

Supplementary Information for:

Brimstone Chemistry Under Laser Light Assists Mass Spectrometric Detection and Imaging the Distribution of Arsenic in Minerals

Swapnil Lal,^a Zhaoyu Zhen,^b Julius Pavlov,^b and Athula B. Attygalle^{*b}

^a Montgomery High School, 1016 Co Rd 601, Skillman NJ 08558 (USA)

^b Department of Chemistry and Chemical Biology, Stevens Institute of Technology, Hoboken NJ 07030 (USA)

Table of Contents

| Figure or Table number | Caption | Page |
|------------------------|--|------|
| Figure S1 | Product-ion (MS ²) spectra of m/z 375 for As_5^- recorded at a transfer collision energy of 10 eV (A), and 15 eV (B). Precursor ions were generated from elemental arsenic. | 2 |
| Figure S2 | Plot of percentage relative intensity of m/z 267 (◆), m/z 171 (■), m/z 139 (▲), m/z 107 (✕), and m/z 64 (✕) ions recorded at Transfer-collision energy settings of 2 eV, 5 eV, 10 eV, 15 eV, 20 eV and 30 eV. Transfer collision gas was argon, and Transfer collision cell pressure was 8.72×10^{-3} mbar. | 3 |
| Figure S3 | Product-ion (MS ²) spectra of m/z 139 for $\text{As}^{32}\text{S}_3^-$ recorded at a transfer-collision energy setting of 10 eV (A), and 20 eV (B). The precursor ion was generated from a mixture of elemental arsenic and S. | 4 |
| Figure S4 | A comparison of the MS ² spectrum of m/z 235 ion for $\text{As}^{32}\text{S}_5^-$ (A), with that of the m/z 237 for $\text{As}^{32}\text{S}_4^{34}\text{S}^-$ (B) recorded at a transfer CE 10 eV. The precursor ion was generated from a mixture of arsenic and S. | 5 |
| Figure S5 | Intensity ratio of m/z 171 (AsS_3^-) and m/z 96 (S_3^-) peaks versus amount of arsenic (ng) deposited on the sample plate. | 6 |
| Table S1 | Correlation between deposited amount of arsenic and $I_{m/z\ 171}/I_{m/z\ 96}$ peak intensity ratios. | 6 |
| Figure S6 | Photographic image of the domeykite mineral sample (the rectangular area used for imaging is demarcated with white lines). | 7 |
| Figure S7 | Photographic image of the latent-print-bearing paper attached to a MALDI plate. | 7 |

