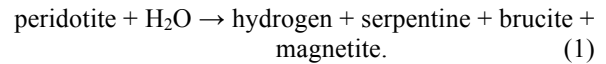**IS SERPENTINIZATION THE SOURCE OF TITAN'S ATMOSPHERIC METHANE?** O. Mousis[1,2], J. I. Lunine[1], M. Pasek[1], D. Cordier[3,4], J. H. Waite Jr.[5], K. E. Mandt[5], W. S. Lewis[5], and M.-J. Nguyen[5], [1]Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, USA (mousis@lpl.arizona.edu), [2]Université de Franche-Comté, Institut UTINAM, CNRS/INSU, UMR 6213, Observatoire des Sciences de l'Univers de Besançon, France, [3]Université de Rennes 1, Institut de Physique de Rennes, CNRS, UMR 6251, France, [4]Ecole Nationale Supérieure de Chimie de Rennes, France, [5]Space Science and Engineering Division, Southwest Research Institute, San Antonio, TX 78228, USA.

Introduction: The Saturnian moon Titan is the second largest satellite in the solar system and the only one that possesses a thick atmosphere. One of the most puzzling characteristics of this mainly nitrogen atmosphere [1] is the large abundance of methane present despite photochemical destruction and escape over the age of the solar system; a source much larger than the atmosphere is implied [2][3]. However, the source, which can be endogenous or exogenous, remains uncertain. It has been proposed that hydrothermal reactions in the interior of Titan could lead to the formation of H_2-rich fluids which may combine with ambient carbon dioxide to produce the observed atmospheric methane [4][5]. On the other hand, alternative scenarios suggest that methane was incorporated in the building blocks of Titan before its formation in the Kronian subnebula [6][7].

Deuterium fractionation during serpentinization reactions: Any scenario describing a possible origin for Titan's methane has to account for its present high D/H atmospheric ratio of $1.32^{+0.15}_{-0.11} \times 10^{-4}$ [8], which represents an enrichment of 4.5 to 7.2 times the protosolar value [9]. It has been proposed that this observed D/H enhancement could be the result of photochemical enrichment of deuterium through that isotope's preferential retention during methane's photolysis [10][11]. However, *Cassini-Huygens* data have been recently used to reexamine this possibility and it was shown that the photochemical enrichment of deuterium is not sufficient to explain the measured D/H value [9][12]. A possible fractionation between CH_3D and CH_4 during the escape process may slightly enhance the deuterium enrichment by a factor of at most 2.6 times the protosolar value [9], but is not sufficient to explain the observed D/H enhancement over the range of escape values proposed in the literature [9][12]. This suggests that D/H in methane is already substantially oversolar when released into the atmosphere of Titan.

Here, we examine the impact of the D/H value in methane on the proposed formation of methane in the interior of Titan from carbon dioxide or carbon grains via the hydrothermal alteration of peridotite [4][5][13]. In this scenario, the H_2 produced during the so-called "serpentinization" process in Titan would react with carbon grains or CO_2 to produce the methane [4][5]. In terrestrial oceans, hydrothermal fluids and seawater interact with peridotite via the following summary reaction [4][13]:

$$\text{peridotite} + H_2O \rightarrow \text{hydrogen} + \text{serpentine} + \text{brucite} + \text{magnetite.} \quad (1)$$

On Titan, a subcrustal liquid water ocean inferred from its asynchronous spin [14] would constitute the free-water reservoir susceptible to interact with rocks. During serpentinization reactions, residual water is deuterium-enriched at the expense of the initial reservoir of free-water. The fractionation factor, α, between OH-bearing minerals and water is then [15]:

$$\alpha_{r-w} = \frac{R_r^f}{R_w^f}. \quad (2)$$

The effect on the D/H ratio of the residual water of a D/H fractionation between the initial water and hydrated peridotite can be readily tested with the following mass balance equation that describes a batch equilibrium mechanism of both hydration and isotopic fractionation between given masses of rock and water:

$$M_w^i \cdot X_w^i \cdot R_w^i + M_r^i \cdot X_r^i \cdot R_r^i$$
$$= M_w^f \cdot X_w^f \cdot R_w^f + M_r^f \cdot X_r^f \cdot R_r^f \quad (3)$$

where M is the mass, X the mass fractions of hydrogen in water ($X_w^i = X_w^f = 1/9$) or rock ($X_r^f = 4/277$), R the D/H ratios before hydration reactions (i) and at batch equilibrium (f). If we neglect the likely small amount of water in primordial peridotites of Titan ($X_r^i = 0$), Eq. 3 can be expressed as:

$$R_w^i = \frac{M_w^f \cdot X_w^f \cdot R_w^f + M_r^f \cdot X_r^f \cdot R_r^f}{M_w^i \cdot X_w^i}. \quad (4)$$

Here, we postulate that the D/H ratio in the methane initially released from the interior is that acquired by hydrated rocks once equilibrium is reached during hydrothermal reactions. The D/H ratio acquired by hydrated rocks would then be preserved in the hydrogen produced from the alteration of peridotites and used in the recombination of CH_4.

