

## Supplementary Materials

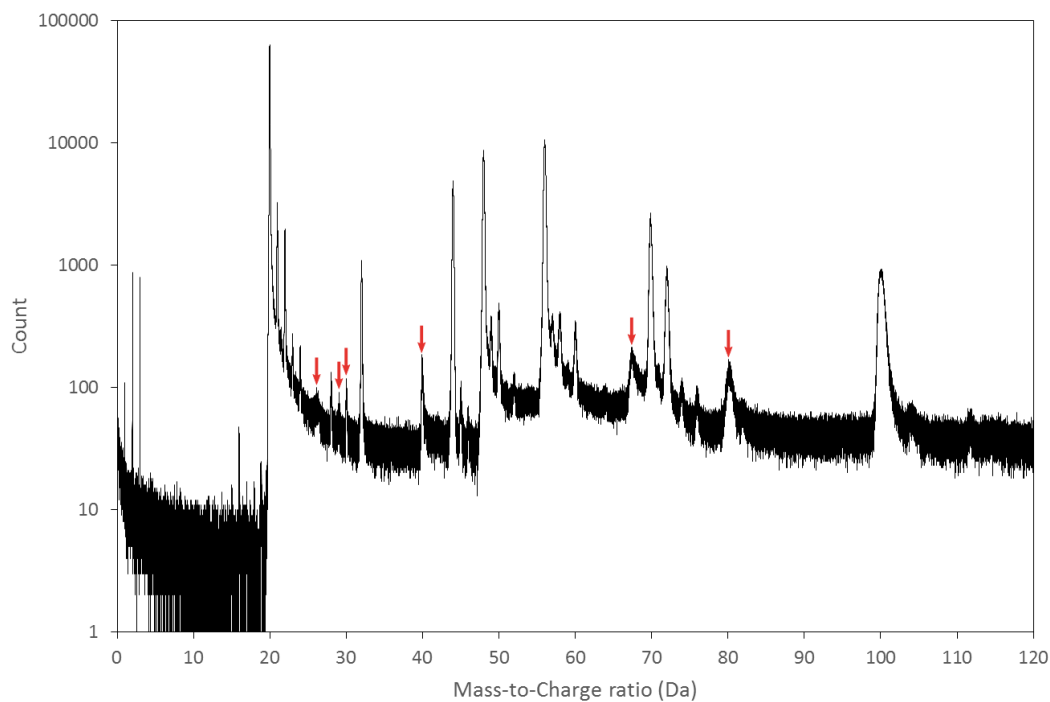
# Atom Probe Tomography (APT) Characterization of Organics Occluded in Single Calcite Crystals: Implications for Biomineralization Studies

Alberto Pérez-Huerta <sup>1,\*</sup>, Michio Suzuki <sup>2</sup>, Chiara Cappelli <sup>1</sup>, Fernando Laiginhas <sup>1</sup> and Hiroyuki Kintsu <sup>2</sup>

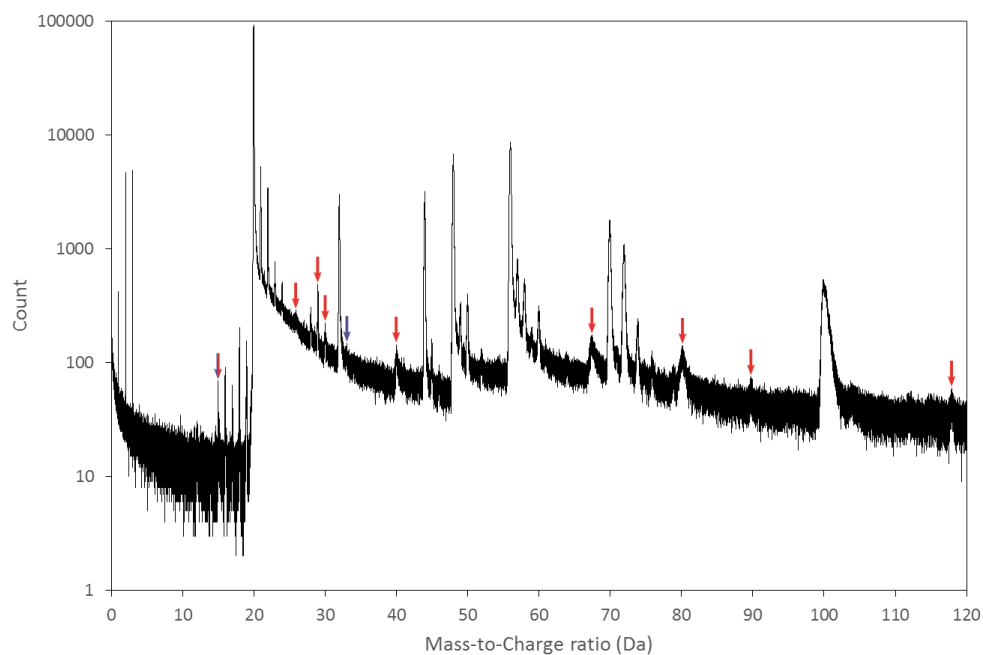
<sup>1</sup> Department of Geological Sciences, The University of Alabama, Tuscaloosa AL 35487, USA

