doi:10.1017/S1431927617004068
Microsc. Microanal. 23 (Suppl 1), 2017

Atomic Elemental Tomography of Heavy Element Biomaterials

Xiaoyue Wang[1,2], Robert M. S. Schofield[3], Michael H. Nesson[3] and Arun Devaraj[1]

[1.] Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, USA.
[2.] Department of Materials Science and Engineering, McMaster University, Hamilton, Canada.
[3.] Department of Physics, University of Oregon, Eugene, USA.

Natural small "tools" of arthropods such as jaw teeth, leg claws or stings are particularly fracture-resistant. Unlike calcified tissues such as bone or teeth of vertebrate, these small functional organs are not biomineralized but instead are predominantly organic with some heavy elements (e.g. Zn, Mn and Cu) [1] However, so far the distribution and binding sites of these heavy elements in these class of biomaterials are unknown. Laser-assisted Atom Probe Tomography (APT) is developing in to an efficient technique to visualize the elemental distribution in biomaterials at near atomic scale spatial resolution [2-3]. Therefor an attempt was made to utilize laser-assisted APT to analyze the elemental distribution in such heavy element biomaterials.

Adult Ant teeth is a typical example of HEBs, which contains Zn. In this work, the distal tooth from adult ants and young ants (*Atta cephalotes*) were fabricated in to APT needle specimens and laser assisted APT analysis was conducted using a CAMECA LEAP 4000X-HR. The steps of sample preparation of Zn ant teeth is provided in figure 1. The distribution of Zn in adult ant teeth was observed to be homogenous and no obvious Zn-rich inclusions were observed. Peaks of Zn+ and Zn 2+ could hardly be discerned in the young ant teeth mass spectra, indicating the limited amount of Zn within young ant teeth. Thus it was observed that Zn is incorporated into ant teeth gradually during the maturation process, which strengthen the mechanical properties by time, which agreed with past studies [1]. Due to significant variability in mass-to-charge spectra and resultant uncertainties in compositional quantification of APT results, such variabilities were investigated systematically as a function of laser pulse energy over the range of 10 pJ to 450 pJ. Also the mass-to-charge spectra of the Ant teeth was compared with the mass-to-charge spectra of standards of Zn reference compounds (Zinc Picolinate, Zinc Acetate and Zinc Glycine). Additionally the effect of FIB milling current during sample preparation of such biomaterials on mass-to-charge spectra was investigated by using extra low milling currents and comparing with results from FIB preparation by normal milling currents used for inorganic materials.

Figure 2 shows the mass-to-charge spectra comparison of adult ant teeth, young ant teeth and other Zinc-reference compounds with Zn binding environments similar to what is expected in adult ant teeth. A detailed analysis of mass spectra from adult ant teeth was made possible by comparing the spectra from reference standards. Such systematic mass-to-charge spectra analysis is crucial since APT is considered as a prospective high spatial resolution compositional analysis method of choice for biological materials [4].

References:

[1] R. M. S. Schofield, *et al*, Journal of Insect Physiology **49** (2003), p.31.

[2] A. Devaraj, *et al*, International Materials Reviews (2017).
[3] B. Langelier, X. Wang, K. Grandfield, Scientific Reports **7** (2017), p 39958.
[4] This project was funded as a part of NSF Biomaterials grant. The APT analysis was conducted at Environmental Molecular Sciences Laboratory at PNNL, which is a national user facility funded by Department of energy Office of Biological and Environmental research office.

