

Supplemental data for Am Min MS #8362

It is the opinion of the authors that the major impact of our manuscript is the application to large-geometry SIMS labs working on elemental and isotope ratio measurements of light elements. If they choose to use Si^{2+} or Si^{3+} ions for normalization purposes to minimize magnetic field jumps (possibly allowing multi-collection), this *may* lead to unintended matrix effects.

The other attribute of multiply charged ions is their low intensity relative to singly charged silicon ions. The analyst can then increase the primary beam current to remove more trace elements from the sample and increase precision while still allowing the matrix ion to be counted on the same detector as the trace elements and also saving time.

This type of application also requires the same study as in the main manuscript, addressing the question: are there additional effects on the analysis when using multiply charged silicon ions? Note that this supplement only addresses selected lithophile elements sputtered as positive ions using a primary beam of negatively charged oxygen.

The analytical conditions are described in more detail in the full paper. Briefly, the sample is held at a potential of 4925V and positive ions with initial kinetic energies of 75 ± 20 eV are detected (the energy window is set to only allow ions with 5000 ± 20 eV energy to be allowed into the secondary magnet). This is referred to as conventional energy filtering. The same samples were examined: USGS basalt and NIST high-silica glass standards.

The elements (and isotopes) in each analysis included $^{28}\text{Si}^{2+}$ at mass/charge ~ 14 , $^{30}\text{Si}^+$, ^{85}Rb , ^{88}Sr , ^{89}Y , ^{90}Zr , ^{138}Ba , ^{140}Ce , ^{208}Pb , ^{232}Th , and ^{238}U . The results (from an analysis session on 15 August 2019) were not corrected for the abundance of the isotopes and are shown as calibration curves with the trace elements normalized either to $^{30}\text{Si}^+$ or $^{28}\text{Si}^{++}$ in Figures S1-S9. The regressions in each of the figures were forced to the origin, and the ratios of the slopes of these regressions between the basaltic glass and the high-silica glass (similar to Table 2) are given in Table S1. The analyses and uncertainties are from Jochum et al. (2005) and Jochum et al. (2011).

Results

Figures S1 through S6 show similar behavior: Rb, Sr, Y, Zr, Ba, and Ce ions, when normalized to the Si^+ ion (and to the silica abundance in the matrix glass) generate similar calibrations whether sputtered from basaltic or the high-silica, soda-lime glass represented by the NIST 61X materials. If there is a difference in calibration, the NIST glasses show slightly greater slopes in the regressions (all forced through the origin). In contrast selecting the doubly charged silicon ion results in two distinct calibration curves, with the basaltic glasses consistently displaying curves with larger slopes. These results are similar to those presented in the main paper.

Regardless of the normalizing Si ion, the basaltic glasses show a much higher probability of generating a lead ion (Fig. S7), although the difference is greater when the doubly charged silicon ion is used for normalization.

The heavy elements Th and U (Fig. S8 and S9) also show different calibrations from the two matrices, but we observe higher probabilities for forming Th and U ions from the high silica glass when Si^+ is used as a normalizing ion (opposite from lead). Normalizing to Si^{2+} increases the differences.

Discussion

Matrix effects for Rb, Sr, Y, Zr, Ba, and Ce (possibly a proxy for other REE) do not show matrix effects larger than ~10% between basaltic and the NIST high silica compositions as long as the ion signals are normalized to that for Si^+ . The effect is much larger when using Si^{2+} . This is similar to results on Be and B presented in the main part of this contribution.

Heavier elements show larger matrix effects. Using NIST glasses as a standard for Th or U when analyzing basaltic glass would lead to an error of ~25% in their absolute abundances, at least when using conventional energy filtering. The error would increase if Si^{2+} was used.

We note that USGS basaltic glass “D” is well aligned with the other glasses when normalized to Si^+ in Figures S1 through S9. However, this glass (between the lowest and highest abundance glass in the basaltic glass suite) is consistently off the trend set by the low trace element abundance glass “A” and the high trace element abundance glass “E” when the trace signal is normalized to Si^{2+} ions. While we observed a higher than expected intensity for Si^{2+} ions from glass “D” (which resulted in the displacement), we do not have an explanation for this behavior. Instead, we use this result to emphasize that the production of doubly charged reference ions is not completely understood.

