Appendix 3: Suitability of samples as reference materials for SIMS

The original goal of synthesizing the Fe-free glasses was to create reference materials for SIMS analysis, and the utility of reference materials fundamentally depends on sample homogeneity. On a broad scale, agreement within mutual uncertainties between the N concentrations measured by EPMA and laser-extraction mass spectrometry (Fig. 2) demonstrates the general veracity of the EPMA technique we used. On the other hand, the reasons for the discrepancies between these two methods, which are particularly severe for the glasses with lowest low N contents, are unknown.

Having fully degassed the fragments used for laser-extraction measurements, we are no longer able to assess whether there were systematic differences in N content between the glasses used for this technique versus those used for SIMS. One possibility for the discrepancies is that small graphite inclusions may have been missed during handpicking of the glasses used for the laser-extraction measurements. Assuming N solubility in graphite is low compared to the glasses, this could have potentially skewed the measurements at low N concentration relative to the EPMA measurements, which were conducted with a broad beam. Another possibility is that there are non-systematic artifacts in our EPMA data that we have not identified. We view differences in matrix correction algorithms for N (which are not as well developed as those for major elements) as unlikely to be the culprit, because the major element composition of the glasses is relatively constant. Importantly, these issues do not affect our conclusions with regards to the shape of the working curves shown in Fig. 5, because our curve regressions are pinned by the high-N content samples that have the highest reproducibility in N

concentrations via both EPMA (measured directly on the chips used for SIMS) and the laser-extraction method.

Our study sheds no new light on analysis of N in silicates at trace levels (below ~500 μg/g) and it is unclear whether our Fe-free glasses could be used for accurate calibration in this concentration regime. Previous studies on N at trace levels have used ion-implanted reference materials (Li et al. 2013; Regier et al. 2016; Yoshioka et al. 2018). We note that the outlook for low-N analysis is bright, as concentrations as low as 10 μg/g have been reported even when using samples mounted in epoxy (Yoshioka et al. 2018). This suggests that contamination in the vacuum (e.g., owing to outgassing of epoxy) does not represent as much of an impediment to analysis of trace N as it does to H and other volatile elements, which have been best measured on samples mounted in indium. Further details on N analysis at low levels can be found in Regier et al. (2016).