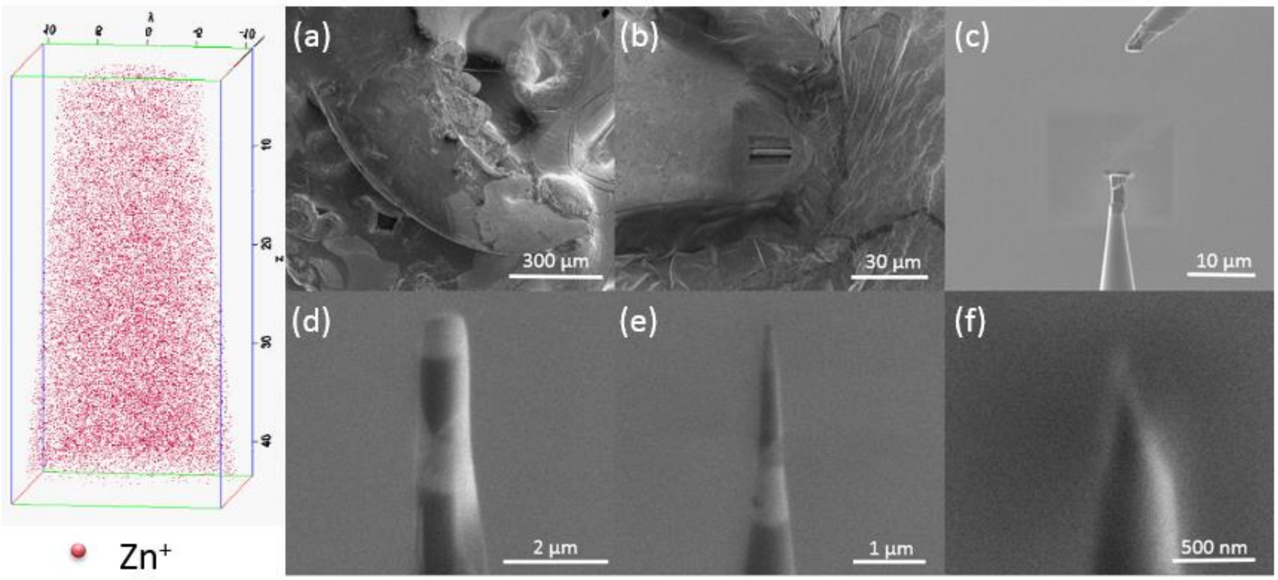

Figure 1. Zn+ ions distribution in APT reconstructed volume of adult ant teeth (left); Preparation of an APT sample from an ant tooth (right). (a) a single distal tooth from an adult leaf cutter ant; (b) lift-out wedge from the tip of the ant tooth; (c) mounting one piece of the lift-out wedge onto the Si-microtip; (d&e) annual milling to sharpen the tip; (f) final polishing the tip with low voltage.

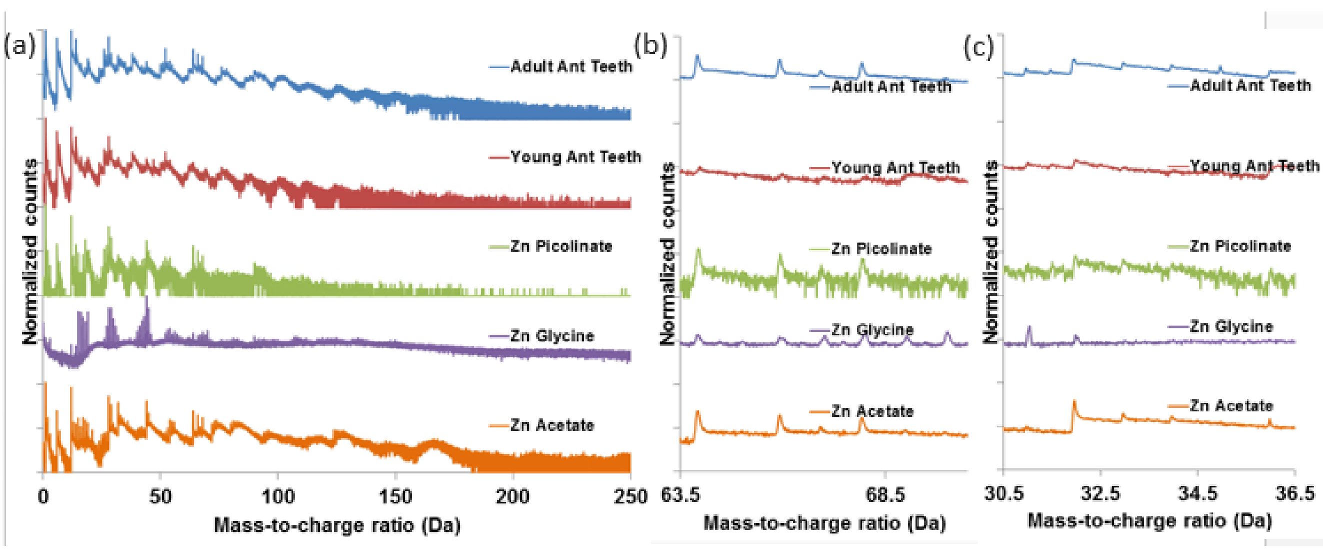

Figure 2. Comparing mass-to-charge spectra of adult ant teeth, young ant teeth and other standard Zinc-compounds with laser pulse energy at 100 pJ. (a) Overall mass spectra comparison; (b) Zn + peaks comparison; (c) Zn 2+ peaks comparison.

https://doi.org/10.1017/S1431927617004068 Published online by Cambridge University Press