

Dissociation temperatures of methane hydrates at high pressure: Implications for the differentiation of Titan's interior

L. Bezacier, G. Tobie, O. Bollengier, O. Grasset, E. Le Menn and A. Oancea

Université de Nantes, CNRS, Laboratoire de Planétologie et de Géodynamique de Nantes, UMR 6112, Nantes, France

(lucile.bezacier@univ-nantes.fr / Fax: +33-251125268)

Abstract

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 to the observed value. However, the reservoir localization in the interior as well as the timing and mechanism of outgassing remain unconstrained. 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 e.g. [Monteux et al., this meeting] of the interior. In order to determine the stability of methane in undifferentiated layers of Titan and its potential effect of its dissociation on the differentiation process, we conduct high pressure experiments in a Diamond Anvil Cell on synthesized samples of methane clathrates.

Clathrate hydrates are non-stoichiometric inclusion compounds with an ice lattice forming molecular cages, in which gases, here methane, are trapped. Clathrate hydrates are common on Earth and are believed to play a key role in the origin and storage of volatiles in icy moons [2]. Many studies have been carried out in order to determine phase relations, crystal structures and physical properties of these clathrate hydrates. Most of them are focused on physical properties at low pressure and low temperature. Previous measurements on methane hydrates at high pressure show that they are stable at ambient temperature up to 42 GPa [4] with phase transitions reported at 0.8-1 GPa and 2 GPa [5], but their dissociation

temperature has been determined only up to 1.5 GPa [1, 2] (see Figure 1a). Before full separation of ice and rock on Titan, a large fraction of ice, and therefore a large fraction of methane, should exist at pressures larger than 1.5 GPa (see Figure 1b). Depending on the dissociation temperature relative to the melting temperature of high-pressure ices, the consequences for the core differentiation and the release of methane would be totally different.

In order to study the dissociation curve at temperature and pressure conditions relevant for the undifferentiated proto-core, we propose a synthesis of methane hydrates in a high pressure vessel and then a high pressure - high temperature study of the methane hydrates in a Diamond Anvil Cell. The Raman spectroscopy will be used as a tool to discriminate free methane gas from the methane trapped into the clathrates as well as their structures at high pressure (between 1.5 and 5 GPa). In a second step, the effects of CO₂, NH₃ and other contaminants will be studied. These results will also be applicable for water-rich exoplanets, where methane hydrates may remain stable at high pressure and affect the composition of their atmosphere.

Acknowledgements

The research leading to these results has received funding from the European Research Council under the European Community's Seventh Framework Programme (FP7/2007-2013 Grant Agreement no. 259285).

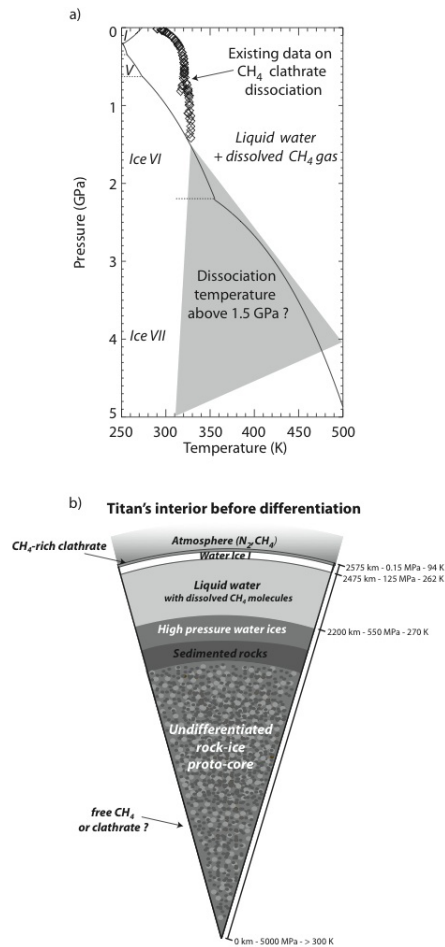


Figure 1: (a) Dissociation curve of methane hydrates compared to the melting curve of water ices and (b) possible internal structure before differentiation. Black diamonds are experimental data obtained by [2] up to 1.5 GPa.

References

- [1] Choukroun, M., Grasset, O., Tobie, G., Sotin, C.: Stability of methane clathrate hydrates under pressure: Influence on outgassing processes of methane on Titan. *Icarus*, pp 581-593, 2010.
- [2] Choukroun, M., Kieffer, S., Lu, X., Tobie, G.: Clathrate Hydrates in the Outer Solar System. In: Gudipati, M., Castillo-Rogez, J.C. (Eds), *The Science of Solar System Ices 3rd ed.*, Springer, 2011 (*in press*).
- [3] Dyadin, Y.A., Aladko, E.Y., Larionov, E.G.: Decomposition of methane hydrates up to 15 kbars. *Mendel. Comm.*, 7, pp. 34-35, 1997.
- [4] Iess, L., Rappaport, N. J., Jacobson, R. A., Racioppa, P., Stevenson, D. J., Tortora, P., Armstrong, J. W., and Asmar, S. W.: Gravity Field, Shape, and Moment of Inertia of Titan. *Science* 327, pp 1367-1369, 2010.
- [5] Hirai, H., Tanaka, T., Kawamura, T., Yamamoto, Y., Yagi, T.: Retention of methane hydrate up to 42 GPa. *Phys. Rev. B* 68, pp 172102, 2003.
- [6] Loveday, J.S., Nelmes, R.J., Guthrie, M., Belmonte, S.A., Allan, D.R., Klug, D.D., Tse, J.S., Handa, Y.P.: Stable methane hydrate above 2 GPa and the source of Titan's atmospheric methane. *Nature* 410, pp 661-663, 2001.
- [7] Lunine, J.I., and Stevenson, D.J.: Thermodynamics of clathrate hydrate at low and high pressures with application to the outer solar system. *The Astrophysical Journal Supplement Series*, 58, pp 493-531, 1985.
- [8] Tobie, G., Lunine, J.I., Sotin, C.: Episodic outgassing as the origin of atmospheric methane on Titan. *Nature*, 440, pp 61-64, 2006.