

# Solar System Deuterium/Hydrogen Ratio

François Robert

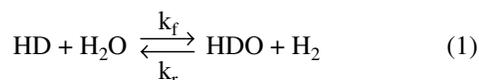
Muséum National d'Histoire Naturelle

The D/H variations in chondritic meteorites are reviewed and compared with astronomical observations in the interstellar medium. The observed D enrichment in organic molecules — and to a lesser extent in water — is a general rule in the universe. The D is preferentially transferred from the universal reservoir ( $H_2$ ) by low-temperature reactions (10–100 K) from neutral molecules ( $H_2$  or H) to hot radicals or ions. The signature of this process is preserved in meteorites and comets. Although this D-enrichment procedure is well understood, in this review a special emphasis is placed on the unsolved issues raised by solar system D/H data. Specifically, it is shown that (1) the usual interstellar interpretation for the origin of the D-rich compounds in chondrites is not quantitatively substantiated and (2) the isotopic heterogeneity observed in LL chondrites is difficult to reconcile with any known natural reservoir or process.

## 1. INTRODUCTION

The origin of organic compounds and water in the solar system is an important problem that has increasingly attracted the interest of astronomers and cosmochemists following the recognition that H-bearing molecules in comets, planets, and chondritic meteorites show a systematic D enrichment relative to the molecular hydrogen of the solar nebula (Robert *et al.*, 1979, 1987; Kolodny *et al.*, 1980; Robert and Epstein, 1982; McNaughton *et al.*, 1981, 1982; Kerridge, 1985, 1987; Deloule and Robert, 1995, 1998). Because there is no nuclear source for D in the universe (Epstein *et al.*, 1976; Galli, 1995), the observed isotopic enrichment must have its origin in chemical reactions having faster reaction rates for D than for H (deuterium and hydrogen, respectively). Such processes lead to “kinetic isotopic fractionation.” The D/H ratio in  $H_2$  (or H) in the interstellar medium (ISM) represents the universal isotopic abundance ratio, the D-rich molecular species representing only a minute fraction of the total H present in the ISM. Therefore, deciphering the origin of D/H variations in organic compounds and in water in the solar system hinges on a correct identification of these reactions and their respective magnitude of isotopic fractionation.

The isotopic exchange between water and molecular hydrogen is a classical example that can be used for the definition of the isotopic fractionation parameters (Geiss and Reeves, 1972; Lécluse and Robert, 1996)



The D enrichment factor  $f$  in equation (1) is defined as

$$f_{(H_2-H_2O)} = \frac{\{1/2[HD]/[H_2]\}}{(D/H)_{H_2O}/(D/H)_{H_2}} = \quad (2)$$

The factor 1/2 is explicitly written in equation (2) to emphasize that the molecular isotopic abundance in  $H_2O$  and  $H_2$  is twice the elemental D/H ratio. Equation (1) does not imply that the thermodynamical equilibrium is reached between the reactants. The notation  $f_{(H_2-H_2O)}$  indicates that the isotopic exchange takes place between  $H_2O$  and  $H_2$  (this notation will be used hereafter for all types of reactions). In this reaction, water is systematically enhanced in D relative to molecular hydrogen; i.e.,  $f_{(H_2-H_2O)} \geq 1$ . Under equilibrium conditions, the enrichment factor,  $f_{equi}$ , stands for the forward to reverse reaction rate ratio; i.e.,  $f_{equi} = k_f/k_r$ .  $f_{equi}$  depends exclusively on the temperature (Richet *et al.*, 1977). In the geochemical literature  $f_{equi}$  is often noted as  $\alpha(T)$  and is referred to as “the isotopic fractionation factor.” Reaction (1) can be extended to all kinds of H-bearing molecules (organic molecules, ions, etc.) and (almost) always yields an enrichment in D in H-bearing molecules relative to  $H_2$ ; i.e.,  $f_{(H_2-XH)} \geq 1$ .

In space, isotopic exchange reactions can take place primarily in three environments: (1) In the solar nebula via a thermal isotopic exchange between molecular hydrogen and H-bearing compounds (Geiss and Reeves, 1972; Lécluse and Robert, 1994). (2) In the dense ISM at  $T < 50$  K via isotopic exchanges between ionized species and molecules (Brown and Millar, 1989; Brown and Rice, 1981; Watson, 1976; Willacy and Millar, 1998; Yung *et al.*, 1988). (3) In denser interstellar clouds (the so-called hot cores), at intermediate temperatures ( $T < 200$ K), via isotopic exchanges between radicals (H or D) and neutral molecules (Rodgers and Millar, 1996). Calculations and/or experimental determinations of the  $f$  values for different molecules and for these three types of environments are available in the literature. The present paper compares these theoretical  $f$  values with the galactic and planetary data in order to investigate the possible relations between solar system and interstellar molecules.

Unequilibrated meteorites contain clay minerals ( $\approx 90\%$  of their bulk H content) and insoluble organic macromol-

TABLE 1. Selected D/H ratios in the galaxy and solar system.

D/H ( $\times 10^6$ )	Species	Location	f	References
Galactic <sup>[6]</sup>				
20–50	H	Big Bang (theoretical)		<i>Schramm (1998)</i>
$16 \pm 1$	H	Local interstellar medium		<i>Linsky (1993)</i>
110 (+150/–65)	H <sub>2</sub> O	Hot cores	7	<i>Gensheimer et al. (1996)</i>
900–43 <sup>[8]</sup>	H <sub>2</sub> O	ISM (20–80 K, respectively)	36–1.7	<i>Brown and Millar (1989)</i>
$1 (+3/-0.2) \times 10^3$	OM <sup>[1]</sup>	Interstellar clouds (hot cores)	63	Personal compilation <sup>[3]</sup>
$2 (+0.7/-1.8) \times 10^4$	OM <sup>[1]</sup>	Cold interstellar clouds	(<20 K) 1250	Personal compilation <sup>[3]</sup>
Proto-Sun				
$25 \pm 5$	H <sub>2</sub>	Protosolar nebula $4.5 \times 10^9$ yr ago	=1	<i>Geiss and Gloecker (1998)</i>
Gaseous Planets <sup>[7]</sup>				
$21 \pm 8$	H <sub>2</sub>	Jupiter (spectroscopic)	=1	
$26 \pm 7$	H <sub>2</sub>	Jupiter (MS <i>in situ</i> )	=1	<i>Mahaffy et al. (1998)</i>
15–35	H <sub>2</sub>	Saturn (spectroscopic)	=1	<i>Griffin et al. (1996)</i>
65 (+2.5/–1.5)	H <sub>2</sub>	Neptune (spectroscopic)	2.6	<i>Feuchtgruber et al. (1998)</i>
55 (+35/–15)	H <sub>2</sub>	Uranus (spectroscopic)	2.2	<i>Feuchtgruber et al. (1998)</i>
Comets <sup>[7]</sup>				
$310 \pm 30$	H <sub>2</sub> O	Comet P/Halley	12.4	<i>Eberhardt et al. (1995)</i>
$290 \pm 100$	H <sub>2</sub> O	Comet Hyakutake	11.6	<i>Bockelée-Morvan et al. (1998)</i>
$330 \pm 80$	H <sub>2</sub> O	Comet Hale-Bopp	13.2	<i>Meier et al. (1998a)</i>
$2300 \pm 400$	OM <sup>[1]</sup>	HCN in Comet Hale-Bopp	92	<i>Meier et al. (1998b)</i>
Interplanetary Particles <sup>[7]</sup> (IDPs and Antarctic Micrometeorites)				
90–4000		Bulk	3.6–160	Personal compilation <sup>[3]</sup>
1500–4000	IOM		60–160	<i>Messenger (2000)</i>
150–300	H <sub>2</sub> O	(four determinations)	6 to 12	<i>Aléon et al. (2001)</i>
Telluric Planets <sup>[7]</sup>				
$149 \pm 3$	H <sub>2</sub> O	Bulk Earth	6	<i>Lecuyer et al. (1998)</i>
$16\,000 \pm 200$	H <sub>2</sub> O	Venus (atmosphere <i>in situ</i> )	640	<i>Donahue et al. (1982)</i>
$780 \pm 80$	H <sub>2</sub> O	Mars (atmosphere <i>in situ</i> )	31	<i>Owen et al. (1988)</i>
100–780	–OH	SNC (Mars mantle?)	4–31	<i>Leshin et al. (1994); Gillet et al. (2002)</i>
LL3.0 and LL3.1 Meteorites <sup>[7]</sup>				
$730 \pm 120$	–OH	in clays and in chondrules (MgSiO <sub>3</sub> )	29	<i>Deloule and Robert (1995)</i>
$88 \pm 11$	–OH	in chondrules (glass)	3.5	<i>Deloule et al. (1998)</i>
800–1100	IOM <sup>[1]</sup>	IOM	32–44	Personal compilation <sup>[3]</sup>
Carbonaceous Meteorites <sup>[7]</sup>				
$140 \pm 10$	–OH	Mean statistical value <sup>[2]</sup>	5.6	Personal compilation <sup>[3]</sup>
380–620	IOM <sup>[1]</sup>	(CM,CV,CR) <sup>[4]</sup>	15–25	Personal compilation <sup>[3]</sup>
$370 \pm 6$	IOM <sup>[1]</sup>	(Orgueil CI) <sup>[5]</sup>	14.8	<i>Halbout et al. (1990)</i>
$170 \pm 10$	–OH	(Orgueil CI) <sup>[5]</sup>	6.8	Personal compilation <sup>[3]</sup>
315–545	SOM <sup>[1]</sup>	Amino-acids from CM	12.5–22.0	<i>Pizzarello et al. (1991)</i>
185–310	SOM <sup>[1]</sup>	Hydrocarbons, carboxylic acids from CM	7.5–12.5	<i>Epstein et al. (1987)</i>

