FORMATION CONDITIONS OF ENCELADUS AND ORIGIN OF ITS METHANE RESERVOIR

Mousis, O.[1], Lunine, J. I.[2] and Waite, J. H.[3]

Abstract. We describe a formation scenario of Enceladus constrained by the deuterium-to-hydrogen ratio in the gas plumes as measured by the Cassini Ion and Neutral Mass Spectrometer (INMS). We propose that, similarly to Titan, Enceladus formed from icy planetesimals that were partly devolatilized during their migration within the Kronian subnebula. In our scenario, at least primordial Ar, CO and N_2 were devolatilized from planetesimals during their drift within the subnebula, due to the increasing temperature and pressure conditions of the gas phase. The origin of methane is still uncertain since it might have been either trapped in the planetesimals of Enceladus during their formation in the solar nebula or produced via serpentinization reactions in the satellite's interior. If the methane of Enceladus originates from the solar nebula, then its D/H ratio should range between $\sim 4.7 \times 10^{-5}$ and 1.5×10^{-4}. On the other hand, if the methane of Enceladus results from serpentinization reactions, then its D/H ratio should range between $\sim 2.1 \times 10^{-4}$ and 4.5×10^{-4}.

1 Introduction

The composition of the gas plume emanating from Enceladus' southern pole has been measured five times by the INMS instrument aboard the *Cassini* spacecraft. From these data, Waite et al. (2009) inferred that the composition of the plume is dominated by H_2O vapor, a few percent of CO_2, CH_4, NH_3, H_2S, and organic compounds ranging from C_2H_2 to C_6H_6. Signatures of possible CO, N_2, and H_2 are seen but the presence of such species cannot be confirmed from the data alone. ^{40}Ar has also been detected and is probably the decay product of ^{40}K (Waite et al. 2009).

Among the compounds observed by the INMS instrument, at least H_2O, NH_3, H_2S and CO_2 are expected to be primordial (Waite et al. 2009). Indeed, the possible presence of N_2 can be explained as a result from the thermal decomposition of NH_3 in the interior of Enceladus (Matson et al. 2007). The measured CO is likely the product of fragmentation of primordial CO_2 during collection by the INMS (Waite et al. 2009). Moreover, the origin of CH_4 and high order hydrocarbons is uncertain because these compounds might have been trapped by the planetesimals of Enceladus at the time of their formation (Waite et al. 2009) or might also result from hydrothermal reactions in the interior of the satellite (Matson et al. 2007).

In the present work, we propose that Enceladus formed from icy planetesimals initially produced in the solar nebula that, once embedded in the subnebula of Saturn, have been partly devolatilized due to the increasing gas temperature and pressure conditions during their migration inwards within the subdisk. The idea of a solar nebula origin for the planetesimals of Enceladus is supported by the recent D/H measurement in H_2O in the satellite's plume ($D/H = 2.9^{+1.5}_{-0.7} \times 10^{-4}$), which is close to the cometary value (Waite et al. 2009). Here, we aim at providing observational tests that may allow characterization of the importance of the devolatilization undergone by the planetesimals of Enceladus during their migration within Saturn's subnebula. Our attention is focused on the origin of CH_4, which is directly tied to the magnitude of this devolatilization. We show that the resulting D/H ratio in CH_4 differs as a function of its source.

[1] Université de Franche-Comté, Institut UTINAM, CNRS/INSU, UMR 6213, 25030 Besançon Cedex, France

[2] Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, USA

[3] Center for Excellence in Analytical Mass Spectroscopy, Southwest Research Institute, San Antonio, Texas, USA
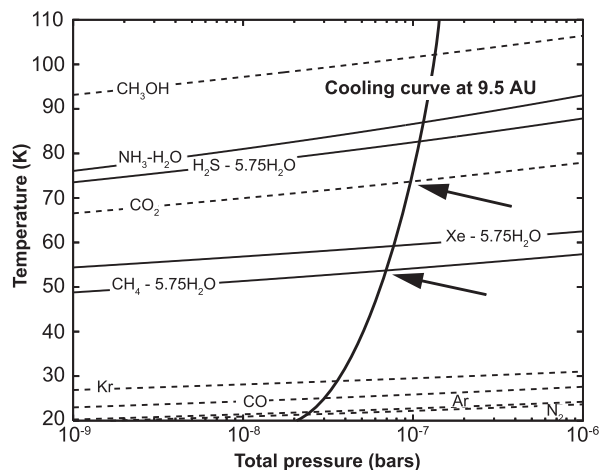
Fig. 1. *Formation sequence of the different ices in Saturn's feeding zone.* Equilibrium curves of ammonia monohydrate, clathrates (solid lines), and pure condensates (dotted lines), and cooling curve of the solar nebula at the heliocentric distance of 9.5 AU, assuming a clathration efficiency of 25%. The bottom and top arrow designate respectively the maximum temperatures at which the planetesimals of Enceladus can be heated during their migration within the Saturn's subnebula if methane observed in the plumes is primordial or if it is produced in the satellite.

