

## Supplemental Methods

### *Isotopic and Isotopologic Ratios*

An isotopic ratio for  $^{13}\text{C}/^{12}\text{C}$  of  $1.22 \times 10^{-2}$  was obtained using  $^{13}\text{CO}_2$  and  $^{12}\text{CO}_2$ , which was consistent with estimates from Hoffman et al ( $1.19 \times 10^{-2} \pm 0.06 \times 10^{-2}$ ) and the terrestrial value ( $1.08 \times 10^{-2}$ ; or 1.07%). Hoffman et al. (1980a) reported a  $^{18}\text{O}/^{16}\text{O}$  ratio of  $2.0 \times 10^{-3} \pm 0.1 \times 10^{-3}$ , which was similar to terrestrial values ( $2.05 \times 10^{-3}$ ; or 0.21%), and was calculated using counts for  $\text{C}^{16}\text{O}_2$  and  $\text{C}^{16}\text{O}^{18}\text{O}$ . By inference, this calculation assumed 100% abundance of  $\text{C}^{16}\text{O}^{18}\text{O}$  at **31.990 amu**, and negated the presence of similar mass gases such as  $\text{NO}_2$  ( $\Delta\text{amu} = 0.002$ ). Under the same assumptions, we obtain a value of  $4.50 \times 10^{-3}$ , which represented either the extreme upper bound in the statistical error for the  $^{18}\text{O}/^{16}\text{O}$  ratio ( $>2$ -sigma from the average) and/or an indication of appreciable  $\text{NO}_2$  abundances at this altitude.

Across  $\text{H}_2\text{O}^+$  and  $^+\text{OH}$ , the calculated  $^{18}\text{O}/^{16}\text{O}$  ratios of  $2.76 \times 10^{-2}$  and  $1.69 \times 10^{-2}$  were  $\sim 4$ -10-fold greater than the value of  $4.50 \times 10^{-3}$  obtained from  $\text{CO}_2$ . This was indicative of significant mixing of an unidentified species with  $\text{H}_2^{18}\text{O}$ , and mixing of  $\text{HDO}$  with  $^{18}\text{OH}$ . Perhaps relatedly, isotopic and isotopologic ratios of  $^{37}\text{Cl}/^{35}\text{Cl}$  ( $6.00 \times 10^{-1}$ ) and  $\text{H}^{37}\text{Cl}/\text{H}^{35}\text{Cl}$  ( $2.16 \times 10^{-1}$ ) were not identical. Similarly, when using atomic species, ratios for  $^{34}\text{S}/^{32}\text{S}$  ( $1.17 \times 10^{-1}$ ; 10.5%),  $^{37}\text{Cl}/^{35}\text{Cl}$  ( $6.00 \times 10^{-1}$ ; 37.5%), and  $^{78}\text{Se}/^{80}\text{Se}$  ( $6.00 \times 10^{-1}$ ; 37.5%) were respectively  $\sim 2.6$ , 1.9, and 2.1-fold higher than terrestrial values ( $2.2 \pm 0.4$ ). These comparisons potentially revealed insights into the statistical error of the counts. Hence, for this analysis, any corrections for isotopic oxygen or sulfur content assumed Earth abundances.

Estimates for  $\text{C}^{16}\text{O}^+$  counts, which was co-mixed with  $\text{N}_2^+$  between **27.988** and **28.012 amu**, were obtained by using the  $^{18}\text{O}/^{16}\text{O}$  ratio ( $2.0 \times 10^{-3}$ ) to back calculate from  $\text{C}^{18}\text{O}^+$ . This calculation negated a potential minimal contribution from  $\text{NO}^+$ . Calculated counts for total  $\text{C}^{16}\text{O}^+$  were then subtracted from the counts at 28.005 amu (671744) to yield adjusted values for  $\text{N}_2^+$  (**Table 1**); this position represented the highest counts across the unresolved region at 28 amu. In turn, maximum counts for  $\text{C}^{16}\text{O}^+$  arising from atmospheric  $\text{CO}$  were estimated using the difference in  $\text{CO}^+/\text{CO}_2^+$  ratios from the fragmentation plots (**Figure 1A**) across the LNMS and NIST data.

### *Organic Contamination*

Unfortunately, we are aware of no technical reports that describe contamination control for the LNMS. Per our understanding (personal communication, R. R. Hodges), components of the LNMS may have been cleaned with trichloroethylene (TCE;  $\text{C}_2\text{HCl}_3$ ) and treated with xylene (possibly as part of vacuum seals). In addition, after assembly, and pre-launch, the LNMS was also possibly subjected to  $\sim 750$  K for an unknown amount of time to

remove residual organics. When at Venus, the LNMS then performed 4 complete sampling and peak-stepping operations in the upper atmosphere before collecting data at ~ 64 km, and then collected 8 full spectra between ~64 and ~53 km. In the mass spectra collected at 51.3 km (**Table S2**), however, the counts and mass values were suggestive of the presence of the TCE parent ion,  $\text{C}_2\text{HCl}_3^+$  ( $\text{M}^+$ ), along with the ions of  $[\text{M}-\text{Cl}]^+$ , and possibly  $[\text{M}-2\text{Cl}]^+$ , including the isotopologues of  $(\text{M}+2)^+$  and  $[(\text{M}+2)-\text{Cl}]^+$ . These same positions, however, were assigned by *Donahue et al.* (1981) as  $^{129}\text{Xe}$ ,  $^{130}\text{Xe}$ ,  $^{131}\text{Xe}$ , and  $^{132}\text{Xe}$  – thus, suggesting that TCE was not an organic contaminant. In the absence of further technical information, we cannot disambiguate the presence of Xe or TCE, nor the contribution from  $\text{Xe}^{2+}$ . In the event of TCE contamination, then the low counts of 5 for the parent ion  $\text{C}_2\text{HCl}_3^+$  were suggestive of TCE being a minor source of atomic chlorine. In support, the NIST reference spectrum indicated a yield of ~10% for atomic chlorine from the parent ion (base peak). In addition, review of the NIST spectra indicated that ethane ( $\text{C}_2\text{H}_6^+$ ) and ethylene (ethene,  $\text{C}_2\text{H}_4^+$ ), which were observed in the data, were not products of TCE fragmentation.

When considering *o*-xylene, *m*-xylene, and *p*-xylene, evaluation of the NIST reference spectra indicated that the benzene and benzyl radical cations were produced in yields of ~10 and 15% of the base peak (tropylium,  $\text{C}_7\text{H}_7^+$ ; 91.054775 amu). In the LNMS data, counts for benzene ( $\text{C}_6\text{H}_6^+$ ) were 16, which implied the presence of a substantially larger base peak from xylene; however, the mass values for tropylium and the parent and  $[\text{M}-\text{H}]^+$  ions were not sampled by the LNMS. In the absence of technical information, again, we are unable to discern between xylene as a parent source or benzene as an atmospheric constituent. However, we posit that residual xylene, if so used, was sufficiently removed by the pre-launch and pre-data acquisition preparations. Therefore, benzene along with ethane, ethene, propyne, and possibly ethyne may potentially be constituents of the atmosphere.