

Preservation and enrichment mechanisms of organic matter in muddy sediment and mudstone

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The paper deals with the study of interaction of clay mineral with organic matter under different sedimentary environments using multidiscipline research methods and a unique and systematic procedure. The clay fractions of muddy sediments and mudstone have remarkably higher contents of TOC and chloroform-asphaltum A than the coarse fractions. About 76.92-97.44% of TOC contents are enriched in the fine clay fractions, suggesting that clay plays a key role in organic matter enrichment in sediment and dissolvable organic matter dominates the adsorbed component. The interlayer space of clay minerals in mudstone show systematic and regular changes revealed by the XRD curves of unprocessed and H₂O₂- and chloroform-asphaltum- processed samples under temperature of 250°C—550°C. The interlayer space varied from 1.43nm in 250°C to 1.00 nm in 550°C, which is obviously different from smectite and illite that keep on 1.00 nm from 250°C to 550°C. This observation clearly indicates that the adsorbed matter in the interlay space of clay minerals is organic matter, i.e. organic matter can be tightly incorporated into clay minerals to form organo-clay complexes. The DTA curves of unprocessed and processed samples occur several radiative peaks indicative of organic matters in which the 350°C peak stays extraordinary stable, which is in accordance with the XRD observations. This further suggests that organic matter can reside in the interlayer space of clay mineral and form organo-clay matter.

The extraordinary stable interlayer space of clay mineral and the characteristic radiative peak in 350°C in different processed muddy samples demonstrate that organic matter in mudstone is primarily resided in the interlayer of clay minerals to form stable organ-clay complexes, not simple physical adsorbed in the surface of clay minerals. Organic matter can enter interlayer of clay minerals and the formed organo-clay complexes are especially stable in muddy sediment and mudstone, and resistant to depositional and post-depositional alterations. Our findings may have great implication on the estimation of carbon budget in sedimentary strata, especially for the study of global carbon cycle.

Local structure of carboxylic acid groups in natural organics

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Carboxylic acids play a major role in the acidity and reactivity (e.g., metal binding affinity) of natural organic molecules (NOM) in the environment. The chemical behavior of a carboxylic acid is largely influenced by other functional groups neighboring the carboxyl, but little is known about these “local structures” in NOM. Infrared spectroscopy (IR) has proven to be ideal for selectively probing carboxyl groups in NOM, due to their high polarity. Additionally, researchers have shown that the asymmetric stretching vibrations of the carboxylate anion are sensitive to local carboxylate structure (Cabaniss, 1998). In this study, we use the IR spectral signature of the carboxylate to infer structural environments in NOM, including six IHSS soil and fluvial humic substances, and an unaltered pine forest leaf leachate sample.

Results

Comparison of the asymmetric stretching frequencies of the simple organic acids with those of the NOM samples, which occur near 1580 cm⁻¹, suggests that the dominant carboxylic acid contributions are aliphatic, with oxygen (-OH, -OR) and/or carboxylic substitutions α to the carboxyl. Unsubstituted aliphatic acid bands occur too low (~1550 cm⁻¹) and, though likely present in small quantities, do not constitute the majority. Salicylate-type groups may also be present in high quantities, though aromatic carboxyls do not appear to be dominant. Preliminary long-range ¹H-¹³C NMR correlation (HMBC) experiments also point to a predominance of substituted aliphatic carboxylates.

Impacts

Oxygen functional groups neighboring a carboxylic acid tend to increase acidity and may participate in metal chelation. These results will therefore greatly impact further study and modeling of natural organic matter processes.

References

Cabaniss S.E., Leenheer J.A., and McVey I.F. (1998)
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