2   Formation of Enceladus' planetesimals

The process by which volatiles are trapped in icy planetesimals, illustrated in Fig. 1, is calculated using the stability curves of hydrates, clathrates and pure condensates, and the thermodynamic path detailing the evolution of temperature and pressure at 9.5 AU in the solar nebula, corresponding to the position of Saturn. The cooling curve intercepts the equilibrium curves of the different ices at particular temperatures and pressures. For each ice considered, the domain of stability is the region located below its corresponding equilibrium curve. The clathration process stops when no more crystalline water ice is available to trap the volatile species. As a result of the assumed solar gas phase abundance for oxygen, ices formed in the outer solar nebula are composed of a mix of clathrates, hydrates and pure condensates which are, except for CO_2 and CH_3OH[1], produced at temperatures ranging between 20 and 50 K. Once formed, the different ices agglomerated and incorporated into the growing planetesimals. Figure 1 illustrates the case where the efficiency of clathration is only of $\sim$ 25%. Here, either only a part of the clathrates cages have been filled by guest molecules, either the diffusion of clathrated layers through the planetesimals was too slow to enclathrate most of the ice, or the poor trapping efficiency was the combination of these two processes. In this case, only NH_3, H_2S, Xe and CH_4 form NH_3-H_2O hydrate and H_2S-$5.75H_2O$, Xe-$5.75H_2O$ and CH_4-$5.75H_2O$ clathrates. Due to the deficiency in accessible water in icy planetesimals, all CO, Ar, Kr and N_2 form pure condensates in the feeding zone of Saturn.
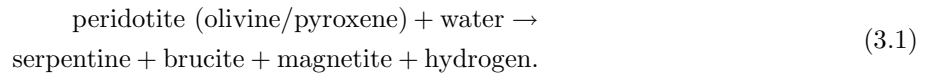
3   What if serpentinization were the source of methane observed in Enceladus?

Two different maximum devolatilization temperatures can be envisaged for the planetesimals of Enceladus. In the first case, similarly to Titan we assume that the methane detected in the plumes is primordial. This corresponds to the hypothesis that the devolatilization temperature of planetesimals never exceeded $\sim$ 50 K during their drift within the subdisk. In the second case, we assume that methane is not primordial and has

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[1]CO_2 is the only species that crystallizes at a higher temperature than its associated clathrate in the solar nebula. Moreover, we consider only the formation of CH_3OH pure ice because no experimental data concerning the equilibrium curve of its associated clathrate have been reported in the literature.

been produced in the interior of the satellite. Here, the maximum devolatilization temperature is then of ~ 75 K because a higher value would not be compatible with the presence of primordial CO_2 in Enceladus (see Fig. 2). In the framework of the second case, we examine the possibility that CH_4 is the result of serpentinization reactions, as proposed by Atreya et al. (2006) in the case of Titan. We first estimate the D/H value in the methane of Enceladus, assuming it was produced in its interior from the association of CO_2 or carbon grains with the H_2 formed during the hydrothermal alteration of peridotite (Moody 1976; Atreya et al. 2006; Oze & Charma 2007), and we compare this value to the one acquired by methane had if it originated from the solar nebula.