<sup>2</sup> Department of Applied Biological Chemistry, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo 113-8657, Japan

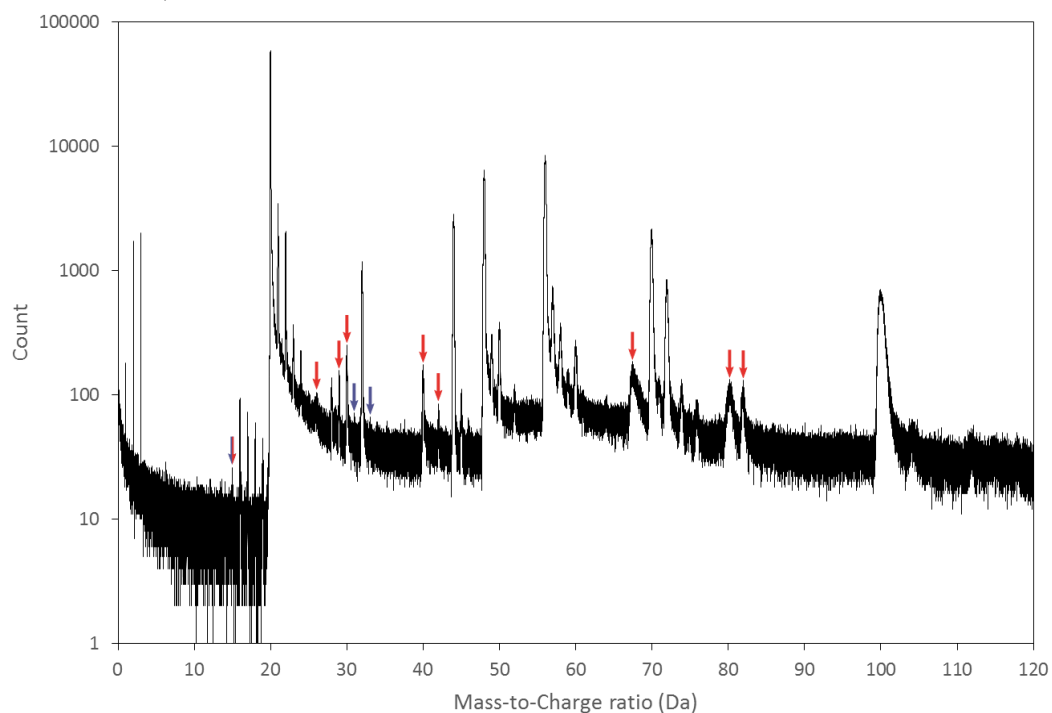
\* Correspondence: aphuerta@ua.edu; Tel.: +1-205-535-0851