The f value is defined as  $(D/H)_{\text{sample}}/(D/H)_{\text{reference}}$ . The “reference” D/H ratio (f = 1) stands for the molecular hydrogen reservoir from which the H-bearing compounds are formed (see notes [6] and [7]).

Notes: [1] IOM = insoluble organic matter; SOM = soluble organic matter; [2] Statistical distribution:  $130 < D/H < 170$  (66%); [3] F. Robert, personal compilation of published data; [4] CM, CV, CR: chondrite types; [5] reference meteorite sample for the protosolar chemical composition; [6]  $(D/H)_{\text{reference}} = 16 \times 10^{-6}$ ; [7]  $(D/H)_{\text{reference}} = 25 \times 10^{-6}$ ; [8] theoretical values.

ecules (hereafter referred to as IOM;  $\approx 10\%$  of H) with IOM systematically enriched in D by a factor of 2 to 3 relative to the minerals. The soluble organic molecules are present at the 100-ppm level and their isotopic compositions are presented in another chapter of this book. Because only a few known natural processes are able to cause such large isoto-

pic heterogeneity, a knowledge of the internal distribution of the D/H ratio in chondrites might become an efficient tool in reconstructing the conditions of synthesis of water and organic molecules. However, little progress has been made in this direction because of the complexity of the organic materials and because of a lack of experimental ef-

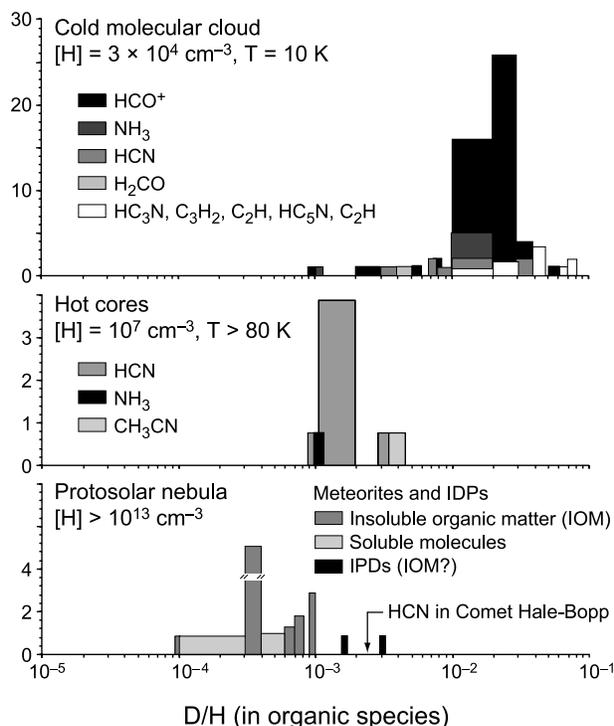
forts to determine precisely the distribution of the D/H ratio at a molecular or mineralogical level.

## 2. NATURAL VARIATIONS OF THE DEUTERIUM/HYDROGEN RATIO

In this section, the natural variations of the D/H ratio in stars, ISM, planets, meteorites, and comets are reviewed. Selected data are reported in Table 1.

### 2.1. The Universal Deuterium/Hydrogen Ratio

Deuterium formed during the “Big Bang” and has subsequently been destroyed in stars. The formation of D in supernova shocks, if possible, does not seem relevant in the galactic context (*Epstein et al.*, 1976). Therefore the D/H ratio of the ISM should have decreased with time as D-free H has been injected into space by supernovae or stellar winds (*Galli et al.*, 1995). However, exact estimates of the overall decrease in D abundance in the galaxies with time remain controversial. Measurements with the Hubble Space Telescope have given an accurate determination of the local ISM: *Linsky et al.* (1993) reports D/H ratios of  $16.5 \pm 1.8 \times 10^{-6}$  and  $14.0 \pm 1 \times 10^{-6}$  within 1 kpc of the Sun and *McCullough* (1991) reported 14 ratios averaging at  $15 \times 10^{-6}$ . The remarkable agreement between these two sets of data suggests that there is a single D/H ratio for the average ISM



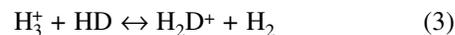
**Fig. 1.** Distributions of the D/H ratio in organic species for three different environments: ISM (cold molecular clouds), hot cores, and solar system (protosolar nebula). The origin of the difference in the D/H ratios between ISM and solar system organic molecules is still an open issue (see discussion in text).

(cf. review by *Linsky*, 2003). Note, however, that *Gry et al.* (1983) or *Vidal-Madjar et al.* (1983) have argued that the D/H ratio may vary according to the line of sight and that the concept of a single ratio for the ISM might be meaningless. In this text,  $(D/H)_{H_2} = 16 \pm 1 \times 10^{-6}$  is used as a reference ratio to calculate the different  $f$  values for the present-day interstellar molecules (see equation (2) and Table 1).

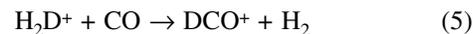
The standard Big Bang model of nucleosynthesis predicts a universal abundance of D that, in practice, depends on the baryon-to-photon ratio (*Schramm*, 1998). The initial D/H ratio of the universe could be around  $50 \times 10^{-6}$  (*Geiss and Gloeckler*, 1998) (see Table 1).

