Supplementary Information

Supplementary Text

Atom Probe Tomography (APT) Technique and Applications in Geosciences:

Atom-probe tomography (APT) is the highest spatial resolution analytical technique in existence for the characterization of materials [1]. The strength of the technique lies in the possibility of combining a 3D reconstruction with chemical composition, including isotopes, at the atomic scale with a near part-per-million analytical sensitivity [1-3]. The analysis of the chosen material often requires a two-step process involving the preparation of tip specimens, usually with a radius of 50-60 nm, using the technique of focused ion beam (FIB), followed by the ionization of material and chemical measurements in an atom probe instrument. Preparation of high-quality tip specimens is crucial, as the technique "uses the principle of field ion evaporation to remove individual atoms from a sample by applying a high electrical field" [4]. The protocols for specimen preparation, mainly using FIB and a subsequent "lift out", are well determined for conductive materials, but they are less explored for insulators and ceramics [4-5]. Once the specimens are fabricated and transferred to a Local Electrode Atom Probe (LEAP) the ionization is initiated using a voltage pulse or a laser pulse focused on the tip of the specimen. Once field ion evaporation is achieved, data are registered through the use of time-of-flight spectroscopy (TOF) for subsequent post-processing. A good summary of the capabilities and limitations of APT can be found in several review articles [1, 3, 5]. As an example, one of the main limitations of the technique, besides an ion detection efficiency up to 80%, is that not all specimens may be run successfully, notably in the case of insulator materials including geological samples [5]. APT data can be divided in two groups. Information obtained from mass spectra, representing the abundance of ions, and the possibility of producing a 3D reconstruction of atoms, or molecules, with a spatial resolution better than 0.3 nm in all directions and high analytical sensitivity of 1 ppm for volumes greater than 10^6 nm^3 [5]. With the advent of a new generation of LEAP instruments, with different flight paths and higher detector efficiencies, APT is becoming increasingly important for the nanoscale analysis of chemical components in minerals. A good summary of APT application in geosciences can be found in [6].

Once the optimal parameters of sample preparation and analysis are determined for different groups of minerals (e.g., silicates and carbonates), the atom probe can potentially provide significant geochemical information. APT should not be contemplated as a substitute for any of the techniques currently available for geochemistry but rather it has to be viewed as a complementary technique to (secondary ion) mass spectrometry and electron microscopy techniques, especially transmission electron microscopy (TEM) for the case of nanoscale samples. In addition, the use of atom probe requires having specific research questions that only can be answered with the increased resolution provided by this technique. Among these questions, some examples are given as follows:

- Analysis of mineral grains, and polycrystalline samples, of less than 5 μm^2.
- Analysis of solid, and even fluid, inclusions (< 10 μm) within minerals.
- Chemical analyses (elements and isotopes) across grain boundaries and zonation in minerals.
- Chemical analyses (elements and isotopes) in relation to crystallographic planes, and crystallographic defects (e.g., dislocations).
- Isotopic analyses of nanoscale mineral grains and particles (e.g., nanodiamonds).

References:

1. Larson, D.J.; Kelly, T.F. Nanoscale analysis of materials using a local-electrode atom probe. *Microsc. Microanal.* **2006**, *May issue*, 59-62.
2. Seidman, D.N. Three-dimensional Atom-Probe Tomography: Advances and Applications. *Ann. Rev. Mater. Res.* **2007**, 37, 127-158.
3. Miller, M.K., Forbes, R.G. Atom probe tomography. *Mater. Charact.* **2009**, *60*, 461-469.
4. McKenzie, W.R., Marquis, E.A., Munroe, P.R. Focused ion beam sample preparation for atom probe tomography. *Microscopy: Science, Technology, Applications and Education* **2010**, 1800-1810. Mendez-Vilas, A., Diaz, J. (eds.), Formatex Publisher, Spain.
5. Kelly, T.F., Larson, D.J. Atom Probe Tomography. *Ann. Rev. Mater. Res.* **2012**, *42*, 1-31.
6. Reddy, S.M., Saxey, D.W., Rickard, W.D.A., Fougerouse, D., Montalvo, S.D., Verberne, R., Riessen, A. Atom Probe Tomography: Development and Application to Geosciences. *Geostand. Geoanal. Res.* **2020**, *44*, 5-50.

