## PHOTOCHEMICAL ENRICHMENT OF DEUTERIUM IN TITAN'S ATMOSPHERE: NEW LIGHTS FROM CASSINI-HUYGENS

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Abstract. We reinvestigate a scenario initially proposed by Pinto et al. (1986) and Lunine et al. (1999), dealing with the photochemical enrichment of deuterium in the atmosphere of Titan, which is based on the possibility that the initial methane reservoir accessible to the atmosphere was larger than what is seen today, in light of the recent Cassini-Huygens measurements (Bézard et al. 2007). We show that this photochemical mechanism is not efficient enough in the atmosphere of Titan to explain its current D/H value, even if the current atmospheric reservoir of  $CH_4$  is postulated to exist since 4.5 Gyr.

## 1 Photochemical model

We define R as the ratio of the total mass of  $CH_4$  expelled from the interior of Titan and constituting the initial reservoir to the current atmospheric mass of  $CH_4$ . If photochemistry is the only source of methane destruction one can write

$$R = f^{\frac{1}{1-q}},\tag{1.1}$$

with f the ratio of D/H observed in Titan's current atmospheric CH<sub>4</sub> to protosolar D/H.  $q = k_2/k_1$ ,  $k_2$  and  $k_1$  being the respective rates for CH<sub>3</sub>D and CH<sub>4</sub> destructions. Alternatively, R can be expressed as it follows:

$$R = \frac{m_{\mathrm{CH}_4} F \tau}{M_{\mathrm{CH}_4}},\tag{1.2}$$

where  $m_{\text{CH}_4}$  is the mass of a CH<sub>4</sub> molecule, F the net photolytic destruction rate of CH<sub>4</sub>,  $\tau$  the time elapsed since the formation of the initial CH<sub>4</sub> reservoir up until now and  $M_{\text{CH}_4}$  is the cumulated mass of atmospheric CH<sub>4</sub> per unit of area, determined by using the Huygens probe data, namely the atmospheric density (HASI data) and CH<sub>4</sub> mole fraction profiles (GCMS data). The fractionation of deuterium in methane photochemistry is plotted in Fig. 1.

## 2 Results and conclusion

Figure 1 shows our calculations of the deuterium enrichment f. Assuming a protosolar D/H in the CH<sub>4</sub> initially released from the interior of Titan, it can be seen that the photolytic fractionation between CH<sub>4</sub> and CH<sub>3</sub>D is never efficient enough to allow a sufficient increase of the atmospheric D/H to match the observed one, even on a 4.5 Gyr timescale. Thus, a higher D/H ratio than the protosolar value must be advocated in the CH<sub>4</sub> of Titan prior its outgassing from the crust. The needed initial enrichment  $f_0$  ranges between 3.2 and 4.0 after 0.6 Gyr, and between 2.2 and 3.2 after 4.5 Gyr of the reservoir existence. Our results substantially differ from those obtained by Lunine et al. (1999) who showed that the deuterium enrichment via photolysis was almost

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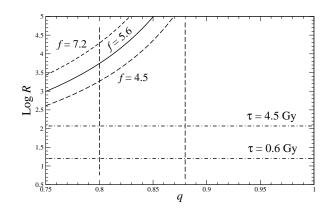


Fig. 1. The fractionation of deuterium in CH<sub>4</sub> photochemistry: plotted is R, namely the initial mass of the methane reservoir, normalized to the mass of the current reservoir (Eq.1). Three curves are shown, corresponding to different present-day deuterium enrichments measured in methane by Cassini/CIRS, with respect to the protosolar D/H abundance. The solid curve corresponds to the central value reported by Bézard et al. 2007 (D/H= $1.32^{+0.15}_{-0.11} \times 10^{-4}$ ) and the dashed curves are related to extreme values obtained with uncertainties. The D/H ratio in the methane initially acquired by Titan is assumed to be protosolar. The two horizontal lines represent values that would be acquired by R if  $\tau$  of the actual methane reservoir reaches 0.6 or 4.5 Gyr (see Eq.2). The two vertical lines represent limits on plausible values of q. It can be seen that, whatever the considered value of  $\tau$ , the reservoir of Titan's atmospheric methane is not initially massive enough to allow a substantial D/H photolytic enrichment that would match the observed values.

efficient enough to explain the current D/H value. Indeed, Lunine et al. (1999) assumed that the satellite was formed in a dense and warm Saturn's subnebula, and that the CH<sub>4</sub> incorporated in Titan was the result of the gas phase conversion of CO in the subnebula. In this scenario, a slight deuterium enhancement in CH<sub>4</sub> would have occurred in the subnebula gas phase, due to a fractionation effect at high temperature and prior the formation of ices and their trapping into proto-Titan. This slight oversolar D/H value in the CH<sub>4</sub> outgassing from the interior of Titan, combined with photolytic enrichment over 4.5 Gyr, would have sufficiently enriched the D/H in CH<sub>4</sub> to allow it to be consistent with the current atmospheric value. However, in the present work, by considering recent data on Titan's atmosphere acquired by Cassini-Huygens, we show that the minimum value required for  $f_0$  is still higher than the one expected from the production of CH<sub>4</sub> in a warm and dense subnebula. We conclude that the isotopic fractionation in the atmosphere of Titan and the isotopic exchange in the Solar nebula are two complementary processes to explain the observed D/H value in methane. The relative importance of these two mechanisms dep ends on the epoch from which started the actual outgassing event.

## References

Bézard, B., Nixon, C.A., Kleiner, I., & Jennings, D. E. 2007, Icarus, 191, 397
Fulchignoni, M., et al. 2005, Nature, 438, 785
Hörst, S. M., et al. 2008, Journal of Geophysical Research (Planets), in press
Lunine, J. I., Yung, Y. L., & Lorenz, R. D. 1999, Planet. Spa. Sci., 47, 1291
Mousis, O., Gautier, D., & Coustenis, A. 2002, Icarus, 159, 156
Niemann, H. B., et al. 2005, Nature, 438, 779
Pinto, J. P., Lunine, J.I., Sang-Joon Kim, & Yuk L. Yung 1986, Nature, 319, 388
Vuitton, V., Yelle, R. V., & Cui, J. 2008, Journal of Geophysical Research (Planets), 113, 5007