### 2.2. The Present-Day Interstellar Deuterium/Hydrogen Ratio

A large enrichment in D is observed in dense molecular clouds in all detectable C-bearing molecules (so-called organic molecules). In these clouds  $T \approx 10$  K and  $H < 10^3$  cm $^{-3}$ . No reliable data exist on H $_2$ O because the low density of HDO in the gas phase prevents its detection. L. D’Hendecourt and F. Robert (unpublished results) estimated from laboratory spectra of deuterated ice the detection limit of HDO in the infrared spectra of the ISM recorded by the Infrared Space Observatory (ISO). According to this laboratory calibration, the D/H ratio of interstellar water vapor should be  $\leq 9 \times 10^{-4}$ . A compilation of the isotopic composition of various interstellar organic molecules is reported in Fig. 1 in the form of histograms; weighted means ( $f > 1000$ ) does not seem explainable by grain-surface chemistry or by gas-phase reactions involving neutrals, but might result from ion-molecule reactions (*Watson*, 1976; *Guélin et al.*, 1982; *Brown and Millar*, 1989; *Duley and Williams*, 1984; cf. review by *Millar*, 2003). Ions are formed in the gas by UV irradiation from nearby stars; UV photons can penetrate deep inside molecular clouds. At a first approximation, the enrichment in D reflects the H $_2$ D $^+$ /H $_3^+$  and CH $_2$ D $^+$ /CH $_3^+$  ratios that result from



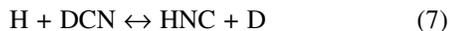
For these two reactions,  $f_{\text{equi}}(H_3^+ \rightarrow H_2D^+) = \exp(227/T)$  and  $f_{\text{equi}}(CH_3^+ \rightarrow CH_2D^+) = \exp(370/T)$ , respectively (*Dishoeck*, 1999). In the form of H $_2$ D $^+$  and CH $_2$ D $^+$ , D is transferred to the organic molecules via reactions such as



leading, in these examples, to  $f_{(HCO^+ \rightarrow H_2)} = f_{(HCN \rightarrow H_2)} \geq 1000$  for  $T < 50$  K (*Guélin et al.*, 1982; *Duley and Williams*, 1984). The steady state is reached in  $10^{6 \pm 1}$  yr, consistent with the estimated lifetime of the cold molecular clouds. *Brown and Millar* (1989) and *Millar et al.* (1989) have shown that, be-

sides reactions (3) and (4), many other reactions are involved in the transfer of D from HD to ions (for example,  $C_2H_2^+ + HD$ ). They have calculated that the measured distribution of D/H ratios in most observed organic molecules corresponds to reaction durations close to  $3 \times 10^5$  yr. In recent and more detailed models, numerous additional reactions are considered (Willacy and Millar, 1998), but these efforts have not changed the main findings described above: Deuterium chemistry in cold interstellar clouds seems well understood.

Determinations of the D/H ratios in organic molecules and in water have been reported in molecular “hot cores.” Hot cores are warm ( $>100$  K) and dense ( $H > 10^7$  cm<sup>3</sup>) and result — as in the case of Orion-KL — from the formation of young massive stars that heat the surrounding ISM. Spatial resolution of the D/H ratio in HCN molecules reveals the occurrence of a transition between the cold molecular cloud and the hot core region (Hatchell et al., 1998; Schilke et al., 1992): the HCN D/H ratio is systematically lower in hot cores than their cold interstellar counterpart (see Fig. 1). It has been proposed that, in hot cores, water results from the evaporation of icy mantles that were condensed at much lower temperature ( $\approx 10$  K) in the surrounding ISM (Rodgers and Millar, 1996). In hot cores the composition of the gas is mainly neutral (Schilke et al., 1992) and the D exchange proceeds via reactions such as



During this reaction  $f_{(HCN-H)}$  decreases with time because D-rich HCN molecules reequilibrate with H at  $\sim 150$  K and becomes isotopically lighter than the surrounding cold ISM ( $\approx 10$  K). A similar situation seems to exist for H<sub>2</sub>O: Measured D/H ratios in H<sub>2</sub>O in hot cores are systematically lower than those calculated for H<sub>2</sub>O in cold molecular clouds. Therefore it has been proposed that, after its evaporation from the grains, water exchanges its D with atomic H, producing a decrease in the D/H ratio as the temperature increases.

### 2.3. The Early Sun and the Giant Gaseous Planets

The D/H ratio in the solar nebula ( $25 \pm 5 \times 10^{-6}$ ) is derived from two independent lines of evidence: (1) the jovian and saturnian D/H ratios and (2) the present-day solar <sup>3</sup>He/<sup>4</sup>He and <sup>4</sup>He/H ratios.

1. Numerous spectroscopic determinations of the D/H ratio in the upper atmospheres of the giant planets have been attempted (Beer and Taylor, 1973, 1978; Bezard et al., 1986; de Bergh et al., 1986, 1990; Feuchtgruber et al., 1997, 1998; Griffin et al., 1996; Lellouch et al., 1996; Mahaffy et al., 1998; Niemann et al., 1996; Smith et al., 1989a,b; cf. review by Owen and Encrenaz, 2003). According to Gautier and Owen (1983) the D/H ratio of the two planets should reflect the value of the solar nebula. In these planets, D is essentially in the form of HD whose abundance has been measured by the Infrared Space Observatory. These obser-

vations are in good agreement with the HD/H<sub>2</sub> ratio measured *in situ* by the Galileo probe mass spectrometer (D/H =  $26 \pm 7 \times 10^{-6}$ ; see Table 1) (Niemann et al., 1996).

2. The D in the early Sun has been converted in <sup>3</sup>He by the thermonuclear reaction  $D + H \rightarrow ^3\text{He}$ . Therefore the D/H ratio of the early Sun can be derived from the present-day <sup>3</sup>He/<sup>4</sup>He measured in the solar wind (<sup>3</sup>He/<sup>4</sup>He<sub>solar</sub>  $\approx 3.8 \pm 0.5 \times 10^{-4}$ ) (Geiss and Gloecker, 1998), provided the initial <sup>3</sup>He/<sup>4</sup>He ratio, <sup>3</sup>He/<sup>4</sup>He<sub>sn</sub>, of the Sun is known

$$\begin{aligned} (D/H)_{\text{early Sun}} = \\ (\text{}^3\text{He}/\text{}^4\text{He}_{\text{solar}} - \text{}^3\text{He}/\text{}^4\text{He}_{\text{sn}}) \times (\text{}^4\text{He}/\text{H})_{\text{sn}} \end{aligned} \quad (8)$$

The (<sup>3</sup>He/<sup>4</sup>He)<sub>sn</sub> estimated from chondrites or from Jupiter data is the most inaccurate parameter in equation (8). Using the recent jovian estimates, a (<sup>3</sup>He/<sup>4</sup>He)<sub>sn</sub>  $\approx 1.5 \times 10^{-4}$  (Mahaffy et al., 1998) corresponds to a (D/H)<sub>early Sun</sub> =  $21 \pm 5 \times 10^{-6}$  (Geiss and Gloecker, 1998) [with (<sup>4</sup>He/H)<sub>sn</sub>  $\approx 10^{-1}$ ].

Combining the two determinations we adopt the usual canonical value for the solar nebula D/H ratio ( $25 \times 10^{-6}$ ). This ratio is therefore used here to calculate the f values reported in Table 1 for all solar system data; i.e., (D/H)<sub>H<sub>2</sub></sub> =  $25 \times 10^{-6}$  in equation (2).

As noted previously, there is a slight difference between this solar ratio and the present-day interstellar ratio (D/H =  $16 \times 10^{-6}$ ). This difference is caused by the destruction of ISM D in stars since the solar system formed, 4.5 G.y. ago. The latter ratio is consistent with the galactic rate of destruction with time of D in stars (Geiss and Gloecker, 1998). Therefore for an identical D/H ratio in the ISM and in the solar system, the calculated enrichment factors f are different.