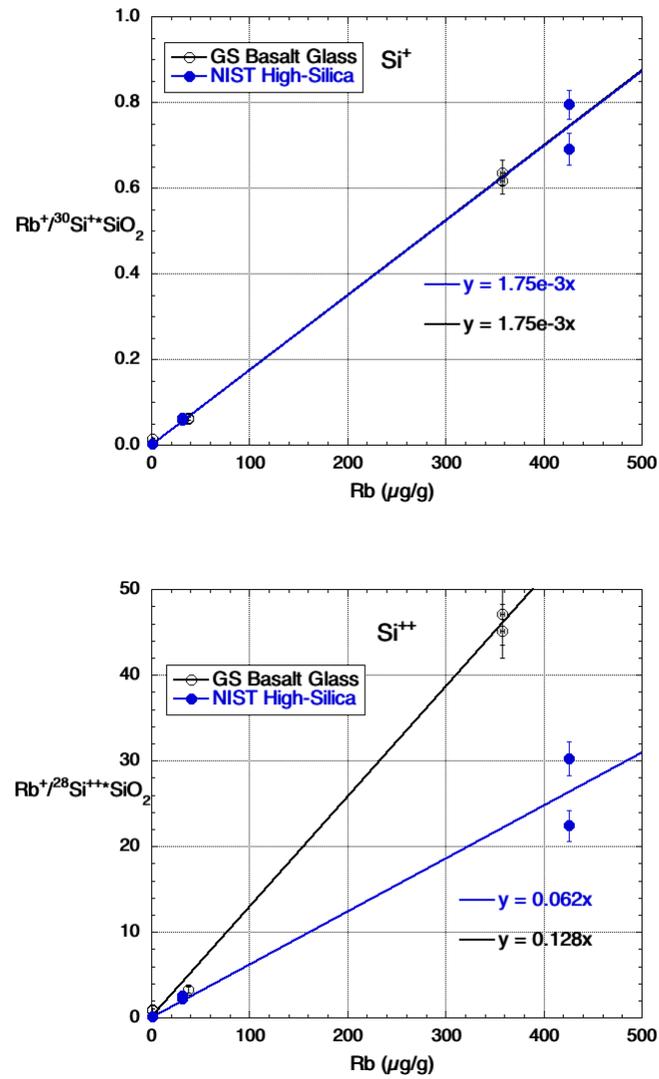


Figure S1. Calibrations for Rb normalized to Si^+ and Si^{2+} .