Supplementary Figures

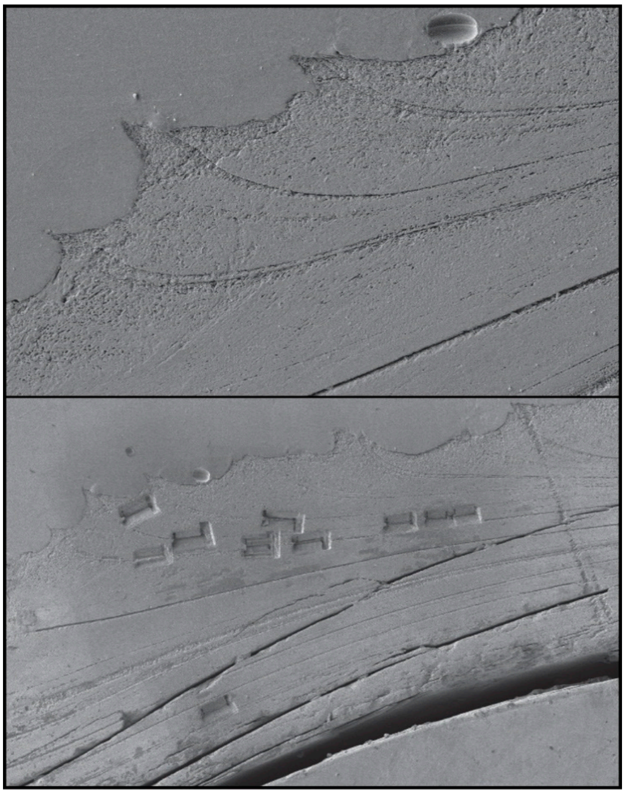

Figure S1. Sample preparation. (**Top**) Detailed SEM image of the polished surface showing the coupled growth lines corresponding to the striae; (**Bottom**) Location of multiple wedges, prepared with FIB, to accurately target the growth lines for APT analysis.

Spectra W7

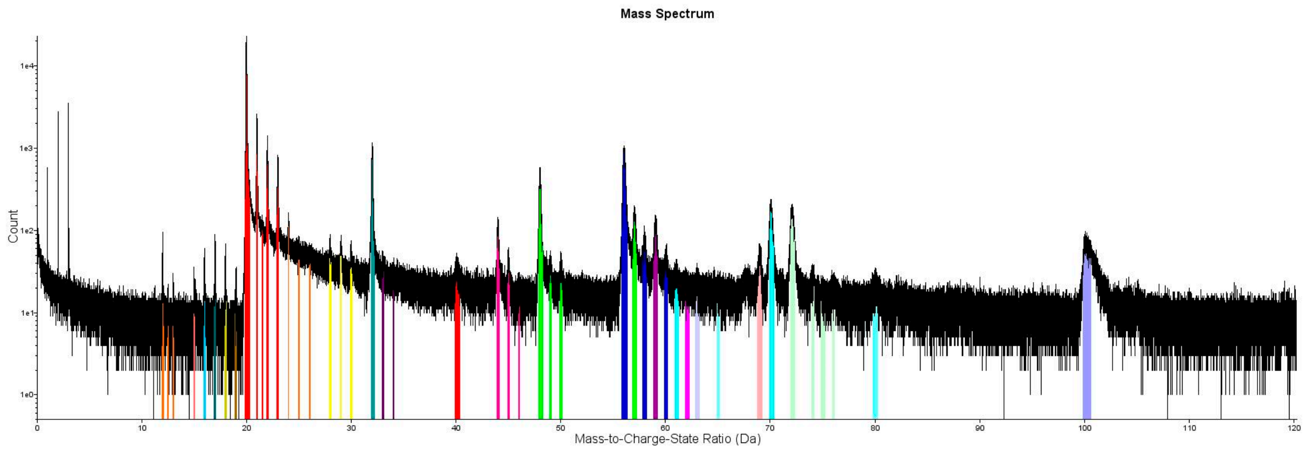

Figure S2. Mass spectrum for tip M13 (run 4173) from wedge 7. Note: For the visualization of peaks and peak identification see Figure 4 and Table 2 respectively in the main text.

