USING MASS SPECTROMETRY TO ANALYZE INTACT OCEANIC SEDIMENTARY PROTEINS

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We have successfully analyzed intact native proteins preserved in oceanic sediments using an electrospray inlet mass spectrometer. This is important because on a global scale, more organic carbon is present in soil humus (1.60×10^{18} gC) and in the oceanic surface sediments (1.0×10^{18} gC), than in all land plants and marine organisms combined (0.60×10^{18} gC). Scientists believe that up to 60% of the residual nitrogen in oceanic samples can be attributed to proteinaceous material >2,000 Da in size. Analyzing and understanding these robust biomolecules can provide us with clues to climate variation and atmospheric oxygen controls over the last 400 million years.

In the past decade, our collective knowledge in proteomics has rapidly grown, yet these techniques have seen relatively little application to environmental problems. Proteins have a great potential as environmental indicators since they typically comprise greater than 50% of the organic matter in organisms and are known to be, at least in part, preserved in sedimentary systems. Previously, most environmental research focusing on proteins involved high temperature hydrolysis of samples, limiting studies to the analysis of amino acid residues. As a result, all information on the size and source of the original biomolecules was lost.

Steady advances in analytical techniques now potentially allow for the examination of protein cycling in environmental samples that have complex matrices such as those present in oceanic systems. The analysis of oceanic proteins is particularly challenging in sedimentary environments because they are present at low concentrations (1-150 mg/ g dry sediment) in a salty, mineral-laden environment where conditions favor sorption to sediment surfaces and/or interactions with other organic matter. As a result, most extraction techniques that isolate proteins also solubilize other organic matter of unknown structure (e.g. humic acids). To ameliorate these problems we are developing chromatographic procedures to isolate protein from other organics to determine their sizes and sequences. We can successfully extract and identify known proteins added to natural sediments at low levels using MALDI-TOF-MS. Unfortunately, the extraction of thousand to million year old native proteins present in oceanic sediments is much more complicated. Using an HPLC-ESI-MS the dominant protein we have isolated from surface sediments off the Washington coast is 36,590 $\pm$ 10 Da. By identifying and eventually sequencing this and other sedimentary proteins, we hope to determine the source organisms that create the proteins and also determine what makes certain proteins resistant to degradation in the environment.