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Research on Geochemistry of Shale Oil and its Derivatives by Sulfur Speciation
Sudipa Mitra-Kirtley, PI

Micro-X-ray Absorption spectroscopy data has been collected from five shale samples belonging to different sites from across the globe. The data was collected at Lawrence Berkeley Laboratory (LBL) synchrotron facility, the Advanced Light Source (ALS), at beam line 10.3.2. The data were later analyzed by three undergraduates during summer of 2018 for six weeks. The goal of the project was to elucidate sulfur chemical structures present in these complex materials. The results were very successful and were presented in two conference presentations, one of which was an invited talk at the annual American Chemical Society conference in New Orleans, Louisiana, in March 2018. The other presentation was at the annual International Petrophase conference at Deer Valley, Utah, in July 2018. These experiments were the first ones to be performed at the micron level on shales to investigate the sulfur chemical species present in them. The Principal Investigator has again submitted a proposal for more synchrotron radiation beam time at LBL for more studies of similar nature in September, 2018. The uniqueness of this particular project (and more of future projects) is that the photon beam was of micron dimensions, thus making it possible to study the whole shale samples at this spatial resolution.

The PI conducted a series of XANES experiments at beamline 10.3.2 at Lawrence Berkeley Laboratory along with Dr. Sirine Fakra, an ALS scientist. Different shale rock samples, were sent to a commercial laboratory, Spectrum Petrographics, where 30 micron thin sections of the shales were prepared. Sulfur K-edge XANES experiments were performed on different spots of each shale section, and concurrently X-ray fluorescence mapping was performed. The latter set of experiments allowed the researchers to gather information of the spatial distribution of different elements. There shales were raw shales, and belonged to a variety of geological eras and depositional environments. All the samples were obtained from U. S. Geological Survey at Colorado. The sulfur speciation was distinctly different between the different spots of the same sample, which was very surprising; this proved the inhomogeneity of the samples at the micron level.

Data Acquisition:
During February 2017, the PI used part her beamtime, which was granted after her submission of a proposal. At the site, she collected μ-XANES, and XRF data using the micron-sized beam. Dr. Sirine Fakra from ALS collaborated with the PI. The energy of the photons was around the 2372 eV which is at the sulfur K-edge. Si (111) crystals were used in the double crystal configuration. The XRF data was collected using a 2.58 keV focused x-ray beam. The energy resolution for the XANES measurements was about 0.2 eV, and all the XANES spectra were energy calibrated to gypsum, whose major peak was at 2482.75 eV.
The in-depth analysis of the samples at the micron level gave insights that were very interesting. Microscale (20 μm pixels) measurements made it possible to determine sulfur speciation in small clusters of organic macerals and mineral structures within the shales. The figure below shows how a typical shale XANES spectrum was fitted with a linear combination of spectra obtained from different known sulfur structures. The table below shows results from different spots of one of the shale samples. The results from this projects shows that the shales have clusters of different sulfur chemical structures dispersed at different sites of the same sample. This finding is significant, and will probably establish new ways of thinking about the presence or absence of homogeneity among sulfur chemical structures within shales. The next set of experiments will involve separated organic and inorganic samples of the same shales, which will be studied under similar conditions with the micro-beam, and this, along extensive imaging of the samples, will reveal possible trends.

On-campus work
During the summer of 2018 three Rose-Hulman students, Wyatt Smith, Martin Narciso, and Zihang Xu worked on the data analysis. The PI made a special trip to start the students on their work on campus, and then corresponded regularly with them from her sabbatical site at Claremont McKenna College for six weeks. Different new computer software programs were written for the purpose, and the results that the different approaches generated were compared for the robustness of the methods. The results came out to be better than expected, and the PI is now preparing a manuscript based on these results. The students gathered extensive experience not only in the data analysis but also in understanding the physics behind XANES, and in the importance of studying heteroatoms, such as sulfur, in fossil-fuel materials.

Presentations

The PI presented an invited oral presentation at the Annual American Chemical Society meeting in New Orleans in March of 2018. Later, in July 2018, the PI did another oral presentation at the Annual International Petrophase Conference in Deer Valley, Utah. The presentations were very well received, and she made several new contacts from interested collaborators.

Two conferences abstracts and presentations:

1. "Microprobe XANES studies of sulfur chemistry of different shales", S. Mitra-Kirtley, W. Smith, S. C. Fakra, J. Birdwell, and A. Pomerantz, Annual Petrophase Conference, Deer Valley, Utah July 2018.
2. "An overview of the utility of sulfur XANES in the study of fossil fuels", S. Mitra-Kirtley, ACS Annual meeting, March 2018.

The next step of the project will be to

1. Collect more data at LBL during a future beam time. The PI has submitted another proposal to LBL for additional beamtime for studies on separated inorganic and organic shales.
2. Analyze all the data for new results and trends.

Figure 1: A typical shale spectrum fitted with a combination of several sulfur standards

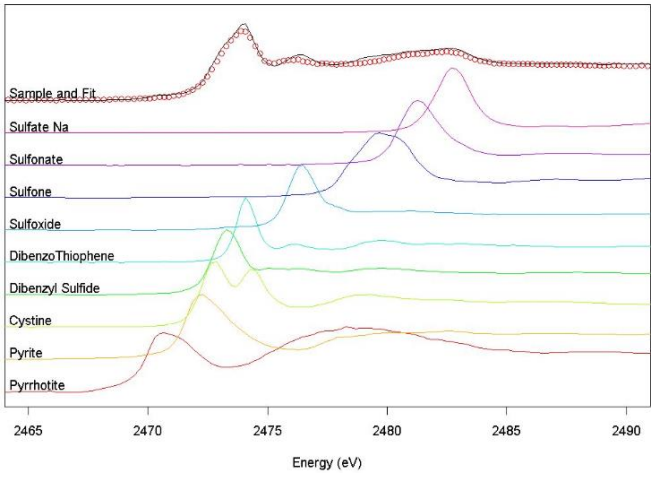

Table I: A typical set of analysis results from different spots of the same shale sample showing variation of sulfur chemical species.

Sample	Pyrrhotite	Pyrite	Sulfur (elem	Dibenzyl Sul	Dibenzothio	Sulfoxide	Sulfite	Sulfone	Sulfonate	Sulfate
2	4.28	0.00	0.00	36.01	20.61	10.69	2.54	0.00	2.63	1.68
3	1.09	70.06	0.00	1.26	10.60	5.55	3.42	5.61	0.22	1.70
4	0.00	83.36	0.00	2.31	6.05	0.38	0.71	1.91	0.71	2.48
5	0.00	0.00	0.00	35.11	57.23	0.00	0.00	0.00	3.86	3.80
6	0.00	0.00	0.00	49.40	37.13	3.67	0.71	0.00	4.58	3.65