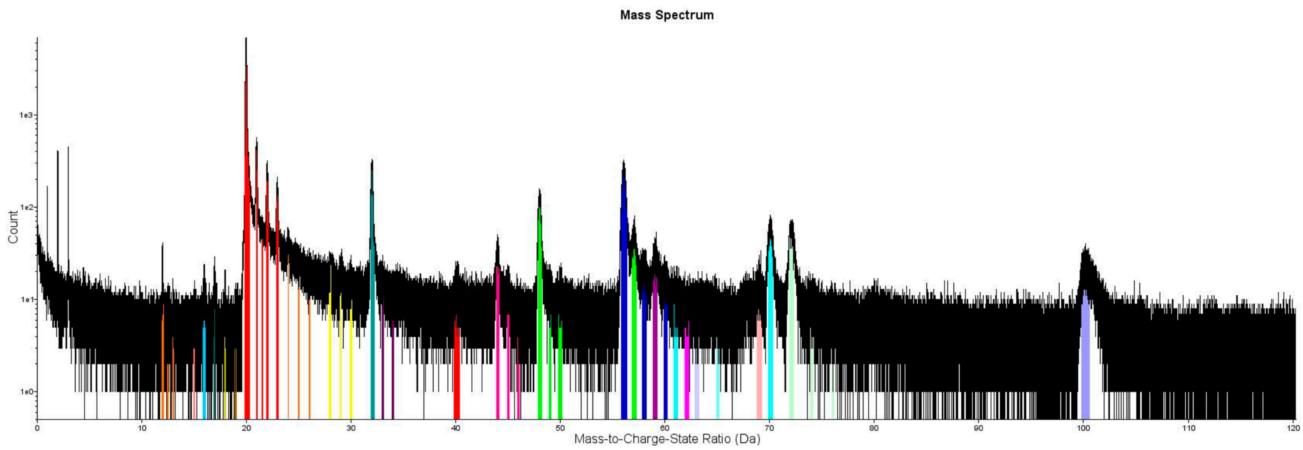

Figure S3. Mass spectrum for tip M19 (run 4174) from wedge 7. Note: For the visualization of peaks and peak identification see Figure 4 and Table 2 respectively in the main text.

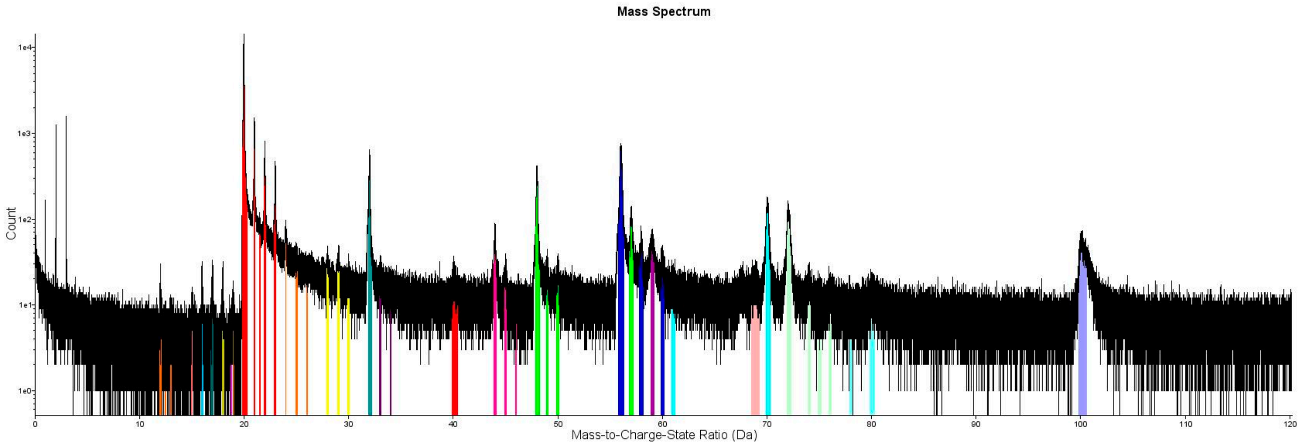

Figure S4. Mass spectrum for tip M21 (run 4176) from wedge 7. Note: For the visualization of peaks and peak identification see Figure 4 and Table 2 respectively in the main text.