### 2.4. The Water-rich Giant Planets

Uranus and Neptune have large icy cores. They exhibit D/H ratios significantly higher than in Jupiter and Saturn (Feuchtgruber et al., 1997). An interpretation of this enrichment is based on formation models of these two planets where the cores of the planets grew up by accretion of icy planetesimals with high (D/H) ratio. Assuming that in the interior, water from the planetesimals and molecular hydrogen from the gaseous envelope was isotopically equilibrated at high temperature [ $f_{\text{equi (H}_2\text{-H}_2\text{O)}} = 1$ ] at least once during the lifetime of the planet, the initial (D/H) ratio of the water must have been somewhat higher than the present-day (D/H) ratio in the H<sub>2</sub>, but lower than the cometary (D/H) ratio. In this model, comets stand as examples of the icy planetesimals at the origin of these two planets. However, the isotopic equilibrium assumption may not apply if the planets are not fully convective.

### 2.5. The Terrestrial Planets

In the case of Mars and Venus, the photodissociation of water in their upper atmospheres produces H and D that is subsequently lost to space. Since H is lost faster than D, the two atmospheres have been enriched in D over the last

4.5 G.y. by a Rayleigh distillation process (Donahue *et al.*, 1982; Owen *et al.*, 1988). However, the theory is too imprecise to accurately derive the primordial D/H ratio of these planets. In SNC meteorites, hydroxylated minerals exhibit D/H ratios similar to the martian atmospheric value (Leshin *et al.*, 1994, 1996). However, Gillet *et al.* (2002) have shown that other mafic minerals in SNCs have D/H ratios even lower than the terrestrial mantle. Thus the exact value of the pristine martian D/H ratio is still considered to be an open question.

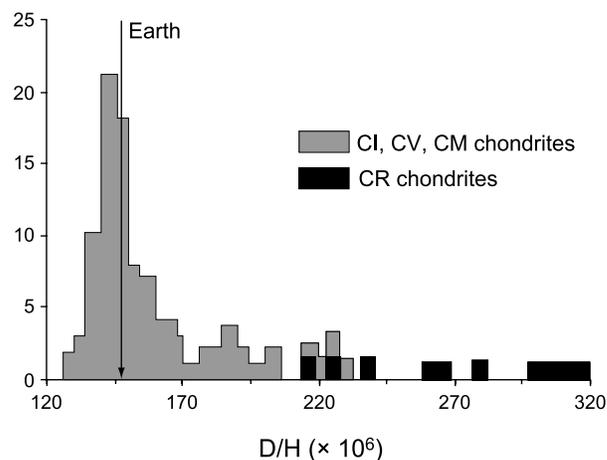
The D/H ratio on Earth has been recently estimated accurately [ $D/H = 149 \pm 3 \times 10^{-6}$  (Lécuyer *et al.*, 1998)]. Escape from the top of the atmosphere should not have decreased the D/H ratio of the oceans significantly (<1%) since the end of the planetary accretion. This has been shown theoretically [by modeling the flux of H escaping to space (Hunten and McElroy, 1974)] and observationally [on Earth, kerogen and mineral D/H ratios are invariable within  $\pm 1\%$  through geological times (e.g., Robert, 1989)].

## 2.6. Meteorites and Some Remarks on Interplanetary Dust Particles

**2.6.1. Variations at the whole-rock scale.** Little attention has been paid to the origin of variations in the whole-rock H-isotopic composition of carbonaceous chondrites [see the review of the available literature data by Robert (2003)]. These meteorites share several common isotopic characteristics: (1) At a bulk scale they are all enriched in D with *f* values between 5 and 12. (2) They contain IOM systematically enriched in D by a factor 2 to 3 relative to the minerals (Robert and Epstein, 1982; Kerridge *et al.*, 1987; Epstein *et al.*, 1987; Robert *et al.*, 1987; Pizzarello *et al.*, 1991).

In Fig. 2, the D/H ratio of the carbonaceous chondrites is reported as a histogram. In meteorites H is present as hydroxyls in phyllosilicates (and to a lesser extent bound to C in organic molecules) but it is collected in the form of water in most experiments when the sample is outgassed by step-heating. All data in Fig. 2 were obtained by outgassing bulk samples under vacuum or in presence of He or molecular oxygen and by analyzing the mass spectrum of the collected molecular hydrogen after the reduction of water.

What fraction of water extracted from an extraterrestrial sample is terrestrial contamination? Surprisingly, detailed experimental studies indicate that this fraction is small, i.e., that the relative contribution of the terrestrial contamination is <15% (Robert and Deloule, 2002). These studies have been performed by comparing the D/H ratio of a sample in contact with liquid D-rich water to the same sample in contact with liquid water having a terrestrial D/H ratio. For example, after outgassing the Orgueil meteorite ( $\approx 10$  wt%  $H_2O$ ) overnight at 50°C under vacuum, water extracted above 50°C shows almost no (additional?) contamination [ $\leq 0.04$  wt%  $H_2O$  (Engrand *et al.*, 1999)]. Similarly, altered olivine in the Semarkona meteorite shows a relative contamination fraction  $\leq 15\%$ , although the water concentration



**Fig. 2.** Distribution of the D/H ratio in whole rock carbonaceous meteorites ( $N = 106$ ). The large range in D/H likely results from variations in the alteration water D/H ratio. This water may have recorded different degree of isotope exchange during parent body hydrothermalism, with D-rich organic compounds. The tail toward high D/H ratios is likely related to a heliocentric distribution, with the highest D/H ratios located in the coldest and remote regions of the solar system (see IDPs in Fig. 3).

in this mineral does not exceed 0.2 wt%  $H_2O$  (Robert and Deloule, 2002). These studies have addressed the specific problem of the terrestrial contamination by isotopic exchange. However, it should be kept in mind that alteration on Earth of meteoritic minerals — by contact with liquid water — yields the addition of terrestrial H in the form of hydroxyl groups. This addition is irreversible at room temperature and the resulting  $-OH$  cannot be separated from the indigenous  $-OH$  by a simple stepwise heating pyrolysis.

Most samples reported in Fig. 2 are “falls” and thus have never been in contact with liquid water on Earth. Therefore the range in D/H ratio reported in Fig. 2 cannot result from different degrees of terrestrial contamination.

In several CI and CM meteorites (Cold-Bokkeveld, Murray, Murchison, Orgueil) the IOM has been chemically extracted and purified and its D/H ratio has been determined by stepwise temperature pyrolysis (Robert and Epstein, 1982; Kerridge, 1987; Yang and Epstein, 1983). Although there are large uncertainties about these determinations because of the contamination linked to the acid-extraction procedures, the IOM D/H ratios lie between  $310$  and  $370 \times 10^{-6}$  for these meteorites. Halbout *et al.* (1990) have argued that all these extracts have a similar indigenous D/H ratio of  $370 \times 10^{-6}$ , with lower values due to acid contamination. In the case of the Renazzo meteorite, the IOM D/H ratio is markedly different from CI-CM with a ratio of  $550 \times 10^{-6}$ . As observed in Fig. 2 the Renazzo-type meteorites (reported as CR meteorites) are systematically enriched in D relative to CI-CM. Mass-balance calculation using the C concentration in the bulk samples and the C/H ratio in the OM indicates that the clay minerals have a D/H ratio close to  $300 \times$

$10^{-6}$  in Renazzo. Thus, the difference between CI-CM and CR cannot be attributed to the presence of D-rich IOM but must be due to an enhancement in D abundance at the scale of the bulk sample. The most puzzling aspect of the variations reported in Fig. 2 is that they greatly exceed the variations observed on Earth for clay minerals formed at temperatures between  $0^\circ$  and  $100^\circ\text{C}$ .

