

## Laser Induced Breakdown Spectroscopy (LIBS) Analysis of H, O, N, C, Li, Ca and S in coal, organic-rich marine sediments and shale.

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Sedimentary rocks rich in organic matter (OM) provide the source material for fossil fuel deposits and record the co-evolution of life and Earth surface conditions. To understand the formation, post-depositional alteration, and economic potential of these deposits, many researchers have successfully used the combined chemical analysis of both their organic and mineral components. The traditional “bulk” analytical techniques for this work require large samples and thus obscure fine spatial variations. While laser ablation ICP-MS has been successfully used to analyze metal concentrations at the micro-scale, few micro-analytical techniques exist that can simultaneously measure the light elements (e.g., C, H, O, and N) that form the bulk of natural OM. With the ultimate goal of contributing to an analytical routine that captures a wider range of elements at sub-millimeter resolution, we explore the potential of Laser Induced Breakdown Spectroscopy (LIBS) for the analysis of marine and terrestrial OM-rich deposits.

We present H, O, N, C, Li, Ca, and S spectra, qualitative and quantitative data obtained by Laser Induced Breakdown Spectroscopy (LIBS) on coal, organic-rich marine sediments and shale reference materials. The reference material analyzed includes the USGS Cody Shale SCo-1 standard, the NIST 1632d, 1635a, 2692c, and 2693 coal standards, and the USGS Mag-1 and Environment Canada PACS-2 marine sediment standards. The instrument used for these analyses was the Applied Spectra J200 LIBS Instrument with dual detector configuration that features a broadband 6 channel CCD detector for simultaneous measurement of major and minor elements and a specialized ICCD detector to measure organic elements such as O, N, and H with highest possible sensitivity. Univariate calibration curves were built for C and H, a multivariate curve was developed for S, and a single standard calibration was performed for N. Reasonable precision and accuracy was achieved for all elements despite non-matrix matched standards, limited sampling area, and potential sample heterogeneities. Improvements can be made with better sample preparation techniques (i.e. pressing pellets), wider sampling area, and fine-tuning laser ablation parameters. These results demonstrate the great potential of LIBS in the analysis of those elements that are difficult, if not impossible, to analyze by LA-ICP-MS in organic-rich geological samples.

Keywords: LIBS, Sediments, Shale