Spectra W8

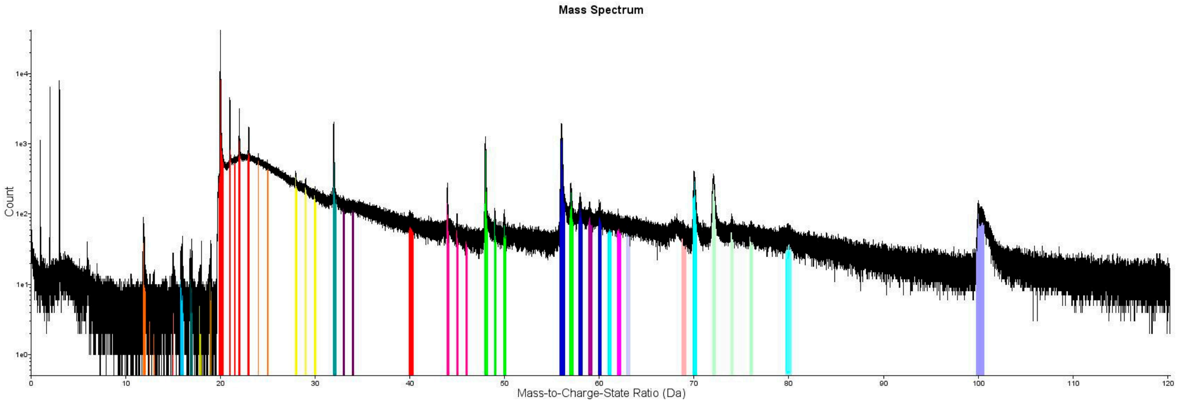

Figure S5. Mass spectrum for tip M3 (run 4149) from wedge 8. Note: For the visualization of peaks and peak identification see Figure 4 and Table 2 respectively in the main text.

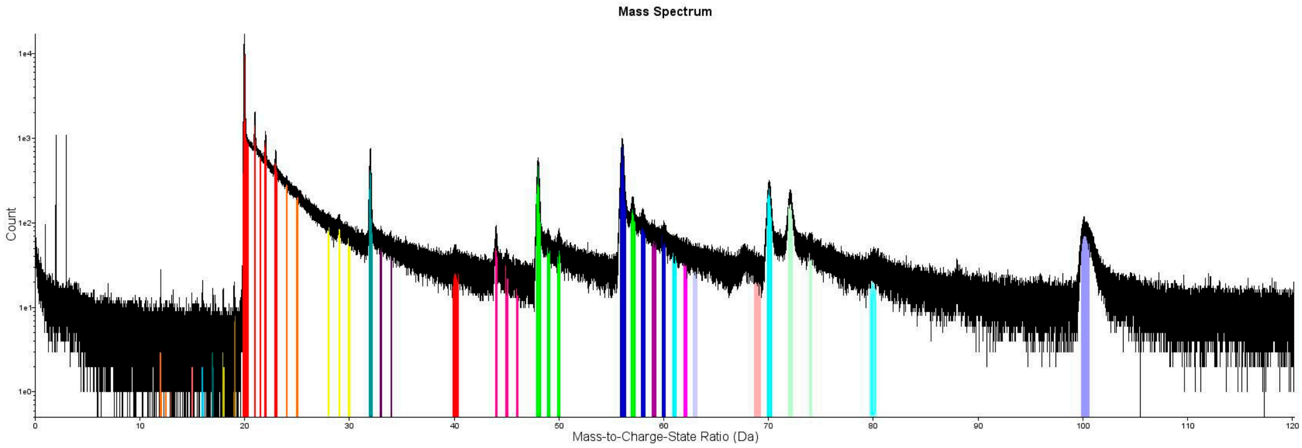

Figure S6. Mass spectrum for tip M4 (run 4150) from wedge 8. Note: For the visualization of peaks and peak identification see Figure 4 and Table 2 respectively in the main text.