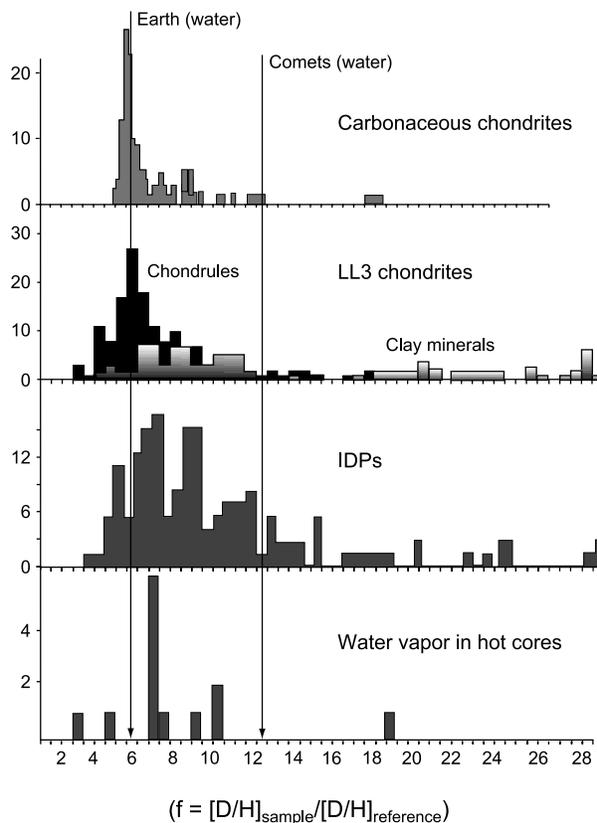
An isotopic fractionation could occur during liquid water circulation in a warm parent body (Bunch and Chang, 1980; Sears *et al.*, 1995). As a general rule, clay minerals are depleted in D relative to water from which they formed. As a rule of thumb, for temperatures  $<100^\circ\text{C}$  one can add  $\approx 10 \times 10^{-6}$  to the measured D/H ratio of the minerals in order to obtain the D/H ratio of the water in isotopic equilibrium with that mineral. This correction is small compared to the total variations reported in Fig. 2. Therefore these variations cannot be attributed to different degrees of isotopic exchange with a water reservoir having a unique D/H ratio.

Part of the observed variations in bulk samples may be caused by different mixing ratios between clays and OM. The maximum value for the relative contribution of the organic hydrogen is  $\approx 10\%$  (i.e., 90% of H is hosted by clays), corresponding to a shift in the D/H ratio of  $\approx 20 \times 10^{-6}$ , i.e., 1 order of magnitude smaller than the total D/H distribution reported in Fig. 2. Several authors have attempted to relate the C/H ratio to the D/H ratio of the carbonaceous chondrites in order to trace the relative contribution of the organic matter to the bulk D/H ratio. Although positive correlations have been found between these two ratios (Kerridge, 1985), these correlations have been met with several counter examples. Thus, the variations in Fig. 2 cannot simply be caused by the differences in the mixing ratio between water and organic matter.

Two small peaks are present in the tail of the distribution in Fig. 2, at D/H equal to  $190$  and  $220 \times 10^{-6}$ . In the distribution reported here, all analyses have been used and thus the same meteorite can be counted more than once. However, reporting an average value for each meteorite — i.e., having a unique D/H ratio per meteorite — does not alter the peaks at D/H equal to  $190$  and  $220 \times 10^{-6}$ . This observation reinforces the statistical value of the distribution. As a firm conclusion of this discussion, the asymmetry of the distribution reported in Fig. 2 results from a wide range of D/H ratios both in IOM and in clays. Eiler and Kitchen (2004) have shown that the least-altered CM samples (e.g., Murchison) have D/H ratios in their matrix and whole rock close to  $150 \times 10^{-6}$ . Conversely, both whole-rock and matrix samples of altered CM chondrites and their chondrules (e.g., Cold Bokkeveld) have D/H close to  $125 \times 10^{-6}$ . The degree of alteration in these samples is traced by several geochemical criteria that correlate with the D/H ratio. Following this interpretation, the lowest D/H ratio of the distribution reported in Fig. 2 stands for the isotopic composition of water that was circulating in the parent bodies and that was at the origin of the mineralogical alteration features; i.e., water D/H  $\approx 120 \times 10^{-6}$ . In this interpretation, each whole-rock sample is an open system and a large fraction of the alteration water has been lost, perhaps to space.

Finally, it should be noted that the observed distribution of the bulk sample D/H ratio (Fig. 2) could be biased by the dynamics of meteorite delivery to Earth. Fragments of disrupted asteroids have a greater chance to intercept the Earth's orbit if the parent bodies were initially located at distances  $<2.5$  AU (Vokrouhlický and Farinella, 2000). At greater distances from the Sun, the fragments have a high probability of being expelled in the outer regions of the solar system. It is thus unlikely that the asymmetry in Fig. 2 reflects the relative proportion of parent bodies in the meteorite source [i.e., the asteroid belt (cf. Meibom and Clark, 1999)], which instead might simply reflect the probability distribution for collecting samples on Earth as a function of the distance of their sources. The D/H distribution of IDPs supports this interpretation (Fig. 3). Although the sources of IDPs extend far beyond the asteroid belt, their distribution mimics that of the carbonaceous chondrites. Therefore, parent bodies located in the far regions of the solar system have higher D/H ratios than those in the inner asteroid belts.

**2.6.2. Molecular and mineralogical hosts of the deuterium/hydrogen ratio.** There are two types of primitive meteorites in which high D/H ratios have been found: LL3 and



**Fig. 3.** Distributions of the D/H ratio in (1) whole-rock samples of carbonaceous chondrites, (2) LL3 chondrites (chondrules and clay minerals in the matrix), (3) IDPs, and (4) water vapor from hot cores (Jacq *et al.*, 1990; Gensheimer *et al.*, 1996; personal compilation of published data). The  $f$  unit is used to normalized the enrichment in D relative to universal H:  $\text{D/H} = 25 \times 10^{-6}$  and  $16 \times 10^{-6}$  for meteorites-comets-IDPs and hot cores, respectively.

carbonaceous chondrites (referred hereafter to as CCs). The IOM has been extracted chemically from these two types of rocks and has been found to be systematically enriched in D:  $f_{(\text{H}_2\text{-IOM})} = 15\text{--}25$  in CCs (with most values around 15; i.e.,  $\text{D}/\text{H} = 375$  to  $625 \times 10^{-6}$ ) and  $f_{(\text{H}_2\text{-IOM})}$  up to 44 in LL3 ( $\text{D}/\text{H} \approx 1100 \times 10^{-6}$ ). The possible contamination of IOM during the chemical procedure has been carefully evaluated and is negligible ( $<7\%$ ) (Halbout *et al.*, 1990).

The usual interpretation of this isotopic enrichment is “interstellar chemistry.” However, as shown in Fig. 1, there is a marked gap in D/H ratios between interstellar and solar system organic matter. Such a difference is impossible to reconcile with a simple temperature effect; i.e., the higher the temperature of ion-molecule reactions, the lower the D/H ratio. The corresponding calculated temperature ( $\approx 120$  K using reaction (4)) is never reached in the ISM (except around massive hot stars). In addition, if such a high calculated temperature corresponded to a protosolar environment, the corresponding gas density would prevent H from being ionized. Therefore the “interstellar interpretation” should be considered more as an analog with the ISM, rather than as a quantitative model supported by facts.

Interstellar medium organic molecules are simple. Chondritic IOM is highly polymerized. It does not seem plausible that the polymerization of such simple D-rich molecules would be associated with a decrease in their D/H ratios because (1) polymerization does not yield an addition of H (or D) and (2) the isotopic exchange between organic H and molecular  $\text{H}_2$  is prohibitively slow at temperatures  $<250$  K. A solution to this problem was proposed (see section 3): In the protosolar nebula, the organic polymer D/H ratio may have decreased by an isotopic exchange with molecular  $\text{H}_2$  at temperatures as high as 650 K. However, this issue should nevertheless be considered open because (1) no D/H determination has been reported for interstellar polycyclic aromatic hydrocarbon (PAH) and (2) although several types of ISM synthesis have been proposed to account for the chondritic IOM [UV photolysis of D-rich ices or gas-grain reactions (Sandford *et al.*, 2001; Sandford, 2002)], a quantitative estimate of their corresponding D/H ratios has not been reached.