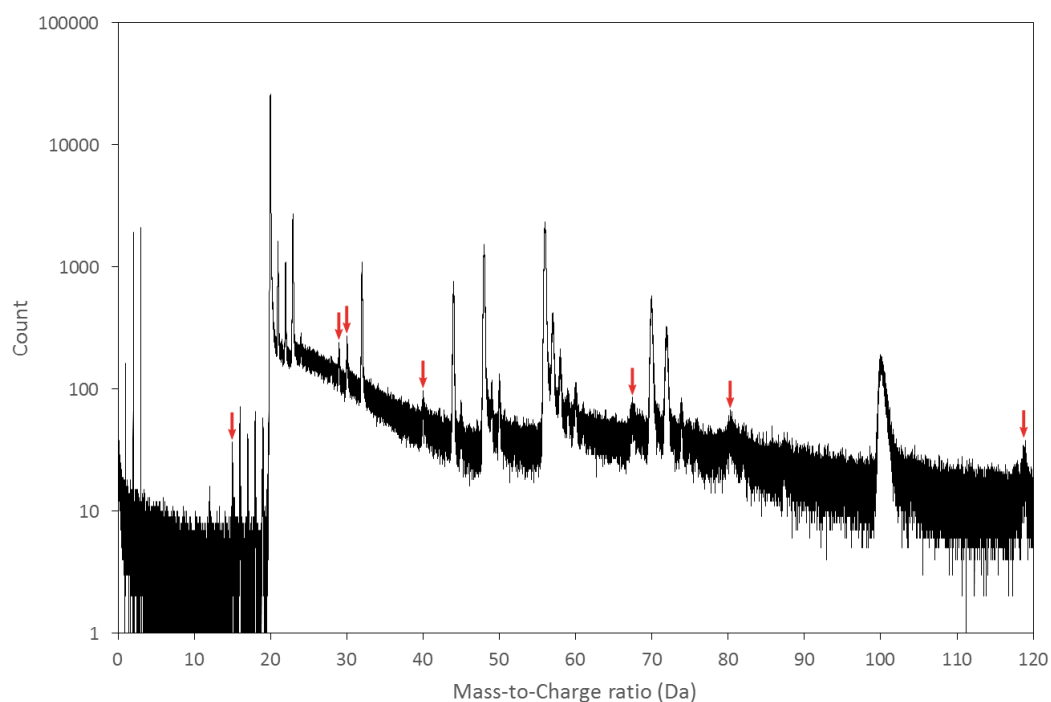
**Figure S1.** Example of representative APT mass spectra for calcite and chitin hydrogel. (Note: **Red** arrows indicate some representative peaks indicative of chitin; more details in Table 2).



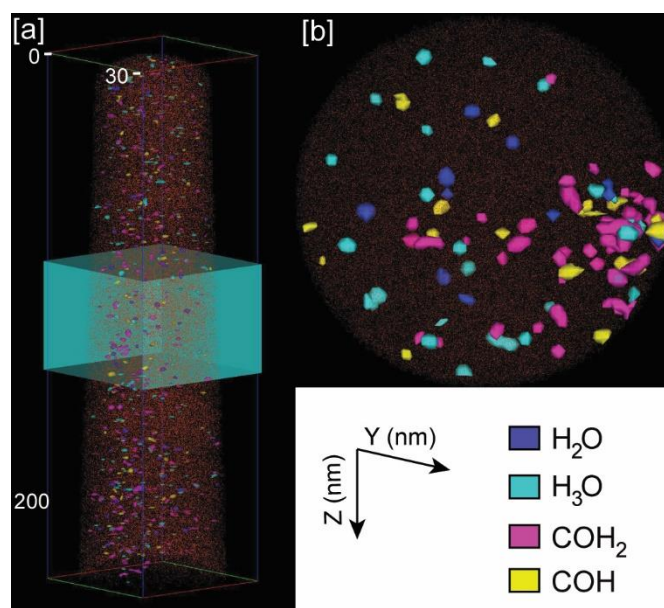
**Figure S2.** Example of representative APT mass spectra for calcite and chitin at 0.12 mg/mL concentration of yatalase. (Note: **Red** and **blue** arrows indicate some representative peaks indicative of chitin and yatalase, respectively; more details in Table 2).



**Figure 3.** Example of representative APT mass spectra for calcite and chitin at 1.2 mg/mL concentration of yatalase. (Note: **Red** and **blue** arrows indicate some representative peaks indicative of chitin and yatalase, respectively; more details in Table 2).



**Figure 4.** Example of representative APT mass spectra for calcite and chitin nanofibers. (Note: **Red** arrows indicate some representative peaks indicative of chitin; more details in Table 2).



**Figure 5.** Example of APT 3D tip reconstruction for calcite with occluded chitin hydrogel fragments; (a) General view; (b) Orthogonal projection view (along Z axis) of a slice of the tip within the blue box in (a). Notes: Dimensions, along Z and Y axes, are in nm; red dots correspond to Ca atoms; chitin fragments recognized by  $\text{COH}^-$ ,  $\text{COH}_2^-$ , and associated water ( $\text{H}_2\text{O}$ ) and hydronium ( $\text{H}_3\text{O}^+$ ) molecules.

