Micro XANES Studies of Oil Shales

SUDIPA MITRA-KIRTLEY[1]

JUSTIN BIRDWELL[2]

WYATT SMITH[1]

[1]Rose-Hulman Institute of Technology, Terre Haute, IN 47803, sudipa.kirtley@rose-hulman.edu

[2] Central Energy Resources Science Center, U. S. Geological Survey, CO, jbirdwell@usgs.gov

Micro X-ray absorption near-edge structure (XANES) and X-ray fluorescence (XRF) spectroscopies have been applied to oil shales from various sources to examine the heterogeneity in sulfur speciation in micron-sized organic macerals and mineral grains in organic-rich mudrocks. The data for this study were collected at beamline 10.3.2 at the Advanced Light Source at Lawrence Berkeley National Laboratory. The twelve samples cover a wide range of depositional and geographical environments (marine and lacustrine), as well as geologic ages (Cambrian to Eocene) and have known oil shale resource potential. Previous bulk analyses performed on the shales and isolated kerogens confirmed their organic richness and were used to identify kerogen types. Based on these analyses, all samples are thermally immature and represent a variety of oil-prone kerogens, including Types I, II, and II-S. XRF was used to map elemental distributions in the samples and then random spots with relatively high sulfur content were selected for XANES measurements. The organic sulfur species detected included organic sulfide, thiophene, sulfoxide, sulfone, and sulfonate structures, and the inorganic sulfur species included pyrite, iron oxides, elemental sulfur, and sulfates. Based on these measurements, we have observed for the first time, variability in the molar concentrations of sulfur moieties between different micro-scale organic matter macerals in source rocks. The variability in sulfur speciation was substantial, though at least one sample showed remarkable homogeneity. Differences in samples showing variability in sulfur species could be attributed to fluctuating conditions in the depositional environment or changes in organic and detrital source material. The large variation of sulfate content within samples suggests preferential oxidation of pyrite, most likely due to post depositional alteration. These results show that micro-scale variation in organic matter composition may be an important factor in some petroleum systems for understanding oil generation processes and product composition related to sulfur chemistry.