In the case of the Murchison carbonaceous chondrite, the soluble organic fraction (amino-acids, fatty acids, hydrocarbons; see Table 1) has been separated from the bulk sample by organic solvent procedures and yields  $f_{(\text{H}_2\text{-SOM})} = 12.5\text{--}22$  [ $\text{D}/\text{H} = 310$  to  $550 \times 10^{-6}$  (Epstein *et al.*, 1987; Pizzarello *et al.*, 1991)]. Such D/H ratios are comparable with those measured in the IOM. Their possible “interstellar” origins face similar issues as those previously mentioned for the IOM.

After the formation of CM and CI chondrites a late circulation of water occurring at (or near) the surface of their parent bodies could have formed the clay minerals (Bunch and Chang, 1980). An often-quoted terrestrial analogy for this mechanism is “hydrothermal alteration.” Consequently, the D/H ratio of these minerals can be used to determine the water D/H ratio because the isotopic fractionation between clay minerals and liquid water is negligibly small

( $\leq 6.5\%$ ) at the scale of the isotopic variations in the solar system. The D/H ratios of these clay minerals has been determined by two methods: (1) by mass balance in CCs [i.e., by subtracting from whole-rock analysis the measured IOM D/H ratio (cf. Robert and Epstein, 1982)] or (2) by *in situ* measurements with the ion microprobe (Deloule and Robert, 1995; Deloule *et al.*, 1998). As general rule, whole-rock D/H ratios in CCs can be taken at face value for the D/H ratio of water that has circulated in these bodies (within  $\pm 10\%$ ). This rule clearly does not apply to the LL3 chondrites.

The LL3 chondrites contain D-rich ( $720 \times 10^{-6}$ ) and D-depleted (hydroxylated?) minerals ( $75 \times 10^{-6}$ ) mixed in various proportions with D-rich IOM ( $\leq 1000 \times 10^{-6}$ ) (McNaughton *et al.*, 1981; Yang and Epstein, 1983; Deloule and Robert, 1995). In LL3 meteorites, pyroxene in chondrules is enriched in D [ $f_{(\text{H}_2\text{-H}_2\text{O})} = 16$ ;  $\text{D}/\text{H} = 400 \times 10^{-6}$ ] relative to other minerals in the same chondrule or relative to the clay minerals of the matrix [ $f_{(\text{H}_2\text{-H}_2\text{O})} = 3.5$ ;  $\text{D}/\text{H} = 88 \times 10^{-6}$ ]. In the matrix surrounding the chondrules, some clay minerals also exhibit high D/H ratios [ $f_{(\text{H}_2\text{-H}_2\text{O})} = 29$ ;  $\text{D}/\text{H} = 725 \times 10^{-6}$ ] that seem to have escaped — along with the pyroxenes in chondrules — the isotopic reequilibration during the late hydrothermal alteration. The mechanism for the incorporation and preservation of these high D/H ratios in chondrules is not understood, nor is the origin of such an isotopic heterogeneity among the matrix clay minerals that are considered to be the products of alteration by water that should be — by definition — isotopically homogeneous! Thus, contrary to CCs, no coherent classification can be proposed to account for the molecular distribution of the D/H ratio in LL3 meteorites.

Interplanetary dust particles have been collected in space and in Antarctic ice. They show extremely large variations in their D/H ratios [ $f_{(\text{H}_2\text{-H}_2\text{O})} = 3.6$  to 161;  $\text{D}/\text{H} = 90$  to  $4000 \times 10^{-6}$ ] (McKeegan *et al.*, 1985; Zinner *et al.*, 1983; Messenger, 2000; Engrand *et al.*, 1999). The organic nature of the D-rich carriers have been unambiguously identified through the correlated variations of the elemental C/H and isotopic D/H ratios (Aléon *et al.*, 2001; cf. review by Messenger *et al.*, 2003). Water in IDPs has D/H ratios either close to the chondritic value or close to the cometary value for water. In the histogram in Fig. 3, it can be seen that bulk IDPs have a distribution of  $f$  values close to CCs, suggesting that cometary fragments are rare in the IDP population.

Important observations have been made through the analysis of IDPs at a 1- $\mu\text{m}$  scale with the ion microprobe (Aléon *et al.*, 2001). In one IDP, three intimately mixed components have been identified: (1) water with  $\text{D}/\text{H} \approx 150 \times 10^{-6}$ , (2) organic molecules with C/H ratios close to those of the CCs and a  $\text{D}/\text{H} \approx 500 \times 10^{-6}$ , and (3) organic molecules with  $\text{C}/\text{H} \approx 1$  (an aliphatic molecule?) and  $\text{D}/\text{H} \approx 1500 \times 10^{-6}$  ( $f = 60$ ). These observations suggest that, under the chemical and physical conditions that prevailed at the formation of IDPs, a wide range of D/H ratios were established in the primitive components of the solar system. It can be thus proposed that the precursors of these different species correspond to different  $\Delta E$  values for ion-molecule reactions ( $\Delta E$  is defined as the exothermicity in reactions

such as reaction (3) or reaction (4)). The isotopic exchange reactions corresponding to these different  $\Delta E$  values have not been yet identified but, as suggested by *Sandford et al.* (2001), may reflect the different isotopic fractionation pathways taking place during homogeneous (gas-gas) or heterogeneous (gas-grain) reactions. In other words, grains and gas may have carried a wide range of different D/H ratios.

## 2.7. Comets

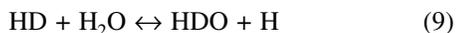
The D/H ratios in water have been reported for three different comets (see Table 1) (*Meier et al.*, 1998a,b; *Eberhardt et al.*, 1995; *Bockelée-Morvan et al.*, 1988) with a mean  $f_{(\text{H}_2-\text{H}_2\text{O})}$  value = 12 (D/H =  $300 \times 10^{-6}$ ). Such a value is a factor of 2 higher than the mean chondritic value but a factor of 2.5 lower than clay minerals in some LL3 chondrites. In HCN molecules (?),  $f_{(\text{H}_2-\text{HCN})} = 92$ ; such a high  $f$  value does not have a chondritic counterpart [the maximum  $f_{(\text{H}_2-\text{IOM})} = 44$  in LL3].

It can be seen (cf. Fig. 3) that the weighted mean composition of CCs corresponds precisely to that of Earth [ $f_{(\text{H}_2-\text{H}_2\text{O})} = 6$ ]. If CCs are taken as the carrier of water on Earth, a minimum  $f$  value can be assigned for the primitive Earth:  $f \geq 4$  (i.e., the minimum  $f$  of the CCs distribution). This implies that (1) no major isotopic fractionation has occurred during the formation of the oceans and (2) no important (>10%) late addition of D-rich water has taken place during the subsequent evolution of the planet.

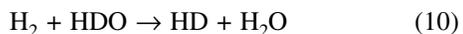
## 3. ORIGIN OF WATER IN THE SOLAR SYSTEM

The D/H variations in Fig. 3 correspond to D enrichments by factors of 5–12 relative to universal  $\text{H}_2$ . Three interpretations for this enrichment have been discussed in detail in the literature. They can be summarized by the following simple reactions:

1. Equilibrium isotopic exchange in the protosolar nebula between molecular hydrogen and water:

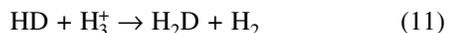


2. Kinetic isotopic exchange in the protosolar nebula between D-rich water and molecular hydrogen:



In this case, the water is enriched in D prior to the formation of the solar nebula, presumably through interstellar ion-molecule reactions at low temperature.

3. Low temperature ion-molecule reactions in the ISM:



The third reaction represents the first step of the synthesis of water whose D/H ratio reflects that acquired by  $\text{H}_3^+$  through reaction (11).