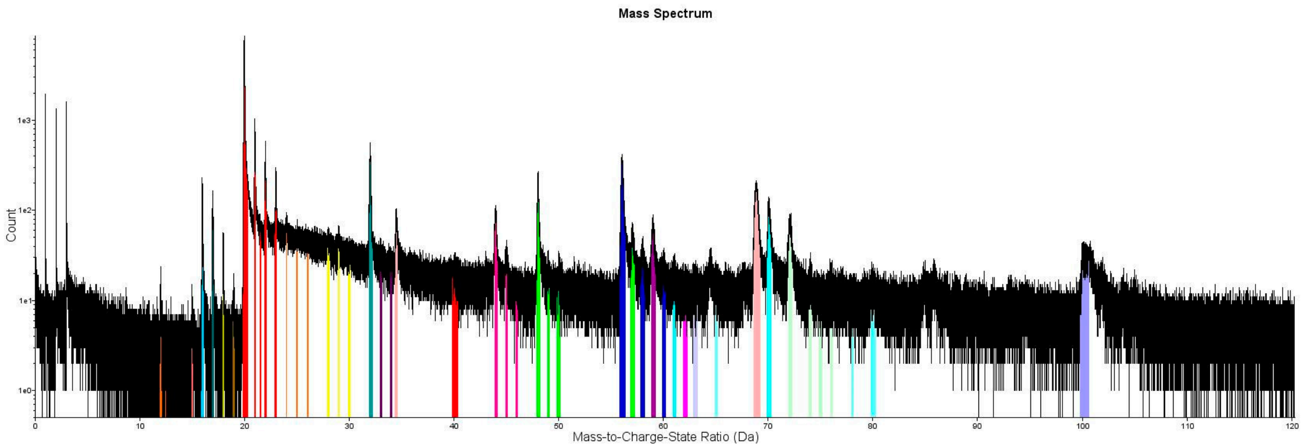

Figure S7. Mass spectrum for tip M10 (run 4148) from wedge 8. Note: For the visualization of peaks and peak identification see Figure 4 and Table 2 respectively in the main text.

3D reconstructions W7

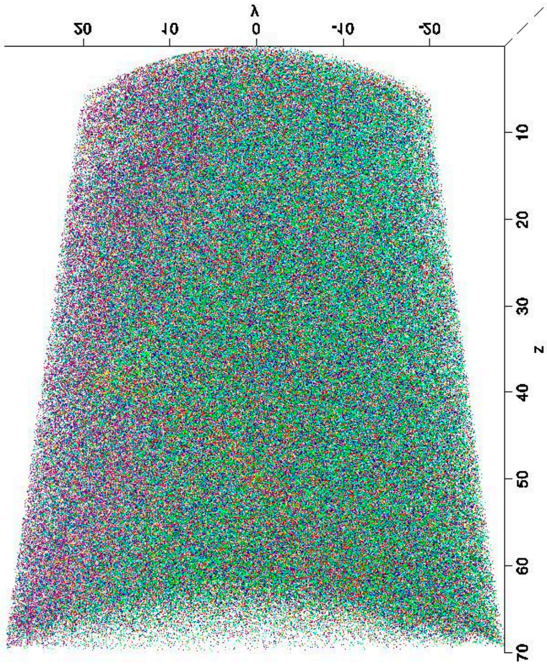

Figure S8. 3D reconstruction of all ions for tip M13 (run 4173) from wedge 7.

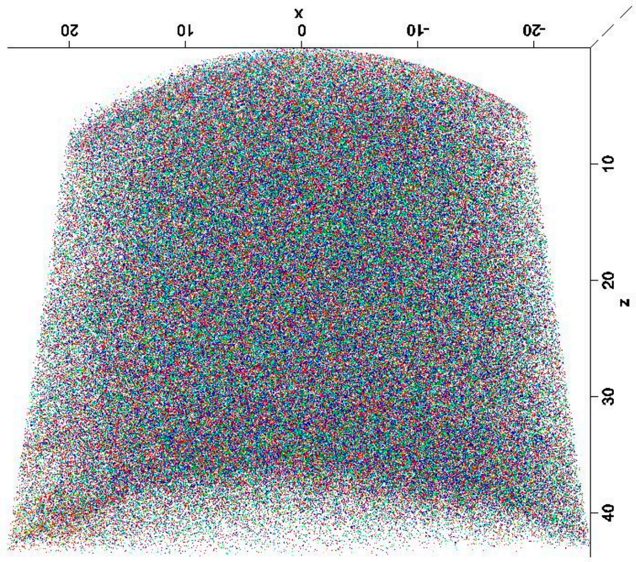

Figure S9. 3D reconstruction of all ions for tip M19 (run 4174) from wedge 7.

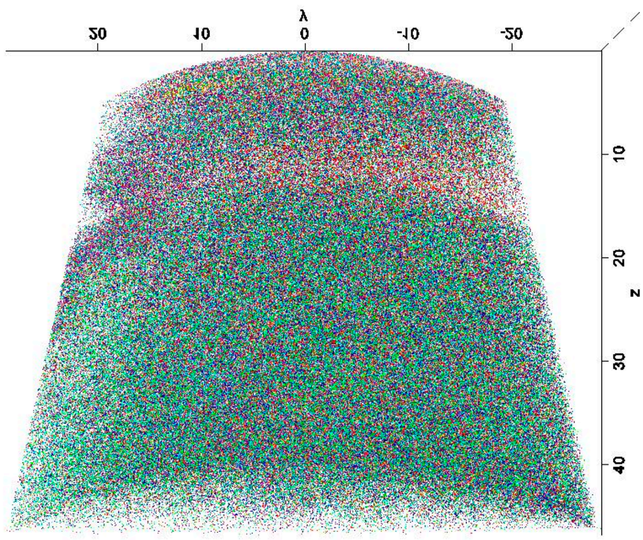

Figure S10. 3D reconstruction of all ions for tip M21 (run 4176) from wedge 7.