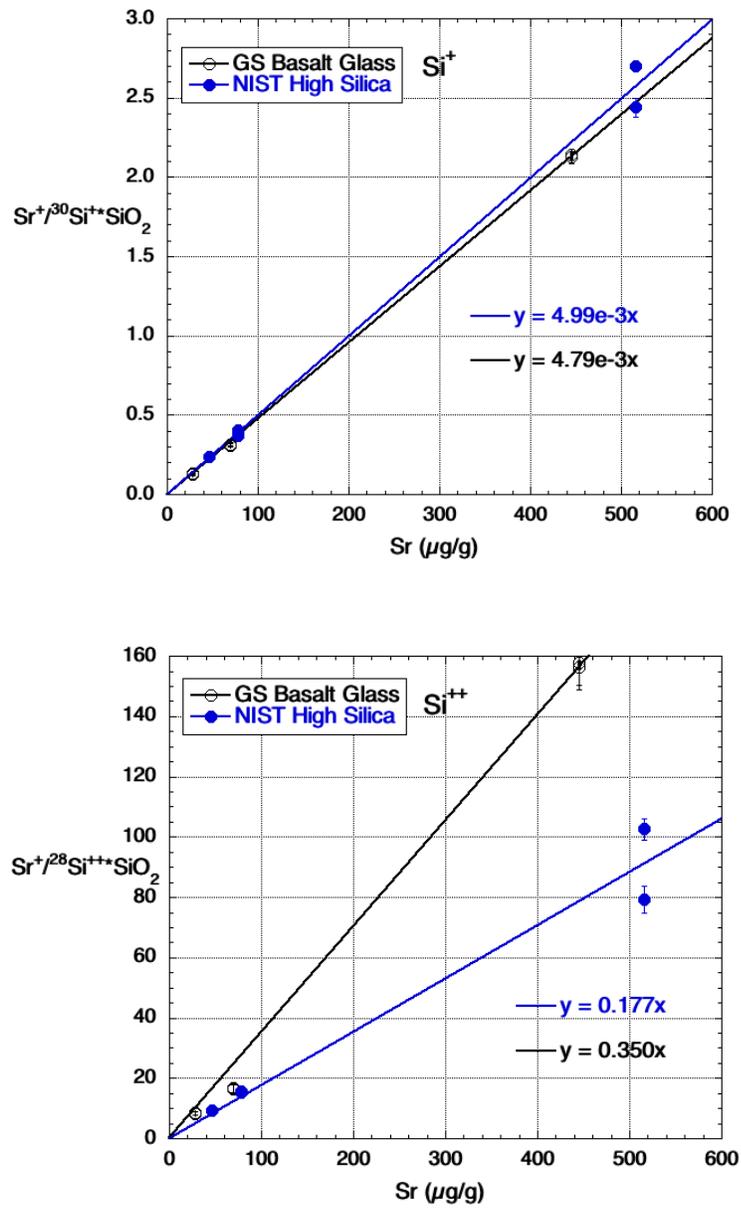


Figure S2. Calibrations for Sr normalized to Si⁺ and Si²⁺.

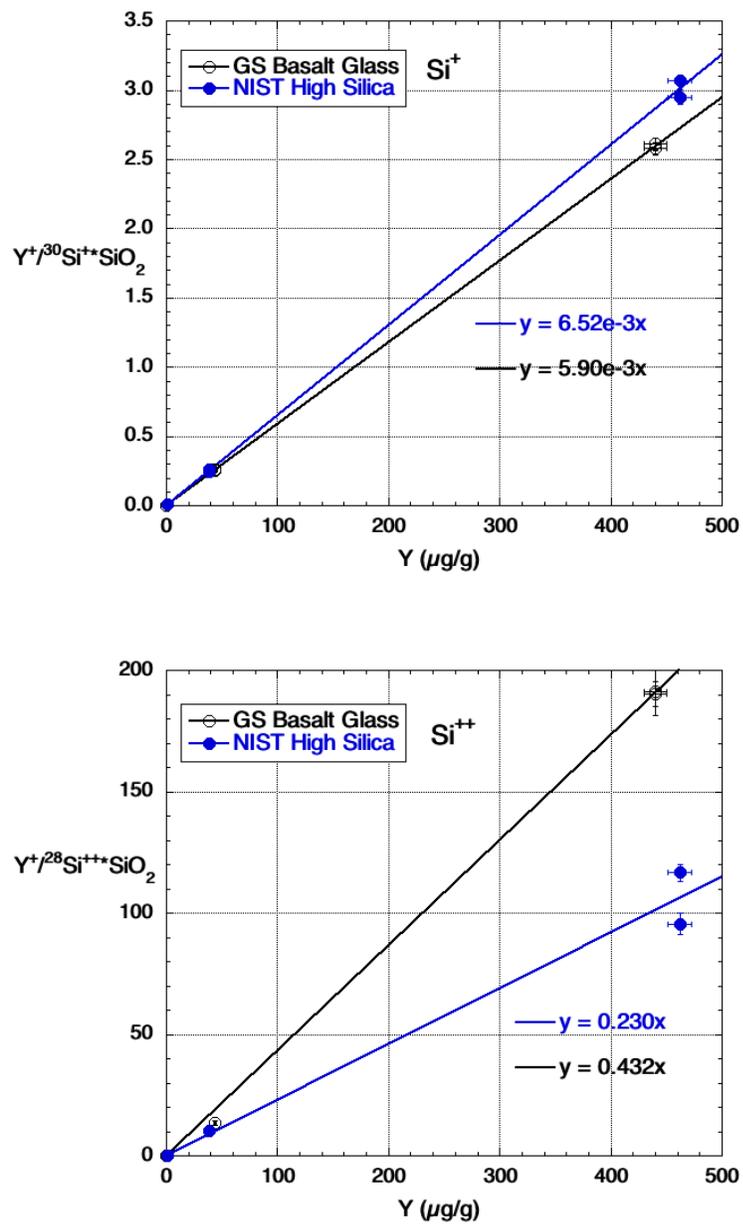


Figure S3. Calibrations for Y normalized to Si⁺ and Si²⁺.

