Molecular characterization of terrestrial and aquatic biomacromolecules that contribute to soil and sediment Carbon burial

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Biologically refractory macromolecules contribute greatly to soil and sedimentary organic matter that persists for extended periods of time. These macromolecules often remain unchanged molecularly for up to millions of years. Understanding their structural makeup is paramount to knowing how organic matter becomes sequestered in sediments. We have recently taken advantage of some modern nuclear magnetic resonance spectroscopy and mass spectrometry approaches that provide a new glimpse of structural makeup of macromolecules from terrestrial and aquatic plants. Using High Resolution Magic Angle Spinning (HRMAS) multidimensional NMR and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS) we can identify specific molecular components of a series of biologically resistant biomacromolecules. These include lignin from modern and ancient woods, cuticular isolates of conifer needles, suberan from tree bark, and algaenan from various ancient and extant algal forms.

It is clear from our studies that some structural elements from modern resistant molecules survive nearly intact. Other structural elements undergo removal or reaction to form other structural elements. Aldehyde, alcohol, acid, and ester functional groups appear to be the reactive centers. Olefinic groups also appear to be sites for cross-linking and polymerization.

Fumarolic alteration and implications for Mars

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Chemical alteration on Mars may have occurred by different types of fluids, including surface water, ground water, and hydrothermal alteration including fumaroles. Each of these scenarios has different implications for interpreting the climate history and potential for life on Mars. Data from the Mars Exploration Rover Spirit strongly suggest hydrothermal alteration in Gusev Crater, both in Paso Robles and Home Plate. Orbital data and observations from Mars meteorites also suggest hydrothermal alteration.

To characterize the weathering environment near fumaroles as an analog for Mars alteration processes, samples were collected near fumaroles in Dixie Valley, Nevada. Samples were also collected away from the fumaroles as a control. These samples are being analyzed to characterize fumarolic alteration products in an acid vapor environment and to prepare for measuring *in situ* alteration rates and secondary product formation. Gas compositions from the fumaroles have been previously analyzed.

Samples were observed by Scanning Electron Microscopy (SEM), and measured for pore water pH and water content. Pore water pH values were approximately 8.4 in the control sample far from the fumaroles, and were approximately 2-7 in samples collected near the fumaroles. Water contents were higher near the fumaroles (10-20%), compared to ~2% in the control. Characteristic results from the SEM observations of samples collected near the fumaroles included the presence of Ca-sulfates, S-rich deposits, Al-sulfates, and Si-rich globules. No sulfates were observed in the sample collected away from the fumaroles as a control, suggesting that the source of the sulfates is the fumaroles.

In situ alteration experiments are ongoing, and will be characterized for weathering rates and secondary product formation.