3D reconstructions W8

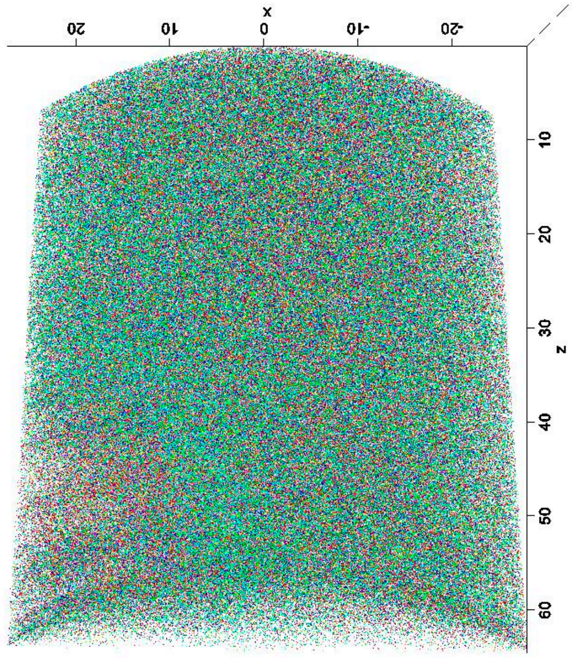

Figure S11. 3D reconstruction of all ions for tip M4 (run 4150) from wedge 8.

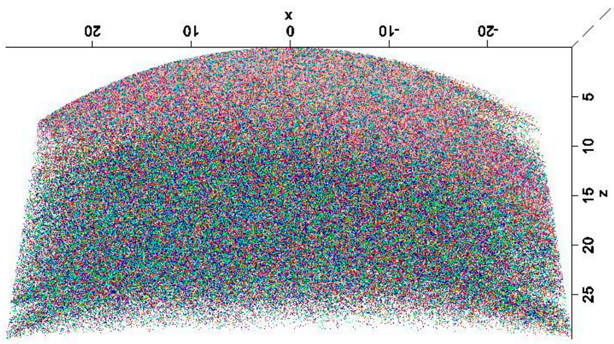

Figure S12. 3D reconstruction of all ions for tip M10 (run 4198) from wedge 8.

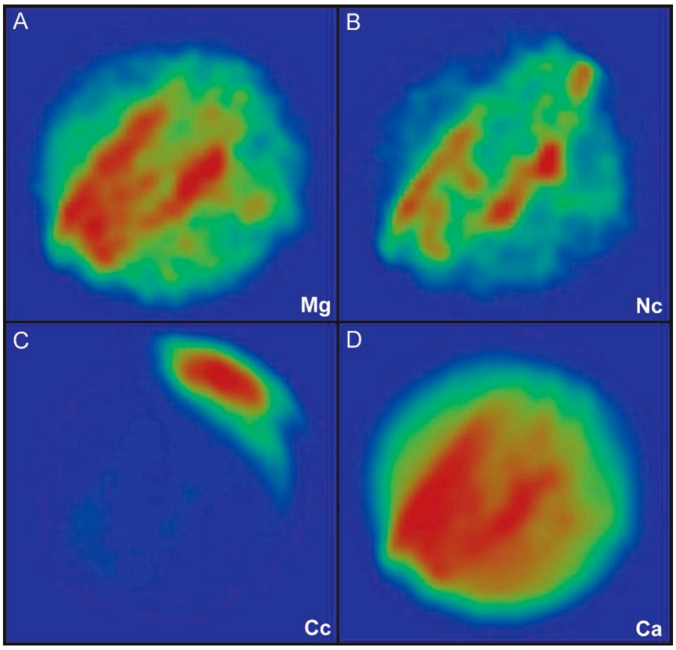

Figure S13. 2D density contour plots taken from the entire specimen through the *z*-axis of the reconstructed volume (red equals to the highest density) showing magnesium (**A**), nitrogen compounds (**B**), carbon compounds (**C**), and calcium (**D**) for tip M13 (W7).