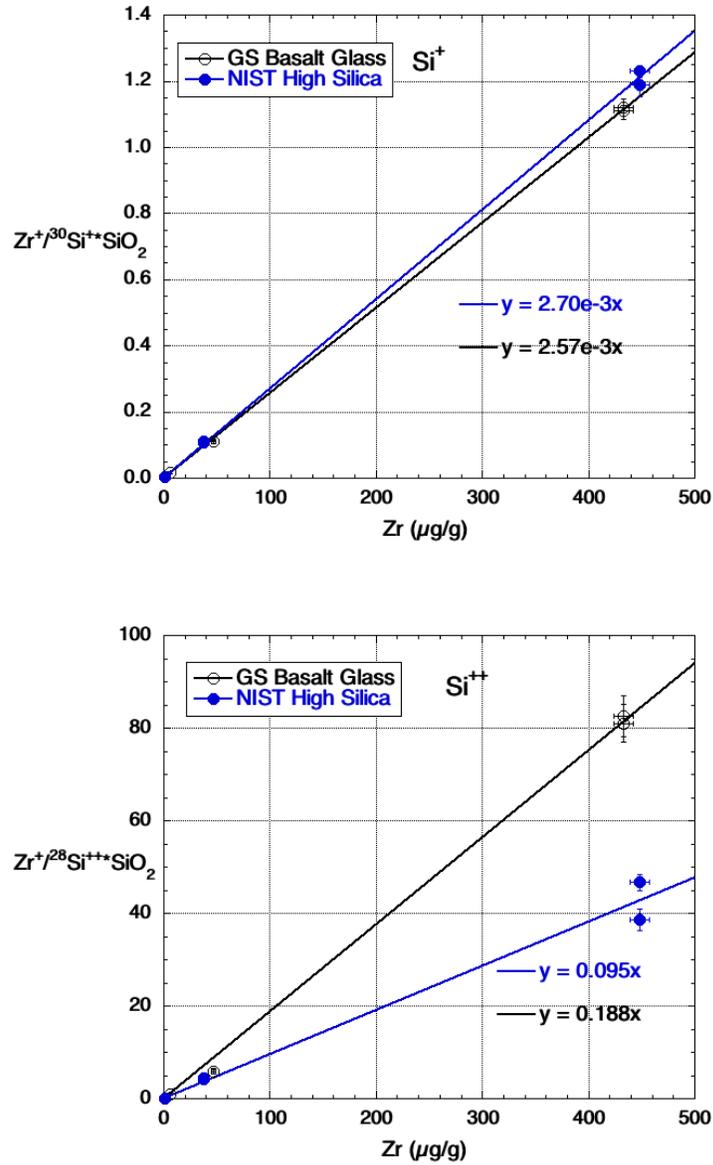


Figure S4. Calibrations for Zr normalized to Si⁺ and Si²⁺.

