

Dynamics and structure of interlayer H₂O in K-saturated hectorite probed by ²H and ³⁹K NMR and neutron spin-echo (NSE) spectroscopy

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²H NMR spectroscopy of K-hectorite/water paste indicates the existence of two unique environments for H₂O in the system: one structurally and dynamically consistent with bulk water between the particles and one attributable to H₂O confined in the clay interlayer. The confined H₂O experiences anisotropic motion between -50 and 0°C via fast rotation (>2 MHz). The spectral changes between -10 and 0°C are interpreted as 'melting' of free and confined H₂O, and as a likely indication of the onset of molecular diffusion. At and above 10°C, all H₂O environments experience motion in excess of 300 kHz through at least three NMR-indistinguishable mechanisms, including translational diffusion of unconfined H₂O molecules, exchange of free and confined H₂O near particle edges, and diffusive motion of H₂O molecules confined within the clay interlayers. The correlation between the rates of ²H and ³⁹K motion and the observed melting transitions for both spin populations strongly suggest that ³⁹K dynamics above the melting transition are linked to an increase in the motional freedom of H₂O.

The neutron spin-echo (NSE) incoherent neutron scattering results for the same K-saturated hectorite sample (79% relative humidity) at $Q=1\text{\AA}^{-1}$ are consistent with the NMR findings and show that the characteristic times of H₂O diffusional relaxation vary over two orders of magnitude from 1.1 ns at -50°C to 0.008 ns at 50°C. A more detailed NSE study covering wider ranges of Q -values and hydration states is planned to fully understand and quantify the dynamics of H₂O molecules in this clay.

The effects of early diagenesis on the composition and $\delta^{13}\text{C}$ signal of lignin from two marsh plants

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Salt marshes constitute productive yet fragile ecosystems at the interface between the land and the ocean. Decomposition of plant material at these sites critically shapes seasonal and long-term cycling of both carbon and major nutrients.

Here, we present a study to quantify the rate of degradation, in concert with the alteration of geochemical characteristics of decomposing plant material. *Spartina alterniflora* and *Juncus roemarianus* leaves were incubated under three different environmental conditions over one year to examine the effect of decomposition on the lignin and isotopic compositions. Litter bags were placed in aerated, oxic seawater in the dark, as well as buried in both surface (0-5 cm) and deep (> 10 cm) sediments of a tidal creek on Sapelo Island, GA. Changes in total organic carbon (OC), bulk tissue $\delta^{13}\text{C}$, and lignin (Λ_6) were monitored.

The extent of decomposition varied with plant type and environment, with the greatest loss of OC occurring in aqueous system for both *S. alterniflora* and *J. roemarianus*. Shifts in bulk tissue $\delta^{13}\text{C}$ values were also dependent on plant type and environment, with greater shifts occurring for *S. alterniflora* than for *J. roemarianus*, and in the aqueous system relative to the sediment incubations. The bulk tissue $\delta^{13}\text{C}$ value of *S. alterniflora* was consistently depleted with degradation, while *J. roemarianus* tissues only exhibited a significant enrichment in $\delta^{13}\text{C}$ during aqueous decomposition. Loss of lignin content was greater for *S. alterniflora* than for *J. roemarianus* and unlike total OC, lignin loss was somewhat similar in all systems.

Compound-specific $\delta^{13}\text{C}$ analysis of lignin-derived phenols indicated variable changes as a result of degradation. The major *S. alterniflora* lignin constituents, vanillin, syringaldehyde, p-coumaric acid, and ferulic acid, were depleted in the aqueous setting by 2‰ to 7‰. However, when incubated in the sediment, the major lignin constituents of *S. alterniflora* exhibited little isotopic alteration, despite large lignin losses, and at most were enriched by 2‰. In contrast, lignin compounds of *J. roemarianus* tissues exhibited smaller and opposite shifts in $\delta^{13}\text{C}$ signals compared to *S. alterniflora*.

These organic carbon characteristics were used in a mixing model to assess the relative contributions and diagenetic losses of different C sources in marsh sediment. These findings indicated that organic matter of marine origin and of C4 plants dominated the study site sedimentary organic carbon.