New gas-hydrate phase: Synthesis and stability of clay–methane hydrate intercalate

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ABSTRACT

Intercalated Na-rich montmorillonite–methane hydrate was synthesized for the first time. The upper limit of stability for the intercalate in pressure and temperature is parallel to that of methane hydrate but at temperatures that are ~0.5–1 °C lower than for methane hydrate. The low-temperature stability of the intercalate is at −11.5 ± 3 °C at ~40 bar, where methane and some H_2O are expelled from the region between the silicate layers (interlayer). In contrast, methane hydrates do not dissociate at these low temperatures. We conclude that at conditions similar to where methane hydrate is stable, smectite may intercalate with methane hydrate and provide additional sinks for methane. The limitation in the stability of smectite–methane hydrate intercalate at low temperatures suggests that, if present in large quantities, it may release at decreasing temperatures sufficient methane to ameliorate a planetary cooling event.

Keywords: clathrate, clay, methane, gas hydrate, montmorillonite, ocean floor, permafrost, smectite, synthesis.

INTRODUCTION

Although gas hydrates have been known for almost two centuries (Davy, 1811), it was recognized only recently that methane hydrate compounds are ubiquitous in continental shelf and ocean-floor sediments and that, combined with methane gas in these sediments, these compounds may represent the main methane repository on Earth (MacDonald, 1990). The possibility that structurally bound methane is present in other solid phases such as clay minerals has been considered (e.g., Gist, 2000; Park and Sposito, 2000; Titiloye and Skipper, 2000), but until now such materials have not been synthesized.

Swelling clays such as montmorillonite usually contains multiple planes of weakly bonded H_2O in the interlayer between the 2:1 (silicate) layers. Because of the weakness of the atomic forces between H_2O and the 2:1 layer, we thought it likely that the stability of a methane hydrate component in a montmorillonite–methane hydrate intercalate would be similar to that of methane hydrate. Therefore, we conducted experiments involving Na-exchanged montmorillonite at temperature and methane pressure conditions that are well within the stability field of methane hydrate (Jager and Sloan, 2001; de Roo et al., 1983). In this paper we present our results on the first synthesis of an intercalated Na-rich montmorillonite–methane hydrate.

EXPERIMENTAL PROCEDURE

Gas hydrates and, by inference, montmorillonite–methane hydrates are not likely to survive exposure to ambient conditions. Therefore, an environmental chamber (Koster van Groos et al., 2003) was developed to analyze in situ materials by powder X-ray diffraction (XRD). The chamber allows pressures to 100 bar and temperatures from −50 to 200 °C and is equipped with Be windows to minimize X-ray adsorption. The chamber is mounted onto a Siemens Theta-Theta powder X-ray diffractometer, model D-5000. The operating conditions were 45 kV and 25 mA, using Cu radiation and a graphite monochromator. A glass specimen slide with an oriented clay aggregate was placed at the center of the chamber, which is the standard geometry for the reflecting condition. The glass slide rested on a Cu base plate to assure that the temperature was uniform. A thermocouple well in the chamber housing allowed insertion of a thermocouple to within 2 mm of the sample. In all experiments, wetted absorbent material was placed in the bottom of the chamber so that the pressurizing gas was water saturated. Temperature was controlled using a Neslab RTE-111 refrigerating bath/circulation unit, which is precise to within 0.1 °C. Sample temperatures were determined using a chromel-alumel thermocouple, placed at 2 mm from the center of the sample. The temperature was calibrated against the melting point of ice and is accurate to within 0.2 °C. Temperatures, therefore, are accurate to within 0.3 °C. Pressures were measured with a calibrated Heise gage and are believed accurate to within 0.2%.