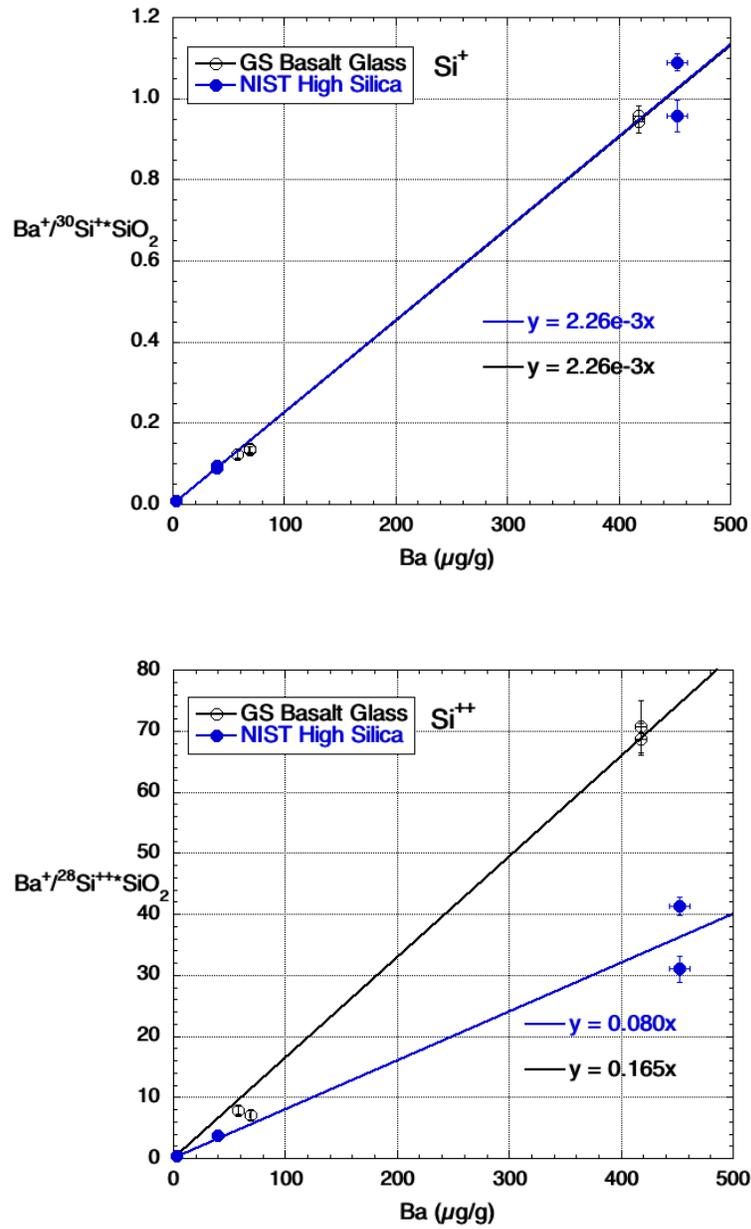


Figure S5. Calibrations for Ba normalized to Si⁺ and Si²⁺.

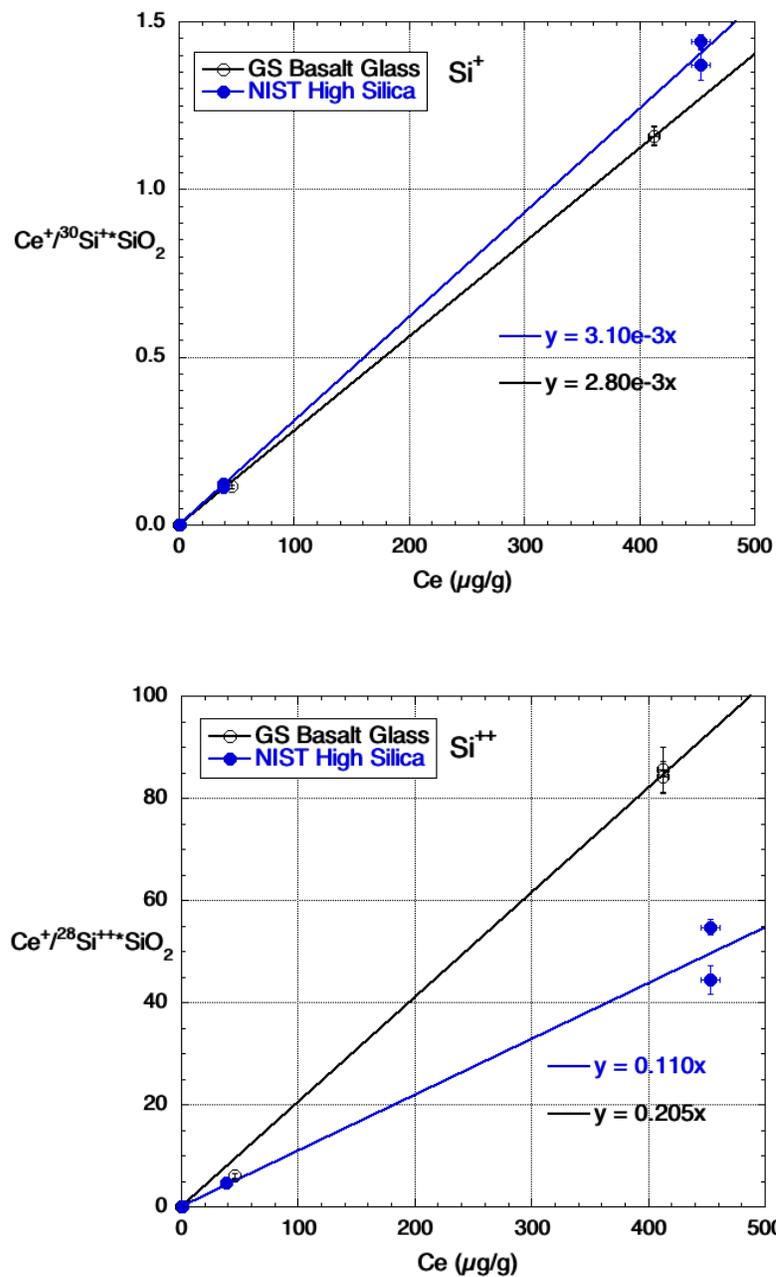


Figure S6. Calibrations for Ce normalized to Si⁺ and Si²⁺.

