

explicit analytical theory on the long-term behaviour of the semimajor axes with which these results can be compared. A comparison is possible for the quantities  $e$ ,  $i$ ,  $\bar{\omega}$  and  $\Omega$  and shows quite good agreement for first-order terms, although serious differences arise for the higher-order ones.

A time of 9.3 Myr is still very short compared with the age of the Solar System, and longer numerical integrations are needed; we and others<sup>9</sup> are working in this direction. For longer integrations to be significant, the round-off error must be carefully controlled to ensure that it will not mask important dynamical features; furthermore, a better physical model must be used to represent the real problem. We are about to start a 100-Myr integration of the outer planets using the same numerical method but improving the physical model. The secular perturbations caused by the inner planets on the perihelia and the nodes of the outer planets are significant over such timescales (for example, the effect of the Earth on the perihelion of Jupiter in 50 Myr is  $\sim 88^\circ$ ). General relativistic corrections are small but not negligible<sup>10</sup>. Moreover, the relative mass loss of the Sun through electromagnetic emission only produces a relative semimajor axis increase of  $6.6 \times 10^{-14} \text{ yr}^{-1}$ . In our integration this effect is already three orders of magnitude larger than the round-off error. However, one might argue that the mass loss

of the Sun will simply rescale the orbits and the periods of the planets and therefore is not likely to have any significant effect on the dynamical structure of the whole system, whereas the numerical errors act in different ways on the different planets and therefore in the long run will affect the dynamical structure. We conclude that the control of the numerical errors, especially the round-off, is at present our most serious problem in elucidating the stability of the Solar System.

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## D to H ratio and the origin and evolution of Titan's atmosphere

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A value of  $1.7 \times 10^{-3}$  has been reported<sup>1</sup> for the ratio of  $\text{CH}_3\text{D}$  to  $\text{CH}_4$  in the stratosphere of the saturnian moon Titan. A lower value of  $6 \times 10^{-4}$  for this ratio in the deeper part of Titan's atmosphere was reported by de Bergh *et al.*<sup>2</sup>. For comparison<sup>3-11</sup> we note that the  $\text{CH}_3\text{D}$  to  $\text{CH}_4$  ratio on Saturn and Jupiter is  $8.7 \times 10^{-5}$  and  $6.7 \times 10^{-5}$ , respectively (see Table 1). We estimate the uncertainties in all these observations and data reduction to be about a factor of 2. Despite these uncertainties it appears that Titan's atmosphere is enriched in deuterium by a factor of  $\geq 3$  relative to Jupiter and Saturn. Potential causative factors examined here for this enrichment are condensation to form tropospheric methane clouds, fractionation occurring over a hypothetical  $\text{CH}_4$ - $\text{C}_2\text{H}_6$  ocean and between the ocean and the clathrate crust beneath, fractionation which occurred during the formation of Titan and fractionation occurring as a result of the evolution of Titan's atmosphere. We conclude that the greater part of the observed fractionation is probably derived from the formation of Titan and the subsequent evolution of Titan's atmosphere driven by photochemistry.

We first consider possible fractionation that occurs during formation of tropospheric methane clouds. Data in ref. 12 indicate the  $\text{CH}_4$ - $\text{CH}_3\text{D}$  liquid solution to be ideal in the sense that the ratio of components in the gas phase is equal to that in the liquid, multiplied by the saturation vapour pressure ratio. As the saturation vapour pressures of  $\text{CH}_4$  and  $\text{CH}_3\text{D}$  are within 2% of the temperature range of Titan's tropopause, we conclude

that no fractionation effects greater than a few per cent can occur with cloud formation.

Of greater concern are the relative solubilities of  $\text{CH}_4$  and  $\text{CH}_3\text{D}$  in the postulated ethane-methane ocean<sup>13</sup>. In the limit that the  $\text{CH}_3\text{D}$ - $\text{CH}_4$  solution is considered as a single component of the ethane-methane system, the  $\text{CH}_3\text{D}/\text{CH}_4$  ratio in the ocean would be within several per cent of that in the corresponding vapour, based on the preceding argument. Alternatively, the deuterated methane could be regarded as a distinct dilute component in the ocean, and its solubility computed from data on binary mixtures. Using data on  $\text{CH}_4$ - $\text{C}_2\text{H}_6$  mixtures<sup>14-16</sup> extrapolated to extreme dilution, and assuming the solubility of  $\text{CH}_3\text{D}$  in  $\text{C}_2\text{H}_6$  is the same for a fixed composition as that of  $\text{CH}_4$  in  $\text{C}_2\text{H}_6$ , we find  $(\text{CH}_3\text{D}/\text{CH}_4)_{\text{atmosphere}}/(\text{CH}_3\text{D}/\text{CH}_4)_{\text{ocean}} \approx 1.3$ . We cannot rule out either limiting estimate in the absence of experimental data, and hence conclude that the enrichment factor is in the range 1.0-1.3.