The starting material in these experiments is Na-exchanged montmorillonite SWy-2 (Costanzo and Guggenheim, 2001), with a grain size <2 μm, hereafter referred to as NaSWy2. This material was selected because Na-rich montmorillonite can easily accommodate multiple planes of H_2O. The Na exchange was performed using three washings with a 1N solution of NaCl, after which the material was washed until the supernatant was chlorine free. The sample was spread as a thin water-rich paste onto a specimen slide, and dried to produce a clay aggregate mount where clay particles are oriented parallel to the glass surface. Proper orientation of the clay particles is essential because clay minerals are poorly crystalline and, thus, are weakly diffracting phases. Using the environmental chamber, the XRD pattern of the starting material at a relative humidity of ~100% and at ambient conditions was obtained (Fig. 1, plot a). XRD patterns were obtained for each experiment before the chamber was sealed to confirm proper orientation of the clay. Next, the sample was sprayed with water by a neb-

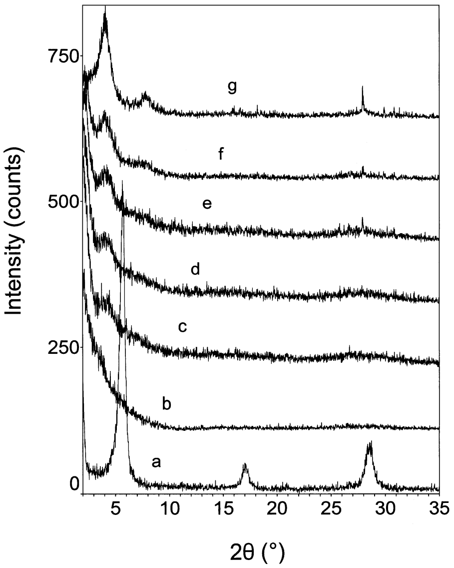

Figure 1. X-ray diffraction patterns of starting material (a, b), and of formation of montmorillonite–methane hydrate intercalate with respect to time at 41.4 bar methane pressure (c–g). (a) NaSWy2 at 100% humidity at 22 °C and 1 atm, peaks at 2θ of ~5.5°, 17°, and 28.5° represent (001), (003), and (005) reflections, respectively. (b) NaSWy2 with additional H_2O at 22 °C and 1 atm. Note lack of distinct peaks but enhanced reflections at 2θ < ~7°. Lack of peaks indicates random interstratification of various H_2O planes between 2:1 layers. c–g: Patterns after (c) 1 h at 1.0 °C; (d) 15 h at 1.0 °C; (e) 28 h at −7.0 °C; (f) 45 h at −7.0 °C; (g) 126 h at −8.0 °C. Note increase over time in peak at 2θ = ~4° (*d* ~22 Å) and, more weakly, in peak at ~8° (*d* ~11 Å). Note also decrease in intensity of peaks (attributed to interlayer H_2O) near 2.5° (*d* ~ 36–41 Å). Developing peak at ~27° represents incipient growth of methane hydrate.

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ulizer to assure that the starting material contained sufficient water to expand the interlayer of the montmorillonite structure and mounted, after which the environmental chamber was sealed. Before the chamber was brought to the desired temperature and pressure, the sample was analyzed by XRD to verify that the clay interlayer had expanded to *d* values >35 Å. The presence of either one peak (or more) at $2\theta < 2.5°$ (*d* values >35Å) or a broad increase in intensity at low angles (Fig. 1, plot b) in the initial XRD patterns confirmed that the added water had become incorporated in the interlayer of NaSWy2.

In most experiments, the chamber was pressurized with methane gas to ~40 bar and cooled to 1 °C for 1 h, after which temperature was cycled 4–8 times between 1 and 4 °C, following recommendations for the synthesis of methane hydrate (Smelik and King, 1997). Duration of each cycle was ~15–30 min. After each cycle, the sample was analyzed by XRD between 2° and 7°. Cycling was terminated when either a 4° peak was present in the XRD pattern or when the sample lost orientation. In other experiments, the sample was held at temperatures between −7 and 1 °C for several days or until a 4° peak appeared. It was not clear if the temperature cycling in this study is a requirement for the formation of this reflection. The overall success rate was ~25%. This low success rate is attributed to the difficulty in controlling the amount of water sprayed onto the sample. In many experiments, it was observed that the clay particles lose orientation, and it was impossible to observe the 4° peak. This loss in orientation is most likely caused by too much water on the sample. In contrast, in several other experiments the 4° peak was not formed, although the clay particles retained proper orientation. In these experiments, the lack of H_2O appears to prevent formation of the 4° peak.

