Appendix 2: quantitative EPMA of nitrogen

This document contains more detailed information on our analytical protocol for nitrogen using EPMA. As noted in the main text of the paper, this protocol takes into account known problems with low fluorescence yields, strong curvature of the background on LDE monochromators, and interference between the N Kα peak and higher-order metal lines.

Analyses were obtained on the JEOL JXA-8900 at the University of Minnesota. Conveniently, this microprobe has two spectrometers with LDE1 monochromators that are positioned opposite from each other, facilitating use of aggregate intensities to improve count rates while monitoring artifacts due to sample preparation that would result in inaccurate data. We also acquired simultaneously on our LDE2 crystal on a third spectrometer, but ultimately decided against using its results. Although this monochromator yields much higher count rates for nitrogen relative to LDE1, it has a more pronounced curvature of the continuum in the nitrogen Kα peak region. We felt that the loss in accuracy due to increased reliance on background model was not sufficiently balanced by the increase in precision using a third spectrometer, and opted for the tandem LDE1 approach throughout this study instead.

Our analytical routine is split into multiple steps that take into account differences between unknowns and standard materials with different concentration levels. This helps to avoid dead time and pulse-height shift problems and to optimize individual background models. This approach was made possible by using the advanced options of the Probe for EPMA software.

In detail, each analytical session proceeded with the following steps:

1) Standards and unknowns were coated together in each analytical session.

2) Major elements were acquired at 15 kV and 20 nA on standards and unknowns.

3) Nitrogen was acquired on nitride standards at 10 kV, 50 nA with wide-set background positions (Fig. 1a).

4) Nitrogen was acquired on unknowns at 10 kV, 150 nA with narrowly set background positions (Fig. 1b). The interference with the Fe Lα1 II peak was taken into account (Fig 1c).

5) Exponential background models were applied (Donovan et al. 2011), fitted to previously acquired wavelength scans (Example for silicate glass is shown in Fig. 1b).

6) Major element and nitrogen data were then combined in Probe for EPMA for each analysis point.

7) Nitrogen data were checked to make sure that spectrometers did not deviate from each other outside of their range of analytical precision.

8) Nitrogen intensities from both spectrometers were aggregated.

9) Final data processing used the PROZA matrix correction (Bastin et al. 1998) and FFAST MACs (Chantler et al. 2005)

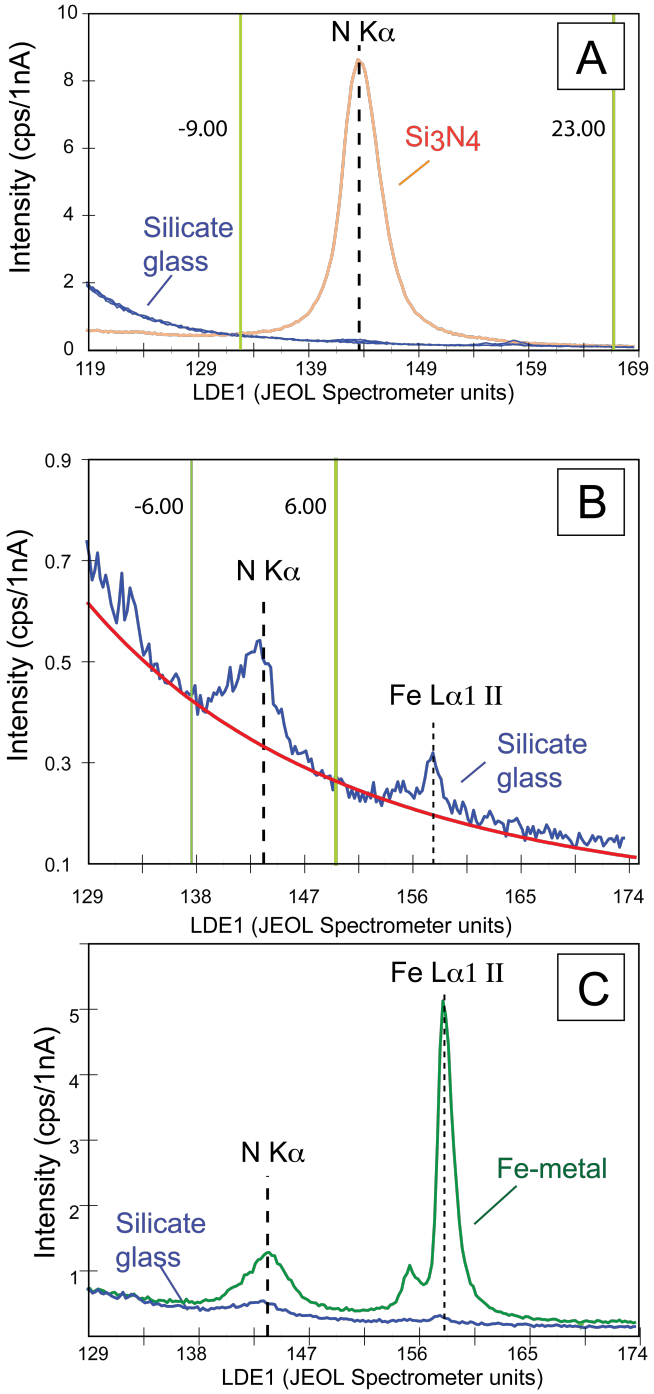

Figure 1: Nitrogen spectra recorded on LDE1 on various materials. Wavescans for glass and metal are on sample B699a from Dalou et al. (2017) (**a)** Comparison of nitrogen spectra of Si_3N_4 and nitrogen-bearing silicate glasses. The background geometry and peak width differs between both materials, necessitating the use of different background positions. **(b)** Detail of background fit for silicate glass. A highly-curved background geometry requires exponential background fits for accurate results. **(c)** Position of higher order metal lines close to the N K-α peak. This interference is present in both materials but especially important in metal analyses.