The ocean is likely to be underlain by a water-ice crust<sup>17</sup>; hence, clathrate formation should occur at the interface. The relative extent of incorporation of molecules of similar shape in the clathrate structure tends to follow their vapour pressure<sup>18</sup>; since these are nearly identical for  $\text{CH}_3\text{D}$  and  $\text{CH}_4$  no partitioning is expected. In any event, the mass of the clathrate layer in contact with the ocean is estimated to be small compared with that of the ocean<sup>17</sup>.

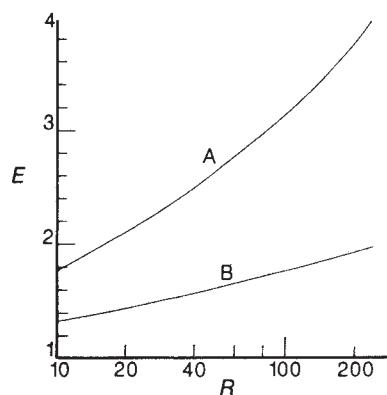
Little is known about the D/H ratio in the primordial gaseous nebula from which satellites formed, because this ratio is sensitive to physical and chemical processes involved in satellite formation which are not well quantified. In a gas containing cosmic abundances of H, O, C and N molecular species, the substitution of a deuterium for a hydrogen in heavier molecules leads to an increase in the binding energy, which becomes increasingly important as the thermal energy per molecule decreases. According to Hubbard and MacFarlane<sup>19</sup> the D/H enhancement for methane in equilibrium with  $\text{H}_2$  is about 2 at 500 K and can be as large as 7 at 200 K. Opposing such enhancements are the rather long equilibration times required in the gas phase. Estimates by Beer and Taylor<sup>20</sup> suggest that for  $\tau \leq 500$  K the equilibration time would exceed  $10^8$  yr, which is considerably longer than the timescale for satellite formation<sup>21,22</sup>. Catalysis on the surface of metal rich grains may lower the equilibration times<sup>23-27</sup>. Recent calculations of D. H. Grinspoon and J. S. Lewis (personal communication) suggest that surface catalysis

**Table 1** Observations of the relative abundances of deuterium and hydrogen in planetary atmospheres

Planetary body	Relevant physical quantity	Notes
Titan	$\text{CH}_3\text{D}/\text{CH}_4 = 1.7 \times 10^{-3}$	Ref. 1, based on $\nu_6$ band of $\text{CH}_3\text{D}$ at $8.6 \mu\text{m}$ ; Voyager IRIS data <sup>3</sup>
	$\text{CH}_3\text{D}/\text{CH}_4 = 6 \times 10^{-4}$	Ref. 2, personal communication based on $6,425 \text{ cm}^{-1}$ band of $\text{CH}_3\text{D}$ ; ground-based data; result probably more certain than that using $\nu_6$ emission feature
Saturn	$\text{CH}_3\text{D}/\text{CH}_4 = 8.7 \times 10^{-5}$	Ref. 5, based on $\nu_6$ band of $\text{CH}_3\text{D}$ ; Voyager IRIS data
Jupiter	$\text{CH}_3\text{D}/\text{CH}_4 = 6.7 \times 10^{-5}$	Refs 4 and 5, based on $\nu_6$ band of $\text{CH}_3\text{D}$ ; Voyager IRIS data; ref. 11
Earth	$4 \times (\text{D}/\text{H}) = 6.2 \times 10^{-4}$	Ref. 8, based on standard mean ocean water (SMOW); for juvenile water see ref. 9
Venus	$4 \times (\text{D}/\text{H}) = 6.4 \times 10^{-2}$	Refs 6 and 7, based on $\text{D}^+$ and HDO measurements on Pioneer Venus
Mars	$4 \times (\text{D}/\text{H}) = 6.2 \times 10^{-4}$	Ref. 10, based on $\delta\text{D} \sim -80$ to $52\%$ in Shergotty meteorite; connection with the martian atmosphere controversial

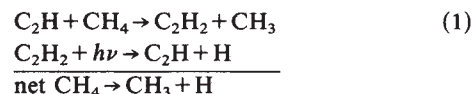
on micrometre-sized nickel grains at 500 K can lead to equilibration times for exchange of deuterium between  $\text{H}_2\text{O}$  and  $\text{H}_2$  of  $3 \times 10^5$  yr, which is roughly the dynamic timescale for the saturnian nebula<sup>21</sup>. The dynamic timescale gives a crude upper limit to the lifetime of material in the saturnian nebula; hence, equilibration times longer than  $10^5$  yr for the exchange reaction are not plausible. This limits the exchange to high temperatures ( $> 500$  K, achievable in the innermost regions of the nebula with gas then being mixed outward to the cooler regions), and the resulting deuterium enrichment in  $\text{H}_2\text{O}$  to at most a factor of 2. We conclude by analogy that an enhancement factor in deuterated methane of 2 is possible in the primordial saturnian nebula out of which Titan formed. This value may be an upper limit because water could dominate the adsorption sites on the grains. Furthermore, once accretion had started the rates of these reactions would have slowed dramatically because the metallic grains would combine chemically to form minerals with a markedly lower catalytic ability<sup>24</sup>.