After completion of an experiment, the sample was quickly removed from the chamber for inspection. In experiments where methane hydrate was present, we observed an effervescent, white gel-like material on the sample, representing the hydrate phase. In several instances no identifiable methane hydrate was observed, but nevertheless, a large number of small bubbles evolved from the montmorillonite sample. This behavior suggests that methane was evolving from the clay, although the possibility that interstitial methane hydrate was present but not detected by XRD cannot be excluded.

RESULTS

In a series of experiments at 41.4 bar methane pressure and at 1 to −8.0 °C, the low-angle peaks attributed to a high H_2O content diminished in intensity with time, while simultaneously a peak at 4° and a weaker peak at 8° formed and intensified (see Fig. 1, plots c–g for XRD patterns after 1, 15, 28, 45, and 126 h). These peaks represent *d* values of ~22 and ~11 Å, respectively. These *d* values suggest the formation of a new clay phase in which these values represent the (001) and (002), respectively, assuming that this phase has a layer structure analogous to montmorillonite. With increasing temperature, this phase became unstable. For example, at 32.9 bar and between 0.8 and 1.85 °C, the 4° and 8° peaks gradually decreased in intensity and disappeared (Fig. 2).

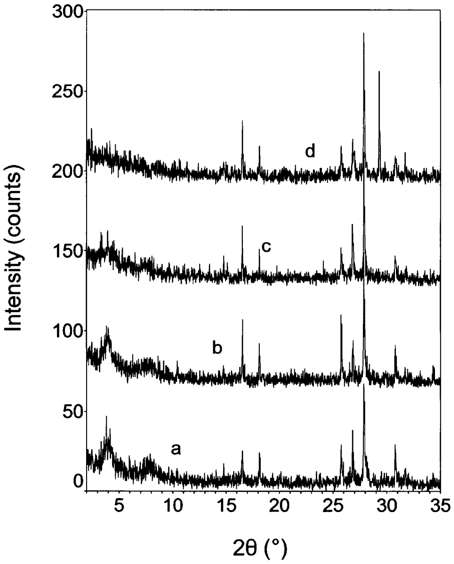

Figure 2. Disappearance of montmorillonite–methane hydrate intercalate with increasing temperature at 32.9 bar. Plots a–d at various temperatures: (a) 0.8 °C; (b) 1.6 °C; (c) 1.75 °C; (d) 1.85 °C. Note diminishing of peaks at 2θ of ~4° and ~8° and their disappearance in d. Sharp peaks near 17° and 25°–35° represent methane hydrate.

A *d* value of ~22 Å is significant, because it may represent the combined minimum thickness of a structural unit involving methane hydrate (cell dimension of ~12 Å; Hirai et al., 2000) and montmorillonite (*d* value of ~9.8 Å of the 2:1 silicate layer; Bailey, 1984). This strongly suggests the formation of a new Na-montmorillonite phase with methane hydrate intercalated between the 2:1 layers. This phase (montmorillonite–methane hydrate intercalate) hereafter is referred to as MMH. A *d* value of ~22 Å may also be produced by an appropriate hydration state of NaSWy2. To investigate if both the growth and the disappearance of the peaks at 4° and 8° are dependent on pressurized methane, a series of experiments was made with helium, which does not form hydrates at these conditions. Montmorillonite was hydrated to show a peak at 4°, and a series of experiments was made at 0 to 20 °C and 41.3 bar He pressure (Fig. 3, plots a–f), and at 20 °C and 1 atm He (Fig. 3, plot g). These experiments show that the XRD patterns are not significantly affected by either changes in temperature or pressure when in the presence of an inert gas. On the basis of these experiments, we conclude that the formation of MMH is dependent on the presence of methane.