Table and Figures

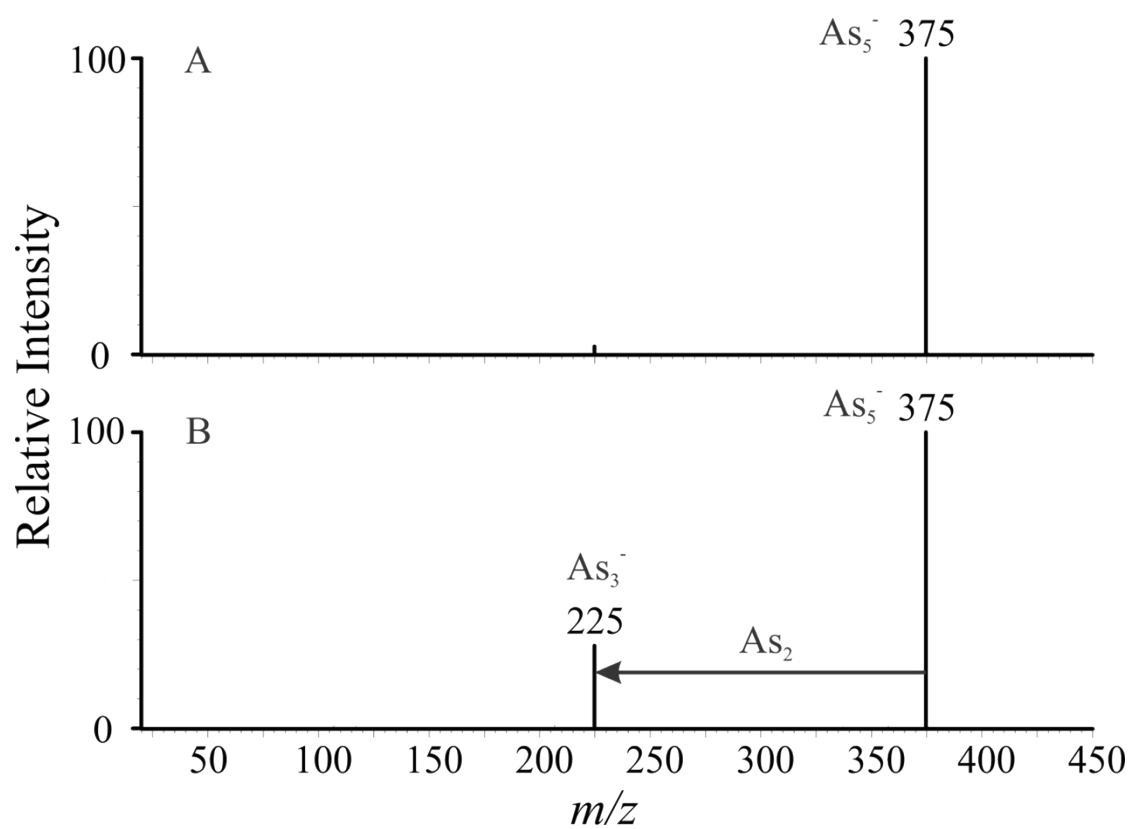


Fig. S1. Product-ion (MS^2) spectra of m/z 375 for As_5^- recorded at a transfer collision energy of 10 eV (A), and 15 eV (B). Precursor ions were generated from elemental arsenic.

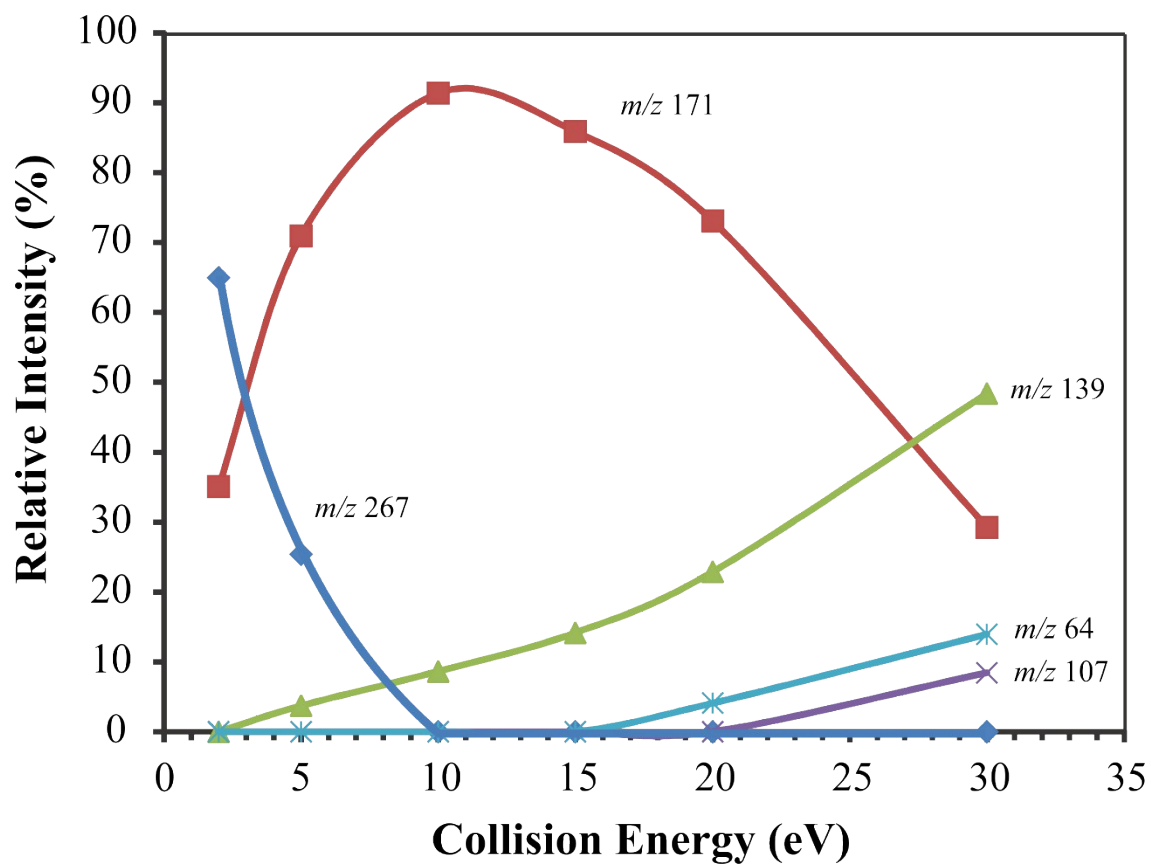


Fig. S2. Plot of percentage relative intensity of m/z 267 (\blacklozenge), m/z 171 (\blacksquare), m/z 139 (\blacktriangle), m/z 107 (\times), and m/z 64 (\ast) ions recorded at Transfer-collision energy settings of 2 eV, 5 eV, 10 eV, 15 eV, 20 eV and 30 eV. Transfer collision gas was argon, and Transfer collision cell pressure was 8.72×10^{-3} mbar.