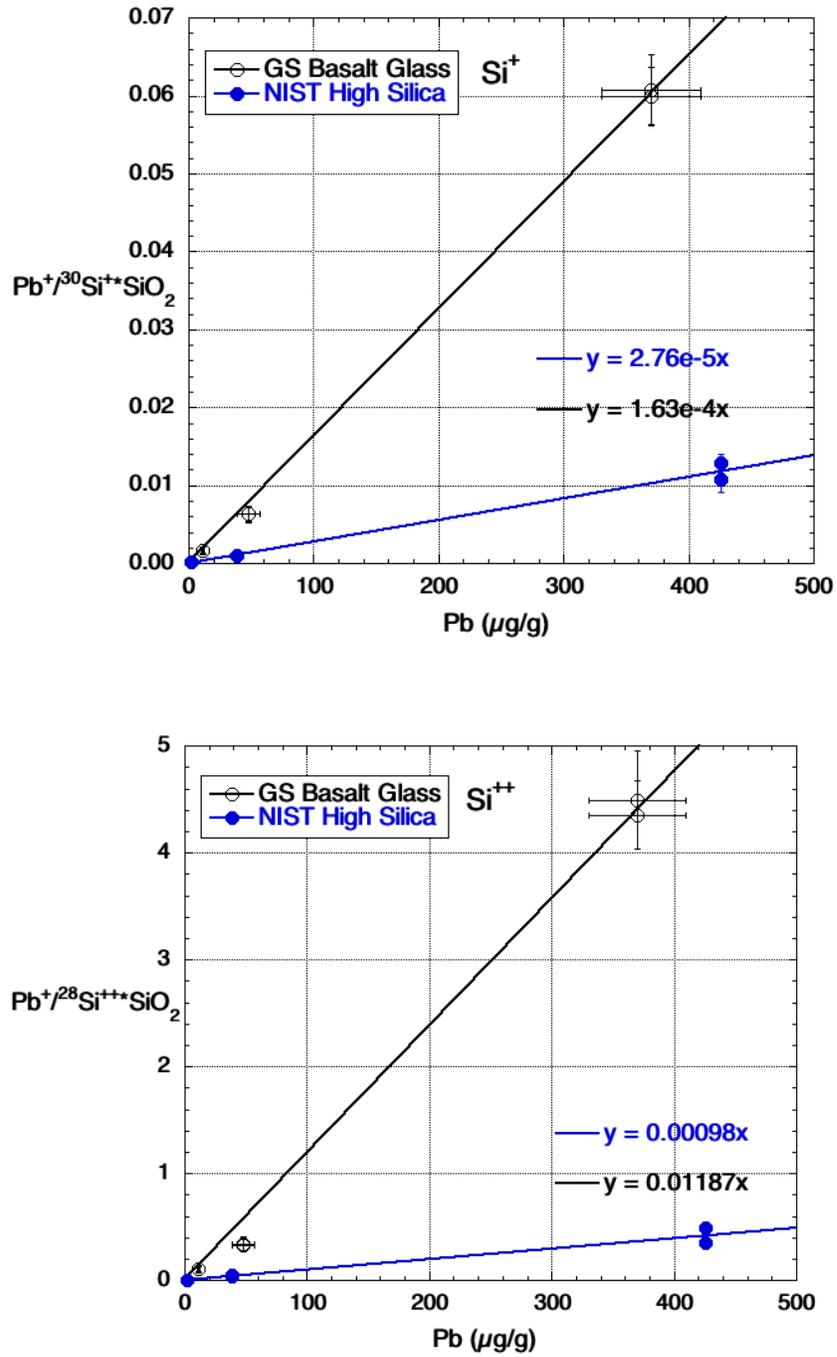


Figure S7. Calibrations for Pb normalized to Si⁺ and Si²⁺.

