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The stability of methane hydrate intercalates of montmorillonite and nontronite: Implications for carbon storage in ocean-floor environments

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ABSTRACT

Sodium-rich montmorillonite, Na-exchanged montmorillonite, and Na-exchanged nontronite form intercalate complexes with methane hydrate, identified by a characteristic *d*(001) value of ~2.2 nm. The upper stability of both Na-rich montmorillonite–methane-hydrate complexes is nearly identical to that of methane hydrate, whereas that of Na-exchanged nontronite–methane-hydrate complex is ~1 °C lower. The low-temperature stability of these complexes is controlled by dehydration reactions of the montmorillonite and nontronite. At temperatures of 2 °C, the *d*(001) value of the montmorillonite complex decreases step-wise with decreasing temperature from ~2.2 nm at 2 °C to 1.6 nm at ≤–5 °C, indicating that H_2O is progressively expelled from the interlayer. All methane is probably expelled at ~0 °C. The *d*(001) value of the nontronite complex did not show a similar step-wise reduction and, consequently, the lower stability of this complex is not well established. We conclude that under conditions of reduced salinity, smectite may sufficiently swell and intercalate with methane hydrate in an intermediate to deep-ocean floor environment. Consequently, these smectite–methane-hydrate complexes in the sub-ocean-floor surface may store substantial quantities of carbon.

Keywords: Methane hydrate, smectite, carbon cycle, carbon storage