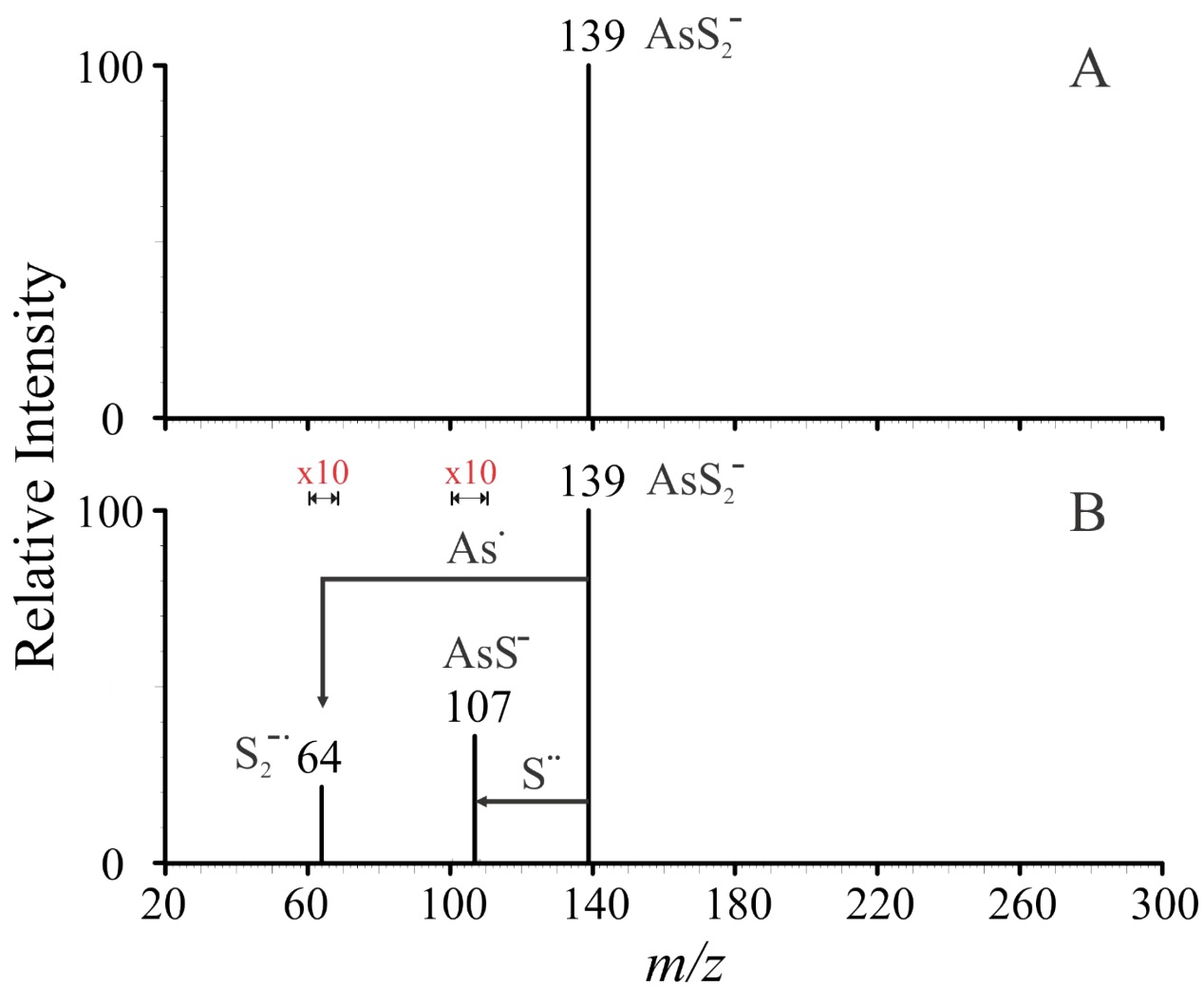


Fig. S3. Product-ion (MS^2) spectra of m/z 139 for $\text{As}^{32}\text{S}_3^-$ recorded at a transfer-collision energy setting of 10 eV (A), and 20 eV (B). The precursor ion was generated from a mixture of elemental arsenic and S.

