Direct characterization of kerogen: Part 1 - XPS and S-XANES Methods

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Understanding the molecular structure and chemistry of complex organic solids is often aided by developing representative chemical structural models of the material. In the past, significant advances were made by using an indirect characterization approach where the strategy was to mildly decompose the solid and then separate, identify and quantify the components using liquid and gaseous characterization methods. Incomplete decomposition of the organic solid and unknown chemical transformations that occur during decomposition are inherent limitations and impose associated uncertainties. Recent advances in X-ray methods enable direct characterization of organic carbon nitrogen, sulfur and oxygen. X-ray methods have been applied to study kerogens that represent a wide range of organic matter types and maturities. A van Krevelen plot, based on elemental H/C data and X-ray Photoelectron Spectroscopy (XPS) derived O/C data of the kerogens of this study shows the well-established pattern for Type I, Type II and Type III kerogens. XPS is used to speciate and quantify nitrogen forms. A combination of Sulfur X-ray Absorption Near Edge Structure (S-XANES) and XPS are used to speciate and quantify sulfur forms. The XPS carbon (1s) signal is sensitive to chemical shifts caused by bonding to oxygen and is used together with solid-state ^{13}C nuclear magnetic resonance (NMR) to elucidate organic oxygen functional groups in kerogens. XPS results show that the amount of carbon-oxygen single bonded species increases and carbonyl-carboxyl species decrease with increasing amount of aromatic carbon. Patterns for the relative abundances of nitrogen and sulfur species exist in spite of large differences among kerogens in the total amount of organic nitrogen and sulfur. XPS and S-XANES results indicate that the relative level of aromatic sulfur increases with increasing amount of aromatic carbon for all kerogens. XPS results demonstrate that the majority of nitrogen exists as pyrrolic nitrogen in comparable relative abundances in all kerogens studied. The direct characterization results using X-ray and NMR

methods for nitrogen, sulfur, and oxygen provide a basis for developing chemical structural models for different organic matter type kerogens.