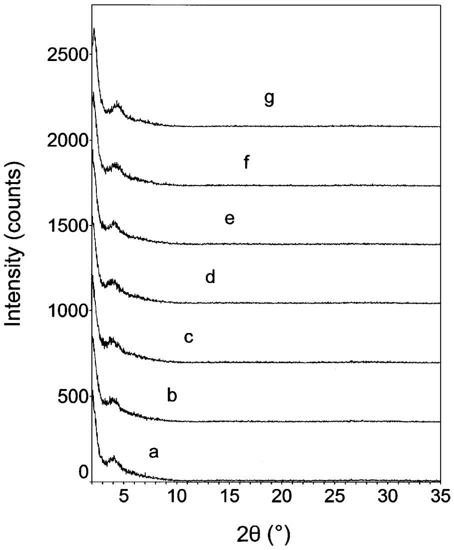

Figure 3. Effect of He pressure and temperature on (001) reflection (~4°, *d* ~22 Å) of montmorillonite. Pressure was ~42 bar He in a–f and 1 atm He in g. Temperature was raised after each pattern was taken. Patterns after (a) 18 h at 0 °C; (b) 1 h at 3.3 °C; (c) 17 h at 4.0 °C; (d) 1 h at 10 °C; (e) 16 h at 15 °C; (f) 2 h at 20 °C; (g) 56 h at 20 °C and 1 atm He. Compare this figure to Figure 2, where peaks at 2θ at ~4° and ~8° disappear above 1.75 °C.

In the next series of experiments, the temperature and pressure stability of MMH were determined. The results, presented in Figure 4, show that the high-temperature stability of MMH is pressure dependent, MMH disappearing at 1.8 °C at 32.9 bar, at 2.3 °C at 35.9 bar, at 3.8 °C at 41.4 bar, and at 5.6 °C at 50.0 bar. In the experiments at 35.9 bar, decreasing the temperature from 2.6 to 1.0 °C reversed the disappearance of MMH. In these experiments, methane hydrate was present even when MMH became unstable. A slight further rise in temperature with ~1 °C resulted in the loss of methane hydrate. The low-temperature stability limit of MMH was not investigated in detail, although a few experiments at much lower temperatures, between −8.5 and −14.5 °C, and at 41.4 bar showed that MMH disappeared while, simultaneously, peaks representing ice (H_2O) developed. In these experiments, methane hydrate was not affected. Low-temperature studies of montmorillonite at 1 atm (Ahlrichs and White, 1962; Anderson and Morgenstern, 1973) showed that, in the presence of excess H_2O, the montmorillonite structure expels part of its H_2O and collapses to a *d* value of ~19 Å at 0 °C and to ~16 Å

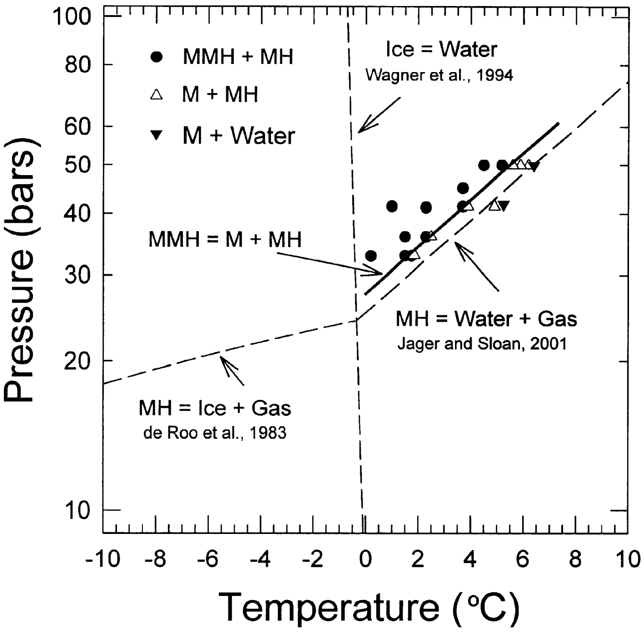

Figure 4. Pressure-temperature (*P-T*) relations for upper-temperature stability of montmorillonite–methane hydrate intercalate (MMH). Shown also are dissociation relations of MH and *P-T* curve for melting of ice.