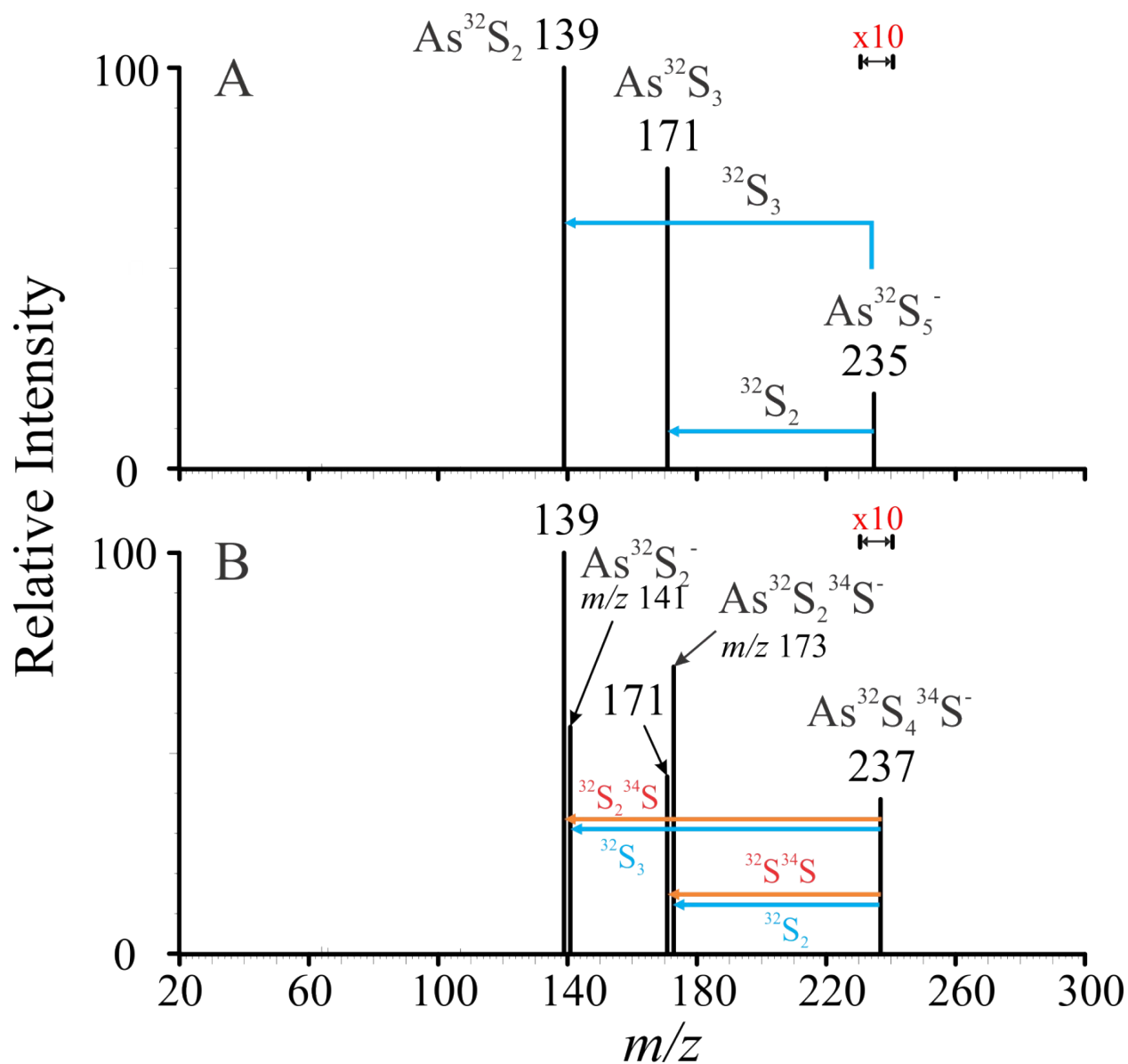


Fig. S4. A comparison of the MS² spectrum of m/z 235 ion for $\text{As}^{32}\text{S}_5^-$ (A), with that of the m/z 237 for $\text{As}^{32}\text{S}_4^{34}\text{S}^-$ (B) recorded at a transfer CE 10 eV. The precursor ion was generated from a mixture of arsenic and S.