The initial mass M_w^i of the free-water reservoir is expected to range between 1.79×10^{22} and 6.73×10^{22} kg. These values correspond respectively to the current and initial masses of the liquid water ocean, whose volume has decreased with time during the cooling of Titan [3][16]. Assuming that methane has been present continuously in the atmosphere of Titan since 4.5 Gyr, destroyed over Titan's history at the current photolytic destruction rate of 6.9×10^{13} molecules m^{-2} s^{-1} [17], the total mass of expelled methane is $\sim 2.17 \times 10^{19}$ kg. Assuming that the hydrogen from the methane is derived from serpentinization reactions only, the equivalent mass of produced H_2 is then 5.42×10^{18} kg. Depending on the composition of peridotite, key geochemical reactions [13] suggest that 4.5 moles of serpentine [$Mg_3Si_2O_5(OH)_4$] are produced per mole of H_2 released during hydrothermal reactions. Hence, the maximum mass of serpentine M_r^f is then 3.38×10^{21} kg, namely about 5% of Titan's rock mass, over 4.5 Gyr, including 10 wt% of H_2O extracted from the free-water reservoir [14]. Because $M_w^i \approx M_w^f >> M_r^f$ and $X_w^i >> X_r^f$, Eq. 4 can be simplified as follows:

$$R_w^i \approx \frac{R_r^f}{\alpha_{r-w}} \tag{5}$$

Equation 5 remains valid independent of the production timescale of methane in the interior of Titan because the mass of hydrated rocks is still small compared to that of the free-water. We consider two extreme values, 0.95 and 1.03, of the hydrogen fractionation α_{r-w} between serpentine and the free-water reservoir in the literature based on laboratory and field data made at temperatures ranging between 298 and 773 K [18]. When neglecting the possibility of photochemical enrichment of deuterium in Titan's methane, the values of R_w^i are about 10–20% lower than that corresponding to Standard Mean Ocean Water (SMOW). The discrepancy becomes even higher when using values of R_r^f that take into account the possibility of deuterium enrichment in Titan's methane, which is the most likely case. Here, the required values of R_w^i are more than 60% lower than the SMOW value.

Discussion: Our calculations show that if the methane of Titan is the result of serpentinization reactions in the satellite's interior, then any measurement of the D/H ratio in the satellite's water ice should be lower than the SMOW value. On the other hand, the measurement of a substantially higher D/H ratio in the water ice of Titan would imply that its methane originates from the solar nebula instead of Saturn's circumplanetary disk. The INMS instrument aboard the Cassini spacecraft has the capability to measure the D/H ratio in the icy grains embedded in the vapor plumes of Enceladus. This measurement would then provide a strong constraint on the origin of Titan's methane because Enceladus and Titan have probably been formed from similar planetesimals [7].

References: [1] Niemann, H. B., and 17 colleagues (2005) *Nature, 438*, 779-784. [2] Lunine J.I. and Atreya, S.K (2008) *Nature Geoscience, 1*, 160-164. [3] Tobie, G., Lunine, J. I., and Sotin, C. (2006) *Nature, 440*, 61-64. [4] Atreya, S. K., Adams, E. Y., Niemann, H. B., Demick-Montelara, J. E., Owen, T. C., Fulchignoni, M., Ferri, F., and Wilson, E. H. (2006) *Planetary and Space Science, 54*, 1177-1187. [5] Oze, C., and Sharma, M. (2007) *Icarus, 186*, 557-561. [6] Mousis, O., Gautier, D., and Coustenis, A. (2002) *Icarus, 159*, 156-165. [7] Mousis, O., Lunine, J.I., Thomas, C., Pasek, M., Marboeuf, U., Alibert, Y., Ballenegger, V., Cordier, D., Elinger, Y., Pauzat, F., and Picaud, S. *The Astrophysical Journal*, in press. [8] Bézard, B., Nixon, C. A., Kleiner, I., and Jennings, D. E. (2007) *Icarus, 191*, 397-400. [9] Cordier, D., Mousis, O., Lunine, J. I., Moudens, A., Vuitton, V. (2008) *The Astrophysical Journal, 689*, L61-L64. [10] Pinto, J. P., Lunine, J. I., Kim, S.-J., Yung, Y. L. (1986) *Nature, 319*, 388-390. [11] Lunine, J. I., Yung, Y. L., Lorenz, R. D. (1999) *Planetary and Space Science, 47*, 1291-1303. [12] Mandt, K. E., Waite, J. H. Jr., Lewis, W., Magee, B., Bell, J., Lunine, J. I., Mousis, O., Cordier, D. *Planetary and Space Science*, submitted. [13] Charlou, J.-L., Donval, J.-P., Fouquet, Y., Jean-Baptiste, P., Holm, N. (2002) *Chemical Geology, 191*, 345-359. [14] Lorenz, R.D., Stiles, B.W., Kirk, R.L., Allison, M.D., Persi del Marmo, P., Iess, L., Lunine, J.I., Ostro, S.J., Hensley, S. (2008) *Science, 319*, 1649-1651. [15] Lécuyer, C., Simon, L., Guy, F. (2000) *Earth and Planetary Science Letters, 181*, 33-40. [16] Grasset, O., Pargamin, J. (2005) *Planetary and Space Science, 53*, 371-384. [17] Vuitton, V., Yelle, R. V., Cui, J. (2008) *Journal of Geophysical Research (Planets), 113*, 5007. [18] Vennemann, T. W., O'Neil, J. R. (1996) *Geochimica and Cosmochimica Acta, 60*, 2437-2451.