In terrestrial oceans, hydrothermal fluids and seawater interact with peridotite via the following summary reaction (Moody 1976; Atreya et al. 2006):

$$\text{peridotite (olivine/pyroxene)} + \text{water} \rightarrow$$
$$\text{serpentine} + \text{brucite} + \text{magnetite} + \text{hydrogen}. \tag{3.1}$$

With a bulk density of 1,610 kg m^{-3}, thermal evolution models suggest that Enceladus is most likely a differentiated body with a large rocky core surrounded by a water ice shell that may be liquid at depth (Schubert et al. 2007). In our calculations, we assume that this liquid layer constitutes the water reservoir that is in contact with peridotite during serpentinization reactions. Under these conditions, residual water is deuterium-enriched at the expense of the initial reservoir of free-water and the fractionation factor, α, between OH-bearing minerals and water is then (Lécuyer et al. 2000):

$$\alpha_{r-w} = \frac{R_r^f}{R_w^f}. \tag{3.2}$$

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 (Lécuyer et al. 2000):

$$M_w^i X_w^i R_w^i + M_r^i X_r^i R_r^i = M_w^f X_w^f R_w^f + M_r^f X_r^f R_r^f, \tag{3.3}$$

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 hydratation reactions (i) and at batch equilibrium (f). If we neglect the amount of water incorporated in primordial peridotites of Enceladus ($X_r^i = 0$) and postulate that $M_w^i \simeq M_w^f$ and $M_w^f.X_w^f \gg M_r^f.X_r^f$, which is a reasonable assumption[2], then Eq. 3.3 can be expressed as:

$$R_r^f \simeq \alpha_{r-w} R_w^i. \tag{3.4}$$

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 (Vennemann et al. 1996). We also 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 serpentinization reactions. Hence, the D/H ratio acquired by hydrated rocks would be preserved in the H_2 produced from the alteration of peridotite and used in the recombination of CH_4. Table 1 summarizes the range of predicted values for D/H in CH_4 produced within Enceladus, assuming that D/H ratio in the primordial water reservoir is the value measured by *Cassini* (Waite et al. 2009). This value is compared to the one acquired by methane if it was initially incorporated by the planetesimals of Enceladus during their formation in the nebula. In this case, since it was established that the methane of Titan originates from the solar nebula (Mousis et al. 2009) and since the buiding blocks of the two satellites share a common origin, the D/H ratio in Enceladus' methane should range between the minimum D/H ratio initially acquired by Titan if a significant photochemical enrichment of

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[2]The CH_4/H_2O volume ratio observed in the plumes is $\sim 0.5\%$ during the E2 encounter (Waite et al. 2006) and is representative of the value existing in the hypothetical internal ocean (Waite et al. 2009). Assuming that all H_2 involved in the formation of CH_4 results from the reaction of peridotite and water, the fraction of used water is only of $\sim 1\%$ and the term $M_w^f.X_w^f$ is more than 11 times greater than the term $M_r^f.X_r^f$.

Table 1. D/H ratio in methane as a function of its postulated origin.

Origin	Range of D/H values
Serpentinization reactions	2.1×10^{-4}–4.5×10^{-4}
Solar nebula	$4.7 \times 10^{-5*}$–1.5×10^{-4}

*Minimum D/H ratio acquired by the primordial methane of Titan in case of strong photochemical enrichment in the atmosphere (see text).

deuterium occurred during the evolution of its atmosphere (Cordier et al. 2008) and the value observed today in Titan by *Cassini* (Bézard et al. 2007). From these values, we infer that the D/H ratio in CH_4 produced by serpentinization should be enriched by a factor of 1.9–6.8 relative to D/H in methane originating from the nebula.

4   Discussion

A word of caution must be given about our estimate of the D/H ratio in CH_4 produced via serpentinization. It is based on the idea that no D-fractionation occurred between the produced H_2 and serpentine, and between the produced CH_4 and H_2. Unfortunately, these points are still not well established in the literature and future laboratory work is required to assess their validity. As noted in Waite et al. (2009), the measured H_2 in recent encounters is most likely a product of H_2O interactions with the instrument's antechamber walls due to the high spacecraft velocity relative to the plume. Therefore the amount of endogenous H_2 and its D/H ratio remains undetermined. Future *Cassini* encounters are currently planned at slower spacecraft speed that may allow separate assessments of H_2 in the plume from that synthesized inside the INMS instrument. In this case determinations of D/H in H_2 during the Cassini mission remain a remote possibility that could tell if this species is produced by serpentinization reactions. Measurement of D/H in CH_4 cannot be made with INMS due to overlapping signals of several species in this portion of the mass spectrum. This measurement requires an instrument with mass resolution (M/ΔM) greater than 6000 and thus must wait for a future spacecraft mission, such as TSSM actually studied by NASA and ESA.

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