The first two interpretations were addressed by *Drouart et al.* (1999) (see also *Dubrulle*, 1992; *Mousis et al.*, 2000;

*Hersant et al.*, 2001; *Robert et al.*, 2000). Reaction (9) has been shown to be impossible because of kinetic limitations (*Lecluse and Robert*, 1994). Reaction (10) has been studied in detail in a model of a turbulent protosolar nebula where the temperature and pressure vary as a function of time and heliocentric distance. It has been shown that the water D/H ratio can decrease in such a nebula by a factor of 10 through the exchange reaction (10), from an initial value of  $750 \times 10^{-6}$  to a final value of  $75 \times 10^{-6}$ . Water condensed in the outer regions of the nebula should exhibit values  $\approx 300 \times 10^{-6}$  (i.e., the cometary value), while water condensed at a close distance from the Sun (1 AU) can reach a value of  $\approx 75 \times 10^{-6}$ . According to this model, the terrestrial and chondritic D/H value is reached in the protosolar nebula at 3–5 AU in  $\leq 10^6$  yr.

Reaction (11) was investigated empirically by *Robert* (2002), who suggested that ion-molecule reactions could have taken place at the surface of the protosolar nebula, where high ion concentration can be reached as a result of UV and/or X-ray irradiation from the early (T Tauri stage) Sun (*Glassgold et al.*, 2000). T. Millar (personal communication, 2003) has performed an unpublished detailed calculation of the D enrichment that can be reached in water through ion-molecule reactions. According to these calculations, the solar system water D/H ratio is also in agreement with that obtained by reaction (11) and would correspond to a formation temperature between 40 and 50 K at densities on the order of  $10 \text{ H cm}^{-3}$ . However, the corresponding D/H ratio in organic molecules — which can be calculated to first order through reaction (4) — exceed by far those measured in chondritic meteorites. Therefore water and organic matter D/H ratios seem to require different temperatures and densities. In this respect, the different interpretations are not consistent.

Following the interpretation according to which hot atom chemistry took place in the early solar system, *Aléon and Robert* (2004) have attempted to calibrate the temperature of ion-molecule reactions by correlating the D/H and  $^{15}\text{N}/^{14}\text{N}$  ratios in solar system organic molecules from several classes of chondrites, cometary data, and IDPs (*Aléon et al.*, 2003); this gives  $70 \leq T \leq 90 \text{ K}$ . If correct, this implies that — contrary to models derived from reaction (10) — water and organic matter formed at the surface of the disk never thermally reequilibrated with  $\text{H}_2$  in the protosolar nebula. This interpretation has not yet been numerically modeled in a turbulent protosolar nebula.

To conclude this section on chondritic data, we emphasize that no quantitative model has successfully accounted for the D/H ratio of coexisting water and organic molecules in comets and carbonaceous meteorites.

## 4. ORIGIN OF WATER ON EARTH

As extensively discussed in the literature (*Balsiger et al.*, 1995; *Bockelée-Morvan et al.*, 1998; *Meier et al.*, 1998a; *Eberhardt et al.*, 1995; *Robert*, 2001), detailed mass-balance calculations between the D/H ratio in CCs and the D/H ratio in comets show that cometary water cannot represent more than 10% [and perhaps as little as 0% (*Dauphas et*

al., 2000)] of the total budget of water on Earth (Deloule et al., 1998). Two scenarios (Drake and Righter, 2002; Morbidelli et al., 2000) have been proposed to import water on Earth during its accretion. The two scenarios are in conflict, but each one has interesting implications.

Morbidelli et al. (2000) proposed on the basis of the dynamical evolution of planetary embryos (1000-km-sized planetesimals) during the first 50 m.y. of the solar system that the carriers of water on Earth originated from  $\approx 2.5$  AU. Few impacts would have been sufficient to import the oceanic mass in the final stages of Earth accretion. This scenario is in agreement with the fact that the terrestrial water D/H ratio [ $149 \pm 3 \times 10^{-6}$  (Lecuyer et al., 1998)] and the mean D/H of the CCs (cf. Fig. 2 and 3) are indistinguishable.

Drake and Righter (2002) suggested that the water-rich planetesimals at the origin of the terrestrial oceans were formed at the same heliocentric distance as the silicate material that formed Earth. According to these authors, the chemical and isotopic compositions of many elements in these planetesimals have to be different from any known type of CCs in order to account for the present-day bulk composition of Earth.

The interpretation of Drake and Righter implies that the D/H ratio of water condensed at a terrestrial orbit had a D/H ratio similar to the mean value defined by the CCs. The Drouart et al. model shows that this may be indeed be the case (F. Hersan, unpublished data, 2002): In a turbulent nebula the D/H ratio in water should not vary significantly for heliocentric distances  $< 2$  AU.

## 5. FUTURE RESEARCH DIRECTIONS

A number of key experimental determinations could shed some light on the problems discussed above. A determination of the D/H ratio of the icy satellites of Jupiter and Saturn would allow a (de)verification that the D/H ratio is indeed correlated with heliocentric distance in the protosolar nebula. A determination of the D/H ratio of comets from the Kuiper belt region may yield new constraints to the problem of water delivery to the early Earth. Similarly, a determination of the D/H ratio of enstatite chondrites might bring us closer to understanding the isotopic composition of indigenous H on Earth, because these meteorites seem to have formed in conditions similar to those under which proto-Earth material formed. Finally, a determination of the distribution of the D/H ratio at a molecular level among the organic moieties of the IOM remains the best possible way to detect interactions between water and organic molecules in space or in meteoritic parent bodies.

## REFERENCES

- Aléon J. and Robert F. (2004) Interstellar chemistry recorded by nitrogen isotopes in solar system organic matter. *Icarus*, *167*, 424–430.
- Aléon J., Engrand C., Robert F., and Chaussidon M. (2001) Clues to the origin of interplanetary dust particles from the isotopic study of their hydrogen-bearing phases. *Geochim. Cosmochim. Acta.*, *65*, 4399–4412.
- Aléon J., Robert F., Chaussidon M., and Marty B. (2003) Nitrogen isotopic composition of macromolecular organic matter in interplanetary dust particles. *Geochim. Cosmochim. Acta*, *67*, 3773–3783.
- Balsiger H., Altwegg K., and Geiss J. (1995) D/H and  $^{18}\text{O}/^{16}\text{O}$  ratio in the hydronium ion and in neutral water from in situ ion measurements in comet P/Halley. *J. Geophys. Res.*, *100*, 5827–5834.
- Beer R. and Taylor F. W. (1973) The abundance of  $\text{CH}_3\text{D}$  and the D/H ratio in Jupiter. *Astrophys. J.*, *179*, 309–327.
- Beer R. and Taylor F. W. (1978) The D/H and C/H ratios in Jupiter from  $\text{CH}_3\text{D}$  phase. *Astrophys. J.*, *219*, 763–767.
- Bezard B., Gautier D., and Marten A. (1986) Detectability of HD and non equilibrium species in the upper atmospheres of giant planets from their submillimeter spectrum. *Astron. Astrophys.*, *161*, 387–402.
- Bockelée-Morvan D., Gautier D., Lis D. C., Young K., Keene J., Phillips T., Owen T., Crovisier J., Goldsmith P. F., Bergin E. A., Despois D., and Wooten A. (1998) Deuterated water in comet C/1996 B2 (Hyakutake) and its implications for the origin of comets. *Icarus*, *193*, 147–162.
- Brown P. D. and Millar T. J. (1989) Models of the gas-grain interaction-deuterium chemistry. *Mon. Not. R. Astron. Soc.*, *237*, 661–671.
- Brown R. D. and Rice E. (1981) Interstellar deuterium chemistry. *Philos. Trans. R. Soc. London*, *A303*, 523–533.
- Bunch T. E. and Chang S. (1980) Carbonaceous chondrites: II. Carbonaceous chondrites phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. *Geochim. Cosmochim. Acta*, *44*, 1543–1577.
- Dauphas N., Robert F., and Marty B. (2000) The late asteroidal and cometary bombardment of Earth as recorded in water deuterium to protium ratio. *Icarus*, *148*, 508–512.
- de Bergh C., Lutz B. L., Owen T., Brault J., and Chauville J. (1986) Monodeuterated methane in the outer solar system. II. Its detection on Uranus at 1.6  $\mu\text{m}$ . *Astrophys. J.*, *311*, 501–510.
- de Bergh C., Lutz B., Owen T., and Maillard J.-P. (1990) Monodeuterated methane in the outer solar system. IV. Its detection and abundance on Neptune. *Astrophys. J.*, *355*, 661–666.
- Deloule E. and Robert F. (1995) Interstellar water in meteorites? *Geochim. Cosmochim. Acta*, *59*, 4695–4706.
- Deloule E., Doukhan J.-C., and Robert F. (1998) Interstellar hydroxyle in meteorite chondrules: Implications for the origin of water in the inner solar system. *Geochim. Cosmochim. Acta*, *62*, 3367–3378.
- Dishoeck Van E. F. (1999) Models and observations of gas-grain interactions in star-forming regions. In *Formation and Evolution of Solids in Space* (J. M. Greenberg and A. Li, eds.), pp. 91–121. Kluwer, Dordrecht.
- Donahue T. M., Hoffman J. H., Hodges R. R. Jr., and Watson A. J. (1982) Venus was wet: A measurement of the ratio of deuterium to hydrogen. *Science*, *216*, 630–633.
- Drake M. J. and Righter K. (2002) Determining the composition of the Earth. *Nature*, *416*, 39–44.
- Drouart A., Dubrulle B., Gautier D., and Robert F. (1999) Structure and transport in the solar nebula from constraints on deuterium enrichment and giant planet formation. *Icarus*, *140*, 129–155.
- Dubrulle B. (1992) A turbulent closure model for thin accretion disks. *Astron. Astrophys.*, *266*, 592–604.
- Duley W. W. and Williams D. A. (1984) *Interstellar Chemistry*. Harcourt, Brace, and Jovanovich, New York.
- Eberhardt P., Reber M., Krankowsky D., and Hodges R. R. (1995)