Geiss and Reeves<sup>28</sup> examined a variety of mechanisms to explain the deuterium enrichment in terrestrial planets and meteorites, and concluded that exchange mechanisms in the solar nebula were probably less important than earlier enhancement processes in interstellar clouds out of which the solar nebula presumably formed. It is possible that some interstellar grains, greatly enriched in deuterium, retained the enrichment during heating processes accompanying the formation of the solar nebula and/or passage through the accretion shock at the solar nebula/interstellar medium boundary. However, such grains, accreting onto Titan during or shortly after its formation could have been subjected to temperatures in excess of 500 K for perhaps as long as  $10^8$  yr after the accretion of Titan, based on detailed models by one of us (J.I.L.)<sup>36</sup>. If the highly deuterated grain material was in thermodynamic contact with a substantial reservoir of non-enriched hydrogen in the primordial atmosphere during this time, dilution of the enrichment could have occurred. This possibility is admittedly very speculative and requires modelling beyond the scope of the present effort. Exchange reactions in the Saturn nebula, therefore, probably

**Fig. 1** Enrichment factor  $E$  as defined in the text versus  $R$ , the ratio of total initial  $\text{CH}_4$  reservoir to the total present  $\text{CH}_4$  reservoir.

produced at most a factor of 2 deuterium enrichment in methane incorporated into Titan from the nebular gas; we acknowledge, however, that highly deuterated material in interstellar grains could have been incorporated in Titan, avoided reprocessing and possibly increased the enhancement of deuterated methane.

In the atmosphere of Titan,  $\text{CH}_4$  is the major observed hydrogen reservoir. Recent photochemical modelling<sup>29,30</sup> suggests that a large quantity of  $\text{CH}_4$  has been converted into heavier hydrocarbons. The destruction of  $\text{CH}_4$  occurs mainly through the catalytic cycle



Following the escape of hydrogen from Titan's atmosphere,  $\text{CH}_3$  radicals combine irreversibly to form  $\text{C}_2\text{H}_6$ . Subsequent reactions lead to the production of smaller amounts of other hydrocarbons. The current rate of destruction of  $\text{CH}_4$  (referred to the surface) is  $\phi = 1.5 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ . Rate coefficients for reactions of deuterated molecules are usually much smaller than the corresponding value for the molecule composed of the lighter isotope<sup>31-34</sup>. The rate coefficient for



has not been measured. Because of the greater binding energy of D compared with H, the rate coefficient for reaction (2) may only be a fraction of that for (reaction 1), that is,  $k_2 = rk_1$  where  $r < 1$ . We adopt two values for  $r$ , 0.75 (case A) and 0.875 (case B), the former being the preferred value (A. H. Laufer, personal communication). We assume that reactions (1) and (2) are the primary cause of isotopic enrichment in the photochemical model.

The theory of isotopic enrichment in a planetary atmosphere due to photochemical processes has been worked out by McElroy and Yung<sup>35</sup>, whose methodology and notation we follow. Let  $N_1(t)$  and  $N_2(t)$  be the total column abundance of  $\text{CH}_4$  and  $\text{CH}_3\text{D}$ , respectively, on Titan at time  $t$ . The evolution of  $N_1(t)$  and  $N_2(t)$  is given by

$$\frac{dN_1(t)}{dt} = -\phi, \quad \frac{dN_2(t)}{dt} = -rf(t)\phi, \quad f(t) = \frac{N_2(t)}{N_1(t)}$$

where  $\phi$  is the column integrated destruction rate of  $\text{CH}_4$  (assumed to be constant with time) defined earlier,  $f(t)$  is  $\text{CH}_3\text{D}$  to  $\text{CH}_4$  ratio, and time is defined so that  $t = 0$  refers to the time of formation of Titan and  $t = \tau = 4.5 \times 10^9$  yr corresponds to the present. We solve this set of equations by using the observed present value  $f(\tau)$  and integrating the equations backwards to  $t = 0$  for a range of assumptions for  $N_1(t)$ . The most interesting results in this computation are the ratio of the initial reservoir

