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Stability of methane clathrate hydrates in Titan's interior: Experimental constraints at high pressure.

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1. Introduction

The origin of Titan's atmospheric methane has long been debated. Its continuous destruction by photochemical processes in the upper atmosphere suggests that it is renewed by internal outgassing in order to maintain its abundance at the observed value. However, the reservoir location in the interior as well as the timing and mechanism of outgassing remain unconstrained.

Methane may be stored in the interior in the form of clathrate hydrates. Clathrate hydrates are non-stoichiometric inclusion compounds with an ice lattice forming molecular cages, in which gases, here methane, are trapped. Previous studies indicated that methane hydrate may be stable at high pressure [1, 2], but their dissociation temperature has never been determined at pressure above 1.5 GPa.

Gravity measurements performed by the Cassini Radio Science Experiment [3] indicate that Titan's interior is only moderately differentiated, suggesting that some internal regions may have remained undifferentiated and relatively cold during most of Titan's evolution. This is also supported by accretion models, which show that the deepest part of Titan's interior is undifferentiated at the end of the accretion stage. In order to determine the stability of methane in undifferentiated layers of Titan and on the fate of methane during the differentiation process, we have conducted high pressure experiments in a Diamond Anvil Cell on synthesized samples of methane clathrates. We determine the temperature at which methane clathrate dissociates and discuss the implications for the methane cycle on Titan.

2. Experimental method

In order to study the dissociation curve at temperature and pressure conditions relevant for Titan's interior, we synthetized methane hydrates in a pressurized vessel and then studied them at high pressure - high temperature in a Diamond Anvil Cell. Raman spectroscopy is used as a tool to discriminate methane trapped into clathrate structures from solid methane mixed with solid water ice and their respective structures at high pressure (between 1.5 and 5 GPa). We also conducted a high pressure study of pure methane to establish the Raman spectra (Figure 1a).

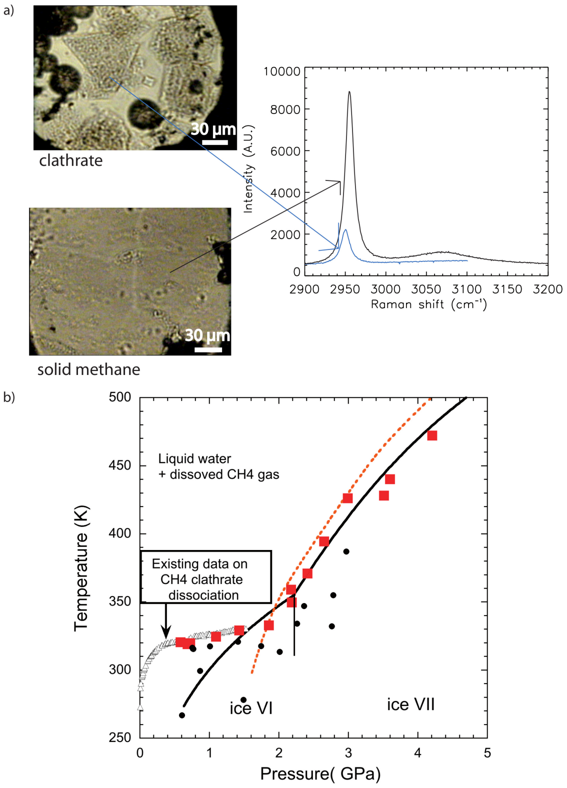

Figure 1: (a) Raman spectra of methane hydrate (blue) and solid methane (black) at high pressure (3.9 GPa) (b) Dissociation curve of methane hydrates compared to the melting curve of water ices. Black diamonds are experimental data obtained by [2] up to 1.5 GPa and the melting curve of methane is plotted in orange.

3. Results

As illustrated on Figure 1a, pure solid methane spectra are different at high frequencies (2900-3300 cm^{-1}) from those of the methane hydrates. The primary peak is shifted by about 4 cm^{-1} in the MH spectra relative to the solid methane spectra. The solid methane spectra also exhibit a secondary peak, which is missing in the MH spectra. These spectra differences permit us to distinguish methane hydrate from a mixture of solid methane and ice [4, 5] and to ensure that we really observe MH dissociation when increasing the temperature. Raman spectra from methane hydrates MH-II and MH-III have also been obtained and they have been used to confirm the phase transition occuring at 2 GPa. As displayed on Figure 1b, we have a good agreement with published data at pressure below 1.5 GPa. In this pressure range, the dissociation of MH is above the melting point of water ice. At higher pressure (> 1.5 GPa), our experiments show that MH destabilizes at temperature very close to those of water ice melting.

This has important consequences for the evolution of methane in Titan's interior. As long as the internal temperature is below the melting point of water, methane should remain trapped in the deep interior in the form of clathrate hydrate. If the interior differentiates slowly without ice melting, large quantities of methane may still be trapped in the outer part of the rock-rich core, and methane clathrate should slowly migrate from the deep interior to the outer ice shell. On the other hand, if significant ice melting occurs during the differentiation process, all the methane should be extracted very rapidly from the core. A large fraction of the released methane should be retrapped in the form of clathrates as they are stable in the ocean conditions ($P < 1$ GPa), and could form a thick layer of methane clathrate above the ocean (e.g. [6]).

4. Conclusion

We have conducted the first high-pressure high-temperature studies on the destabilization of methane hydrates at pressure above 1.5 GPa and we show that their destabilization occurs close to the melting point of ice.

These results are also applicable to water-rich exoplanets, where methane hydrates may remain stable at high pressure and affect the composition of their atmosphere.

Acknowledgements

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