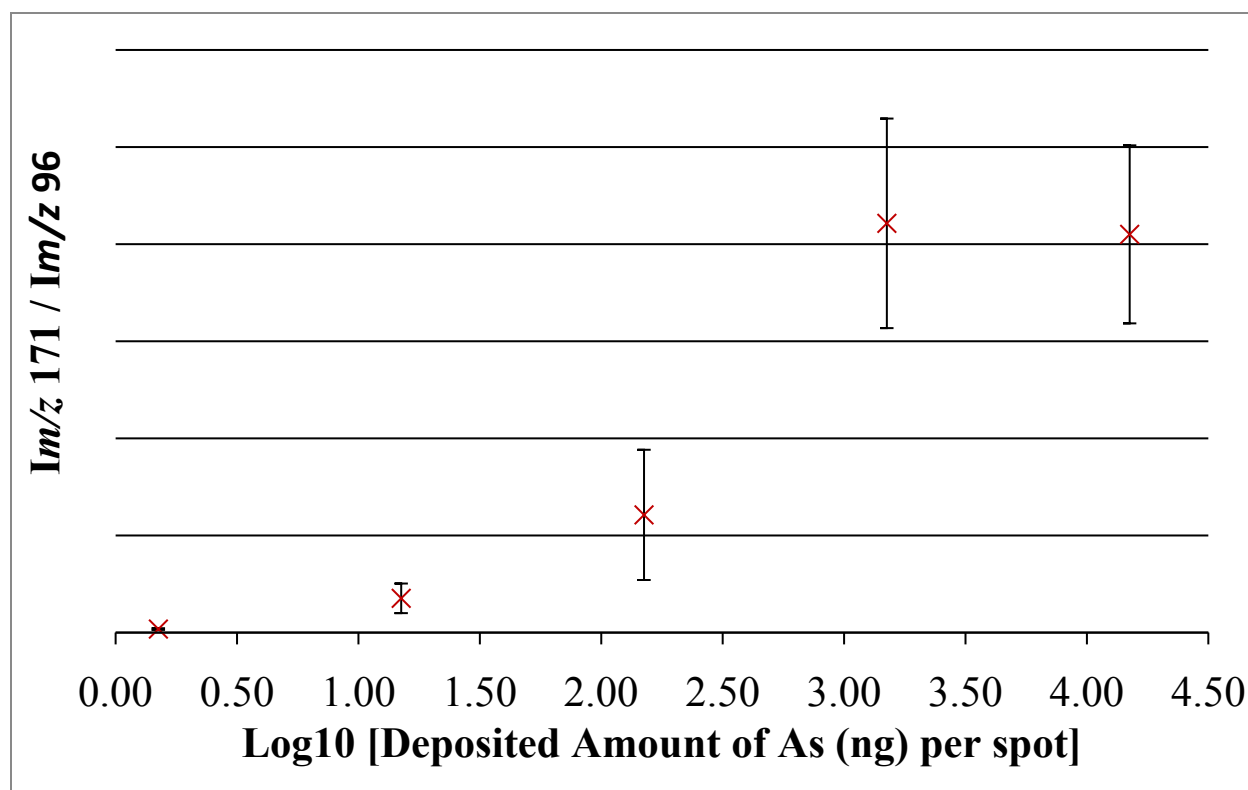


Fig. S5. Intensity ratio of m/z 171 (AsS_3^-) and m/z 96 ($\text{S}_3^{\bullet-}$) peaks versus amount of arsenic (ng) deposited on the sample plate.

Table S1. Correlation between deposited amount of arsenic and $I_{m/z\ 171} / I_{m/z\ 96}$ peak intensity ratios.

| Sample | Conc. of NaAsO_2 (M) | Volume of NaAsO_2 solution deposited (μL) | Amount of As deposited (ng) | Amount of S deposited* (μg) | Observed $I_{m/z\ 171} / I_{m/z\ 96}$ peak intensity ratio |
|--------|-------------------------------|---|-----------------------------|--|--|
| 1 | 1.00×10^{-5} | 2 | 1.5 | 5.16 | 0.04 |
| 2 | 1.00×10^{-4} | 2 | 15 | 5.16 | 0.35 |
| 3 | 1.00×10^{-3} | 2 | 150 | 5.16 | 1.21 |
| 4 | 1.00×10^{-2} | 2 | 1500 | 5.16 | 4.21 |
| 5 | 1.00×10^{-1} | 2 | 15000 | 5.16 | 4.10 |