**Table 2** Enrichment factors for deuterium on Titan

Process	Enrichment factor	Remarks
(1) Cloud formation	1	See text
(2) C <sub>2</sub> H <sub>6</sub> -CH <sub>4</sub> ocean	1-1.3	Assuming 20% CH <sub>4</sub> , 80% C <sub>2</sub> H <sub>6</sub> ocean
(3) Ocean-ice crust formation	1	See text
(4) Equilibrium between CH <sub>4</sub> and H <sub>2</sub> in the saturnian nebula	1-2	Assuming 500 K nebula temperature; isotopic exchange catalysed by metal grains
(5) Atmospheric evolution	1.7	Based on curve A in Fig. 1 and $R = 10$
Total	1.7-4.4	Products of all enrichment factors (1)-(5)

of CH<sub>4</sub> to the present reservoir which is  $R = N_1(0)/N_1(\tau)$ , and the enrichment factor due to atmospheric evolution which is  $E = f(\tau)/f(0)$ .

A simple analytical solution exists, which relates  $E$  and  $R$ ,  $E = R^{1-\tau}$ . The numerical results are summarized in Fig. 1. The enrichment factor  $E$  is plotted against  $R$ , which is a measure of the extent of atmospheric evolution. For both case A ( $r = 0.75$ ) and case B ( $r = 0.875$ ),  $E$  increases with  $R$ , and could become very large if  $R \gg 100$ . For an ocean composition of 20% CH<sub>4</sub> and 80% C<sub>2</sub>H<sub>6</sub> (ref. 13), the value for  $R$  is 9 and the enrichment factor based on our preferred case A is 1.7. It can be shown that isotopic exchanges such as  $H + CH_3D \rightleftharpoons HD + CH_3$  and recombination reactions such as  $H + CH_2D + M \rightarrow CH_3D + M$  are of relatively minor importance on Titan. Isotopic re-equilibration could also occur either in the ocean or deeper in Titan's interior. However, temperatures in the ocean are much too low ( $\sim 90$  K) to permit appreciable thermal decomposition of either CH<sub>4</sub> or C<sub>2</sub>H<sub>6</sub> to form radicals which mediate the isotopic exchange. In addition, since the reactions involve neutral species in an ocean of non-polar molecules CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, we also would not expect solvent interactions to affect reaction rates. While any treatment of chemical processes in the interior of Titan is necessarily speculative, we would not expect significant re-equilibration to occur at greater depths. This inference is based on current theories of the internal structure of Titan, which propose an icy mantle with a maximum temperature at the core-mantle boundary of  $\leq 400$  K. The first condition implies greatly restricted mobility of reactants and the second, that temperatures are still too low for thermally-driven reactions to occur.

The relative abundance of deuterium to hydrogen in a planetary atmosphere is one readily available measure of the origin and evolution of the hydrogen bearing volatiles on the planet (see Table 1). If we take the de Bergh *et al.*<sup>2</sup> value  $6 \times 10^{-4}$  for the ratio CH<sub>3</sub>D/CH<sub>4</sub> on Titan, and the Voyager value of  $8.7 \times 10^{-5}$  for Saturn, we note that deuterated methane is enriched 6.9-fold on Titan. The uncertainty associated with the derivation of this number is about a factor of 2-3. Note that the uncertainty must include not only the errors in measurement, but also the plausible range in the fractionation factor between CH<sub>3</sub>D and HD within the atmosphere of Saturn<sup>20</sup>, since the ratio of interest refers to the bulk saturnian value. The physical and chemical enrichment factors considered in this paper are summarized in Table 2. The cumulative enrichment factor is 2-4, which is below the observed value but within the estimated uncertainties of the observations. It is more difficult to interpret the observed value of CH<sub>3</sub>D/CH<sub>4</sub> obtained by Kim and Caldwell<sup>1</sup>. We have neglected early evolution of Titan's atmosphere driven by planetesimal impacts and early solar extreme ultraviolet which could have increased the atmospheric D/H ratio, allowed some re-equilibration between deuterated species, or

provided an era of enhanced photodissociation of methane. Future observations of deuterated species on Titan and the giant planets are obviously needed to remove the large uncertainties in the D/H measurements. For a more realistic treatment of the photochemically-driven evolution of D/H on Titan, we recommend a laboratory experiment to measure the relative rate constants of the reaction C<sub>2</sub>H with CH<sub>3</sub>D and CH<sub>4</sub>.

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## Antarctic and non-Antarctic meteorites form different populations

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Compared with non-Antarctic falls, Antarctic meteorites include many of hitherto rare, unique or unknown type<sup>1</sup>, such as lunar and putative martian samples<sup>2-4</sup>. Attention has not previously been paid to the more common sorts of Antarctic meteorites and here we focus on the most frequently encountered, H5 chondrites. We find that compositional differences between Antarctic and non-Antarctic specimens of this class, especially those involving thermally sensitive trace and ultra-trace elements, are so substantial that it seems extremely doubtful that the two sample populations are derived from the same parent population. This implies that

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