Table S1. Measured elemental atomic concentration (%) for all analyzed tips.

Specimen 1536_0 Yatalase				Specimen 1619_0.12 Yatalase				Specimen 1560_1.2 Yatalase				Specimen 1644_ChitinFiber			
Element	Atom count	Atomic %	Atomic error %	Element	Atom count	Atomic %	Atomic error %	Element	Atom count	Atomic %	Atomic error %	Element	Atom count	Atomic %	Atomic error %
C	1,884,114.0	7.34%	0.0004%	C	1,165,352.5	5.052%	0.0007%	C	1,550,622.6	7.06%	0.0006%	C	292,215.4	4.71%	0.0009%
Ca	14,417,368.3	56.15%	0.0160%	Ca	14,111,918.7	61.18%	0.014%	Ca	12,089,332.2	55.03%	0.0174%	Ca	3,669,268.5	59.12%	0.0317%
H	535,717.1	2.09%	0.001%	H	962,311.8	4.17%	0.0019%	H	720,779.5	3.28%	0.001%	H	368,606.2	5.94%	0.0018%
N	532.3	0.002%	0.0001%	N	11,753.8	0.05%	0.0005%	N	5520.7	0.03%	0.0005%	N	6534.8	0.11%	0.0007%
Na	14,364.8	0.06%	0.0016%	Na	31,653.7	0.14%	0.0024%	Na	22,726.8	0.103%	0.0018%	Na	290,858.9	4.69%	0.0144%
O	8,824,961.4	34.37%	0.0005%	O	6,764,071.1	29.32%	0.0008%	O	7,549,411.0	34.37%	0.0007%	O	1,577,964.1	25.43%	0.0018%
				P	973.7	0.004%	0.0015%	P	1336.2	0.01%	0.0011%	P	522.0	0.01%	0.0042%
				S	19,683.1	0.09%	0.0387%	S	27,580.3	0.126%	0.0291%				
Specimen 1620_0 Yatalase				Specimen 1592_0.12 Yatalase				Specimen 1618_1.2 Yatalase				Specimen 1643_ChitinFiber			
Element	Atom count	Atomic %	Atomic error %	Element	Atom count	Atomic %	Atomic error %	Element	Atom count	Atomic %	Atomic error %	Element	Atom count	Atomic %	Atomic error %
C	1,090,581.8	7.10%	0.0004%	C	1,346,631.7	5.20%	0.0004%	C	1,306,839.0	6.83%	0.0007%	C	185,700.6	3.05%	0.0016%
Ca	8,470,402.7	55.16%	0.0191%	Ca	15,137,987.9	58.45%	0.0158%	Ca	10,426,381.4	54.51%	0.0168%	Ca	3,934,738.7	64.64%	0.0239%
H	459,295.0	2.99%	0.0028%	H	1,310,097.8	5.06%	0.0015%	H	1,132,041.3	5.92%	0.0020%	H	334,874.9	5.50%	0.0032%
N	8073.5	0.05%	0.0003%	N	4347.5	0.02%	0.0003%	N	30,237.4	0.16%	0.0006%	N	1675.1	0.03%	0.0012%
Na	4268.4	0.03%	0.0037%	Na	71,756.3	0.28%	0.0022%	Na	28,950.2	0.15%	0.0024%	Na	114,442.2	1.88%	0.0086%
O	5,322,273.2	34.66%	0.0010%	O	8,015,026.6	30.95%	0.0008%	O	6,174,461.9	32.28%	0.0008%	O	1,516,022.6	24.90%	0.0018%
				P	279.6	0.00%	0.0009%	P	2664.4	0.01%	0.0013%				
				S	10,989.7	0.04%	0.0217%	S	24,218.6	0.13%	0.0308%				
				Specimen 1670_0.12 Yatalase											
				Element	Atom count	Atomic %	Atomic error %								
				C	577,191.4	4.802%	0.0005%								
				Ca	7,308,407.3	60.800%	0.0205%								
				H	335,378.4	2.790%	0.0049%								
				N	2476.6	0.021%	0.0004%								
				Na	7859.6	0.065%	0.0051%								
				O	3,789,062.4	31.522%	0.0009%								