at -10 °C. It seems likely that, at the lower temperature boundary of MMH, a similar expulsion of interlayer material occurs. Thus, the stability of MMH is limited at the high-temperature boundary by the expulsion of methane from the interlayer component and at low temperatures by the expulsion of H_2O.

The phase relationships of MMH and methane hydrate (MH) are compared in Figure 4, which shows the limiting reactions MMH = MH + M (montmorillonite), MH = water + gas (Jager and Sloan, 2001), and MH = water + ice (de Roo et al., 1983), as well as the melting curve of ice (ice = water) Wagner et al., 1994). Note that our data for the upper stability of methane hydrate are in excellent agreement with earlier work.

DISCUSSION AND CONCLUSIONS

The parallelism of the upper-temperature stability limit of both MMH and methane hydrate is striking. This suggests that the atomic forces between H_2O and methane are not significantly affected by the presence of the montmorillonite component and confirms that a methane hydrate component is present between the 2:1 layers of Na-montmorillonite. We note that the computer simulation model of Titiloye and Skipper (2000) requires that ''Methane particles are solvated by approximately 12–13 water molecules, with six oxygen atoms from the clay surface completing the coordination shell,'' resulting in an $\sim$15 Å layer spacing. We have no direct information about the structure of this methane hydrate component. However, we note that the $\sim$15 Å layer spacing is inconsistent with our experimental data, which show an $\sim$22 Å layer spacing. Thus, it remains to be determined whether the silicate ring of the 2:1 silicate layer acts as part of a cage or whether tetrakaidecahedral ($5^{12}6^2$) or pentagonal dodecahedral (5^{12}) cages exist (Hirai et al., 2000; Gutt et al., 2000) in the interlayer. Using chemical modeling techniques, we expect to clarify the structure of the interlayer hydrate complex.

We conclude that the experimental evidence presented in this study shows that, at relatively low temperatures and modest methane pressures, Na-montmorillonite–methane hydrate intercalate is stable with respect to an assemblage composed of montmorillonite and methane hydrate. This conclusion is based on XRD analysis and on phase equilibria considerations. The observation that the clay sample appears to produce gas bubbles when exposed to ambient conditions in the absence of identifiable methane hydrates provides important supplementary evidence for the formation of MMH.

The synthesis of Na-montmorillonite–methane hydrate intercalate indicates the existence of a new class of hydrates involving swelling clays with intercalated hydrocarbon hydrates. Primary areas for the possible occurrence of these materials are ocean floor sediments and permafrost (Majorowicz and Osadetz, 2001), where swelling clays and methane are known to be abundant. It is interesting to note that clay–gas hydrate intercalates have densities similar to those of ocean-floor clay sediments, whereas gas hydrates are less dense than seawater and require ''anchoring'' with sedimentary material to prevent buoyancy. It should be recognized, however, that the composition of swelling clays on the ocean floor is much more complex than the montmorillonite used thus far.

The dissociation of MMH between -8.5 and -14.5 °C at 41.4 bar to form montmorillonite, ice, and methane gas is an intriguing property of this gas hydrate phase, especially if the methane component is not immediately captured by H_2O to form methane hydrate. Thus, if clay–methane hydrates are present in significant quantities near a planetary surface, cooling of this surface may partly reverse the sequestration of methane. Considering the efficacy of methane as a greenhouse gas, this process could buffer the cooling of a planet during deep-freeze conditions.

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