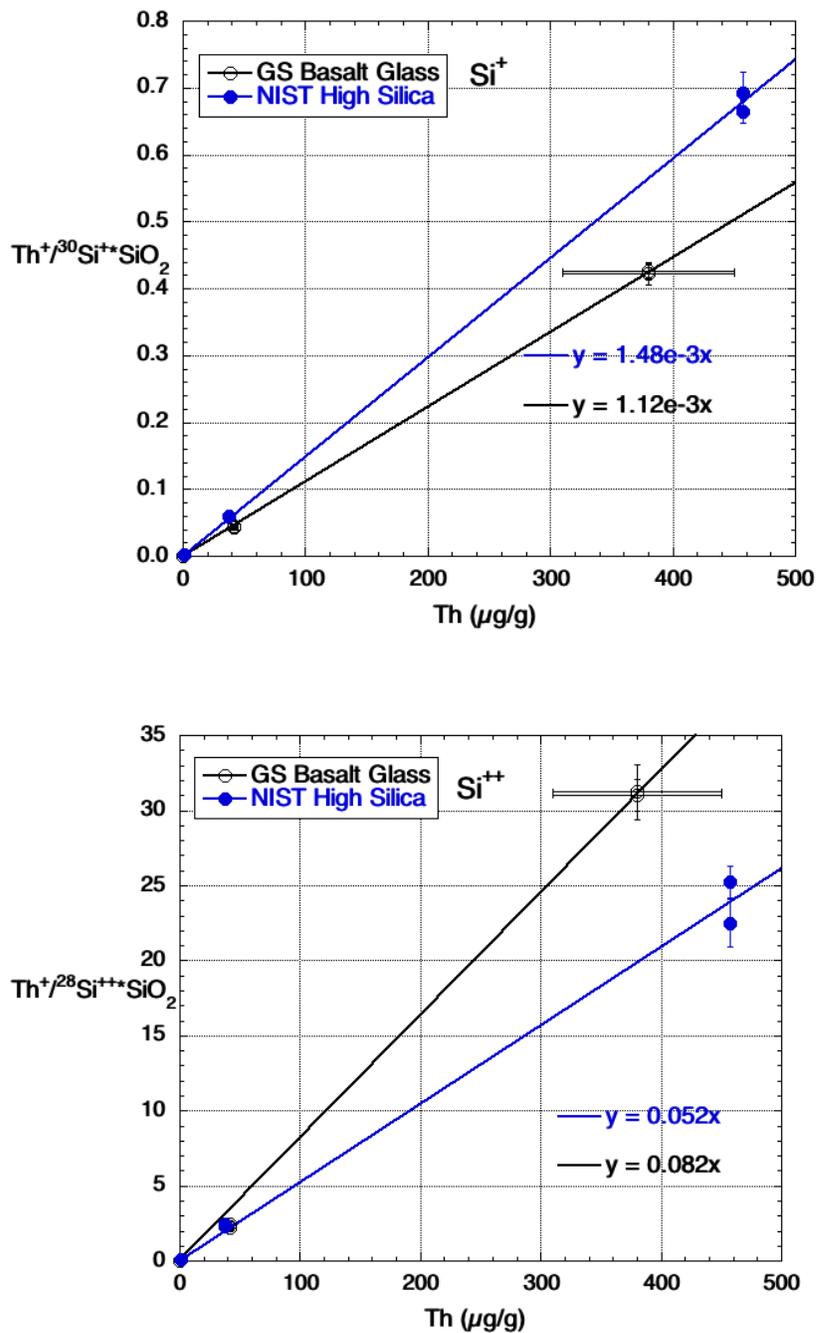


Figure S8. Calibrations for Th normalized to Si⁺ and Si²⁺.

