

### Abnormal Cage Occupancy of Methane Hydrate in Clay Sediments

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Natural methane hydrates in marine clay sediments show heterogeneous phase behavior with high complexity, mainly in the negatively charged interlayer region. Although a small number of computer simulation and model studies are reported, the real clay interlayer effect on natural methane hydrate formation and stability remains still much unanswered. We first observed the chemical shift difference of <sup>27</sup>Al, <sup>29</sup>Si, and <sup>23</sup>Na between dry clay and clay containing intercalated methane hydrates (MH) in the interlayer. We also measured the solid-state <sup>13</sup>C MAS NMR spectra of MH in Na-montmorillonite (MMT) and Ca-montmorillonite (MMT) to reveal unusual methane popularity established during intercalation and performed cryo-TEM and XRD analyses to identify the morphology and layered structure of the intercalated methane hydrate. The present findings strongly suggest that the real methane amount contained in natural MH deposits should be reevaluated under concern of the compositional, structural, and physical aspects of clay-rich sediments. Moreover, the intercalated methane hydrate structure should be seriously considered for building the production technologies of the deep-ocean methane hydrate.