X-ray analysis of reactive C-, N-, P-, and S-functional groups in NOM

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NOM plays an important role in many biogeochemical processes, and the conentration and chemistry of functional groups of NOM dictate their role in different processes. Traditional laboratory techniques, such as NMR and IR, have been used for decades to examine the functional group composition of isolated NOM. In the last decade, synchrotron based X-ray absorption spectroscopy (XAS) and spectromicroscopy methods allowed the examination of functional groups of NOM in their pristine state in soils and sediments at nanometer resolution. A discussion of XAS of reactive functional groups in NOM and their cycling in terrestrial systems will be presented.

Using XAS, we examined isolated NOM from different environments, and NOM in selected soils without any isolation. The XAS of several simple molecules containing different C-, N-, P-, and S-groups were also examined, and their spectra helped in interpreting the electronic states of different functional groups of NOM. X-ray spectra were also collected in different ways (using electron and fluorescence yield, and transmission) to identify the best detection schemes.

While several functional groups are identified using XAS, the ability to detect different C-moieties with X-rays is not as good as NMR. However, XAS contributes new information on the aromatic-N, amides, and nitrosyls. The detection of P groups using XAS is at par with that of NMR. However, small variations in the XAS of P can be used to detect the bonding environments of phosphate or phosphonate groups. The S-XAS spectra of NOM provide unique information on both the reduced and oxidized functional groups of S.

The electronic transitions, probed using XAS, are highly sensitive to small changes in the local coordination environments of functional groups, and the X-ray spectra change with changes in the protonation state, metal complexation (type of metal, and the number of metals), and symmetry of functional groups. The X-ray spectra are also sensitive to sample thickness and the concentration of the reactive groups, which can influence the relative concentration estimates. Ignoring these variations can result in the incorrect identification of the functional groups.

Geochemical monitoring of reactive percolation experiments using carbon stable isotopes

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Reservoir petrophysical property changes (permeability/porosity) are crucial issues, which need to be considered in carbon capture and storage (CCS) and enhanced oil and gas recovery (EOR and EGR). The potential hydrodynamic and geochemical reactions during such initiatives need to be well understood for planning, as well as for monitoring purposes. CO_2-rock-brine interactions are often analysed using geochemical parameters such as ion concentration changes. Stable isotope measurements of carbon ($\delta^{13}C$)are currently used as a method to montor and quantify geochemical changes during CO_2-injection. The applicability of using these isotopes as an additional and new monitoring tool to verify permeabiliy changes in the host rock has been tested in a series of laboratory experiments with a new reactive percolation bench, ICARE 4. Reservoirs, considered suitable for CO_2 injection, often host carbonate phases in contact with brine. Carbonate dissolution, plays a major role in host rock permeability changes during CO_2 injection. In order to test the geochemical effects of such a scenario, supercritical CO_2 was injected into brine in contact with quarzitic limestone. Results indicate good correlations between permeability, $\delta^{13}C$, DIC and calcium concentration data. Once CO_2-breakthrough occurred, permeability increased from a minimum of 0.1 millidarcy (mD) to a maximum of ~ 1.4 mD. This was accompanied by a $\delta^{13}C_{DIC}$ increase from ~ -5 ‰ to 0 ‰; DIC concentration increase from 0 mg L^{-1} to 3000 mg L^{-1} and a calcium concentration increase from below 100 mg L^{-1} to ~ 1400 mg L^{-}. These first data imply that $\delta^{13}C$ is a valid monitoring parameter for observing critical geochemical changes indicating CO_2 rock-brine interaction, which may be used to verify permeability development during CO_2 injection.