*The volume of saturated sulfur solution in toluene (1.979 g/ 100 g toluene at 293.15 K; Ren, Y.; Shui, H.; Peng, C.; Liu, H.; Hu, Y., Solubility of elemental sulfur in pure organic solvents and organic solvent–ionic liquid mixtures from 293.15 to 353.15K. *Fluid Phase Equilib.* **2011**, 312, 31-36) added to each spot was 0.3 μL

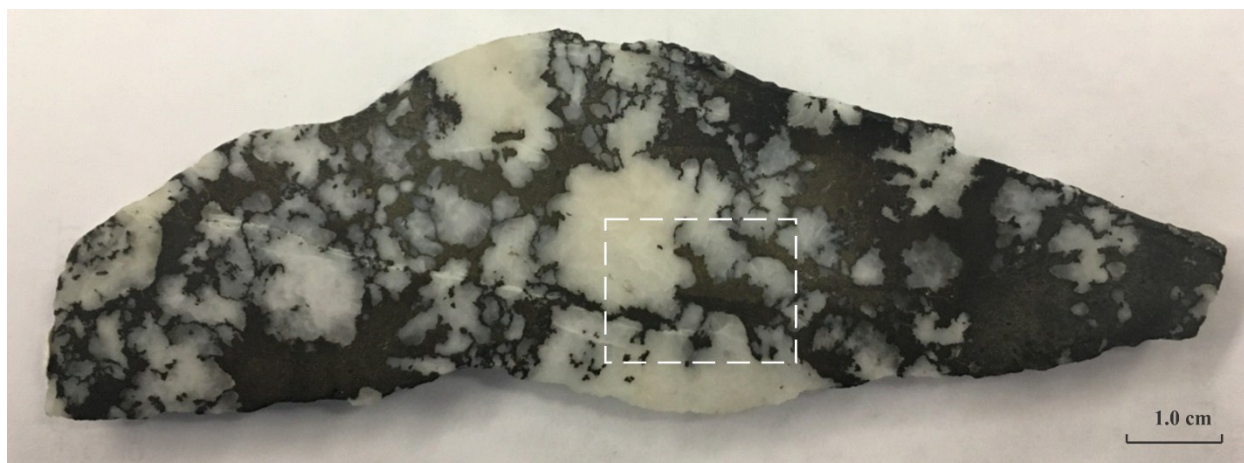


Fig. S6. Photographic image of the domeykite mineral sample (the rectangular area used for imaging is demarcated with white lines).

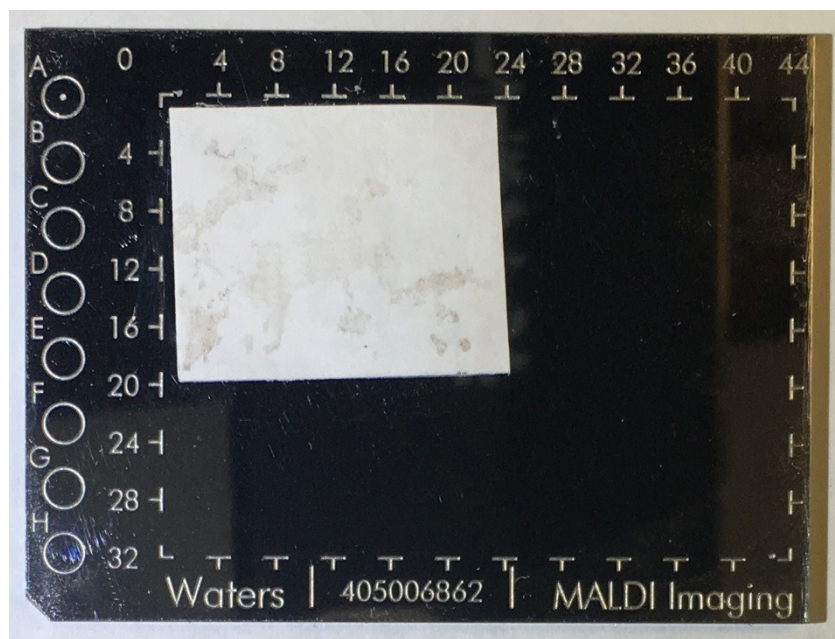


Fig. S7. Photographic image of the latent-print-bearing paper attached to a MALDI plate.