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Imaging isotopic content at the nanoscale using extreme ultraviolet laser ablation and ionization time-of-flight mass spectrometry

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Extreme ultraviolet (EUV) laser ablation and ionization coupled to a mass spectrometer offers unique capabilities to identify and map the chemical composition of solids with unsurpassed three-dimensional nanoscale spatial resolution. We have developed an extreme ultraviolet laser ablation and ionization time-of-flight mass spectrometer (EUV TOF) that uses an EUV laser operating at a wavelength of 46.9 nm (26.4 eV photon energy) [1-3]. The EUV laser beam can be focused down to spots of about 100 nm to ablate and ionize atoms and molecules in the laser-created plasma by single photon ionization [1]. The strong absorption of the 26.4 eV photons in most materials makes it possible to ablate craters that are tens of nanometers deep at fluences of less than 0.5 J/cm² [1]. Previously, we have shown that EUV TOF can analyse trace elements in standard reference materials and can image the isotopic content in uniform materials, both organic and inorganic, with ~80 nm lateral spatial resolution [1-2]. Here, we present results from a recent study that extends EUV TOF's high sensitivity and high spatial imaging capabilities to the analysis of an isotopically non-uniform (heterogeneous) uranium sample at the nanoscale [3]. At the 100 nm spatial scale, we found that EUV TOF reveals more isotopic heterogeneity than previously measured with microscale and bulk mass spectrometry techniques [4]. We also compared EUV TOF results to those obtained on a similar sample at the same spatial scale using nanoscale secondary ionization mass spectrometry (NanoSIMS), the gold standard for isotopic imaging at the nanoscale, and found that EUV TOF possesses similar imaging capabilities to NanoSIMS [3]. The ability of EUV TOF to image isotopic content at the nanoscale makes it a promising tool in fields for which it is critical to identify sources of chemical processes at the submicron scale, such as nuclear forensics, geochemistry, and biology.

- [1] I. Kuznetsov, J. Filevich, F. Dong, M. Woolston, W. Chao, E.H. Anderson, E.R. Bernstein, D.C. Crick, J.J. Rocca, C.S. Menoni, Three-dimensional nanoscale molecular imaging by extreme ultraviolet laser ablation mass spectrometry, *Nature Communications*, **2015**, *6*, 1-6.
- [2] T. Green, I. Kuznetsov, D. Willingham, B.E. Naes, G.C. Eiden, Z. Zhu, W. Chao, J.J. Rocca, C.S. Menoni, A.M. Duffin, Characterization of extreme ultraviolet laser ablation mass spectrometry for actinide trace analysis and nanoscale isotopic imaging, *Journal of Analytical Atomic Spectrometry*, **2017**, *32*, 1092-1100.

- [3] L.A. Rush, J.B. Cliff, D.D. Reilly, A.M. Duffin, C.S. Menoni, Isotopic heterogeneity imaged in a uranium fuel pellet with extreme ultraviolet laser ablation and ionization time-of-flight mass spectrometry, *Analytical Chemistry*, **2020**, submitted for publication.
- [4] D.D. Reilly, C.L. Beck, E.C. Buck, J.B. Cliff, A.M. Duffin, T.G. Lach, M. Liezers, K.W. Springer, S.J. Tedrow, M.M. Zimmer, Focused ion beam for improved spatially-resolved mass spectrometry and analysis of radioactive materials for uranium isotopic analysis, *Talanta*, **2020**, *211*, 1-8.