CO_2, CO counts are automatically high (up to $2 \cdot 10^5$ based on fragmentation at 70 eV), but its isotopologue $^{13}C^{18}O$ could account for at most ~4 counts of the ~150 count signal at 31.01 u. Similarly, from the levels at m/z ~ 30 shown in Fig. 2, ^{15}NO and $^{13}C^{12}CH_6$ could account for at most ~3 and ~11 counts, respectively. As such we presently assign the higher m/z 31 value as HNO. Given the shape of their altitude profiles (Fig. 2), both NO and HNO may be partly reaction products of instrument-derived H_2O with an ambient nitrogen species, albeit Venusian NO has been independently detected and is associated with lightening discharge chemistry [11].

Unambiguously identifying the parent species of P is nontrivial but we find evidence (Fig. 2) for several molecular fragments such as PO, PO_2, PO_3, HPO_4, and H_2PO_4, the last two being tentative. Notably the m/z ~ 95 channel (for PO_4) was not recorded by LNMS.

Detections and relative count rates at these m/z channels are consistent with phosphoric acid (H_3PO_4), and possibly phosphorus acid (H_3PO_3), expected to form along with H_2SO_4 in the clouds. Below the clouds H_3PO_4 aerosol would dehydrate to phosphates such as P_4O_6. While there is evidence for P_2 in the LNMS data

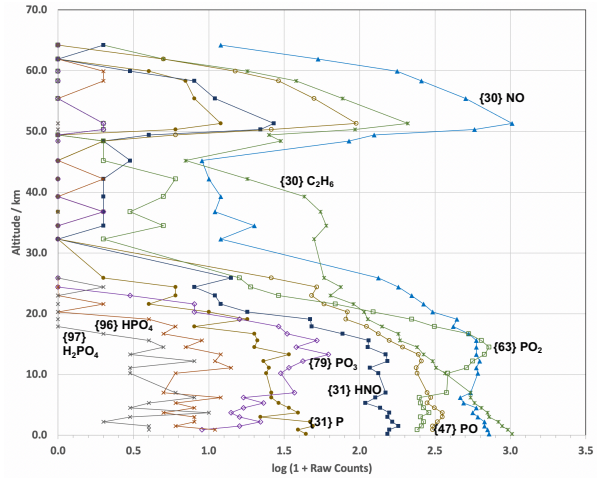

Fig. 2. Altitude profiles for LNMS m/z channels ranging from 30 u to 97 u, showing tentative chemical assignments including evidence of Venusian P- and N-bearing compounds.

(not shown), the lack of higher-m/z signals and the anomalous altitude dependence of P_xO_y masses (similar to sulfur profiles [10]) strongly suggest that residual inlet H_3PO_4 is the dominant contributor below 26 km.

At present we find no distinct evidence for PH_3 within the resolution constraints and limit of detection of LNMS. Among the instrument's three {34} channels (not plotted) – 33.97 u, 33.99 u, and 34.01 u – ranging over 0.04 u or one part in 850, there could be overlapping contributions from the "intended" species ^{34}S (33.968 u), H_2S (33.988 u), and H_2O_2 (34.005), as well as PH_3 (33.997 u). Further analysis including analog peak modeling may help unravel these. All three {34} channels exhibit similar increases with decreasing altitude both from 64.2 km to 51.3 km and again below 26 km, reaching as high as $\sim 2 \cdot 10^3$ counts near the surface. Based on (free-flowing) ^{36}Ar concentrations of 30 ppm, if the ^{31}P signal were entirely from PH_3, the PH_3 mixing ratio would have an upper bound of 250 ppb below 26 km. There does not appear to be any reasonable way to propagate such an estimate to within the clouds themselves. PH_3 is thus only indirectly supported as it would nominally be a minor reaction product of phosphoric/phosphorus acid breakdown.

In Fig. 2 the C_2H_6 profile varies with altitude as a well-mixed atmospheric species as originally reported [10]. Any reduced species such as hydrocarbons should be followed up through further studies and missions.

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