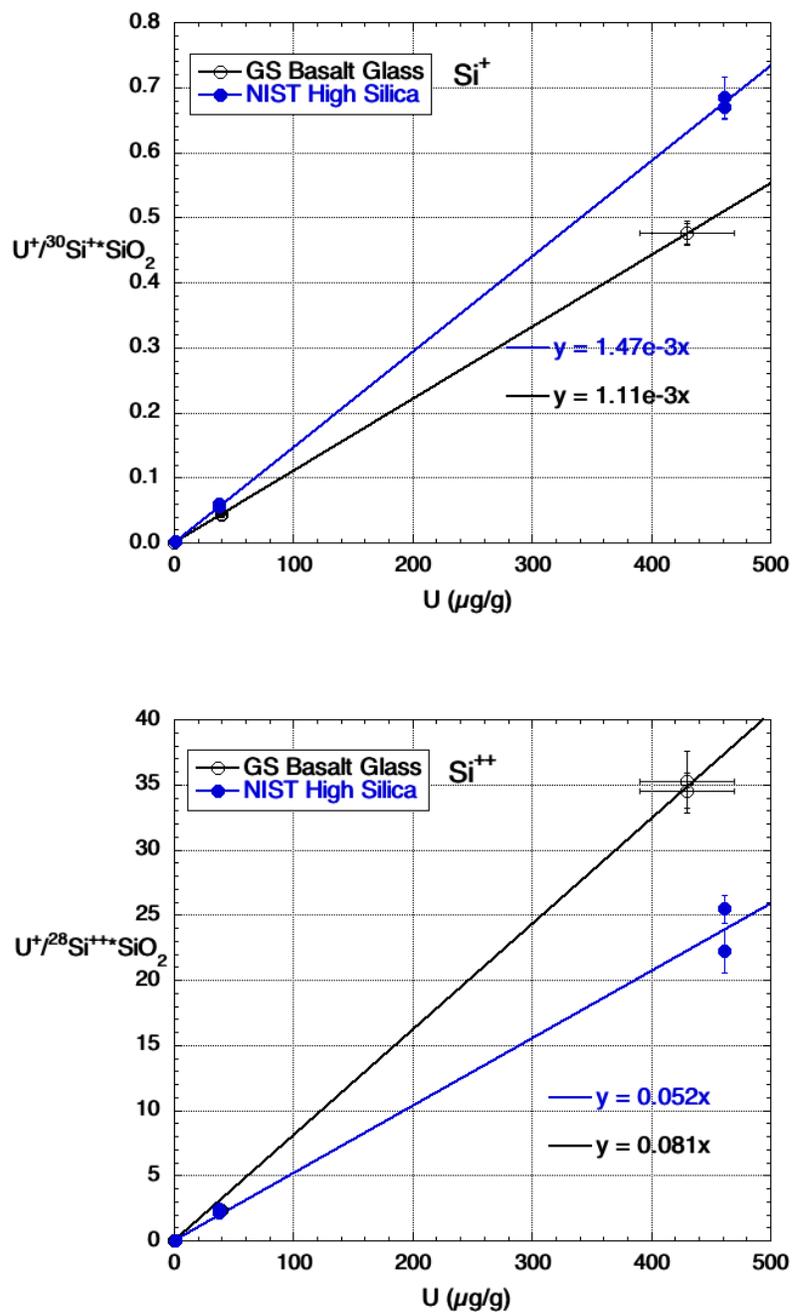


Figure S9. Calibrations for U normalized to Si⁺ and Si²⁺.

Table S1. Relative differences in calibration slopes as shown in Figures S1-S9.

Element	Normalizing Species	
	Si ⁺	Si ²⁺
	Basalt/NIST	Basalt/NIST
Rb	1	2.1
Sr	0.96	2.0
Y	0.90	1.9
Zr	0.95	2.0
Ba	1	2.2
Ce	0.90	1.9
Pb	5.9	12
Th	0.76	1.6
U	0.76	1.6

References

- Jochum, K. P., Willbold, M., Raczek, I., Stoll, B., and Herwig, K. (2005) Chemical characterization of the USGS reference glasses GSA-1G, GSC-1G, GSD-1G, GSE-1G, BCR-2G, BHVO-2G and BIR-1G using EPMA, ID-TIMS, ID-ICP-MS, and LA-ICP-MS. *Geostandards and Geoanalytical Research*, 29, 285-302.
- Jochum, K. P., Weis, U., Stoll, B., Kuzmin, D., Yang, O., Raczek, I., Jacob, D. E., Stracke, A., Birbaum, K., Frick, D. A., Günther, D., and Enzweiler, J. (2011) Determination of reference values for NIST SRM 610–617 glasses following ISO guidelines. *Geostandards and Geoanalytical Research*, 35, 397-429. <https://doi.org/10.1111/j.1751-908X.2011.00120.x>