- The D/H and  $^{18}\text{O}/^{16}\text{O}$  ratios in water from comet P/Halley. *Astron. Astrophys.*, 302, 301–316.
- Engrand C., Deloule E., Robert F., Maurette M., and Kurat G. (1999) Extraterrestrial water in micrometeorites and cosmic spherules from Antarctica: An ion microprobe study. *Meteoritics & Planet. Sci.*, 34, 773–786.
- Epstein R. I., Lattimer J. M., and Schramm D. N. (1976) The origin of deuterium. *Science*, 263, 198–202.
- Epstein S., Krishnamaty R. V., Cronin J. R., Pizzarello S., and Yuen G. U. (1987) Unusual stable isotope ratios in amino acids and carboxylic acid extracts from the Murchison meteorite. *Nature*, 326, 477–479.
- Eiler J. M. and Kitchen N. (2004) Hydrogen isotope evidence for the origin and evolution of the carbonaceous chondrites. *Geochim. Cosmochim. Acta*, 68, 1395–1411.
- Feuchtgruber H., Lellouch E., de Graauw T., Encrenaz Th., and Griffin M. (1997) Detection of HD on Neptune and determinations of D/H ratio from ISO/SWS observations. *Bull. Am. Astron. Soc.*, 29, 995.
- Feuchtgruber H., Lellouch E., Encrenaz Th., Bezaud B., de Graauw T., and Davies G. R. (1998) Detection of HD in the atmospheres of Uranus and Neptune: A new determination of the D/H ratio. *Astron. Astrophys.*, 341, L17–L21.
- Galli D., Palla F., Ferrini F., and Penco U. (1995) Galactic evolution of D and  $^3\text{He}$ . *Astrophys. J.*, 443, 536–550.
- Gautier D. and Owen T. (1983) Cosmological implication of helium and deuterium abundances of Jupiter and Saturn. *Nature*, 302, 215–218.
- Geiss J. and Gloecker G. (1998) Abundances of deuterium and helium in the protosolar cloud. *Space Science Rev.*, 84, 239–250.
- Geiss J. and Reeves H. (1972) Cosmic and solar system abundances of deuterium and helium-3. *Astron. Astrophys.*, 18, 126–132.
- Gensheimer P. D., Mauersberger R., and Wilson T. L. (1996) Water in galactic hot cores. *Astron. Astrophys.*, 314, 281–294.
- Gillet Ph., Barrat J. A., Deloule E., Wadhwa M., Jambon A., Sautter V., Devouard B., Neuville D., Benzerara K., and Lesroud M. (2002) Aqueous alteration in the Northwest Africa (NWA 817) Martian meteorite. *Earth Planet. Sci. Lett.*, 203, 431–444.
- Glassgold A., Feigelson E. D., and Montmerle T. (2000) Effects on energetic radiation in young stellar objects. In *Protostars and Planets IV* (V. Mannings et al., eds.), pp. 429–455. Univ. of Arizona, Tucson.
- Griffin M. J., Naylor D. A., Davis G. R., Ade P. A. R., Oldman P. G., Swinyard B. M., Gautier D., Lellouch E., Orton G. S., Encrenaz Th., de Graauw T., Furniss I., Smith I., Armand C., Burgdorf M., Del Giorgio A., Ewart D., Gry C., King K. J., Lim T., Molinari S., Price M., Sidher S., Smith A., Texier D. N., Trams S. J., Unger S. J., and Salama A. (1996) First detection of the 56 mm rotational line of HD in Saturn's atmosphere. *Astron. Astrophys.*, 315, L389–L392.
- Gry C., Laurent C., and Vidal-Madjar A. (1983) Evidence of hourly variations in the deuterium Lyman line profiles toward Epsilon Persei. *Astron. Astrophys.*, 124, 99–104.
- Guélin M., Langer W. D., and Wilson R. W. (1982) The state of ionization in dense molecular clouds. *Astron. Astrophys.*, 107, 107–127.
- Halbout J., Robert F., and Javoy M. (1990) Hydrogen and oxygen isotope compositions in kerogens from the Orgueil meteorite: Clues to solar origin. *Geochim. Cosmochim. Acta*, 54, 1453–1462.
- Hatchell J., Millar T. J., and Rodgers S. D. (1998) The DCN/HCN abundance ratio in hot molecular clouds. *Astron. Astrophys.*, 332, 695–703.
- Hersant F., Gautier D., and Huré J-M (2001) A two dimensional model for the primordial nebula constrained by D/H measurements in the solar system: Implications for the formation of giant planets. *Astrophys. J.*, 554, 391–407.
- Hunten D. M. and McElroy M. B. (1974) Production and escape of terrestrial hydrogen. *J. Atmos. Sci.*, 31, 305–317.
- Jacq T., Walmsley C. M., Henkel C., Baudry A., Mauersberger R., and Jewell P. R. (1990) Deuterated water and ammonia in hot cores. *Astron. Astrophys.*, 228, 447–470.
- Kerridge J. F. (1985) Carbon, hydrogen and nitrogen in carbonaceous meteorites: Abundances and isotopic compositions in bulk samples. *Geochim. Cosmochim. Acta*, 49, 1707–1714.
- Kerridge J. F., Chang S., and Shipp R. (1987) Isotopic characterisation of kerogen-like material in Murchison carbonaceous chondrite. *Geochim. Cosmochim. Acta*, 51, 2527–2540.
- Kolodny Y., Kerridge J. F., and Kaplan I. R. (1980) Deuterium in carbonaceous chondrites. *Earth Planet. Sci. Lett.*, 46, 149–158.
- Lécluse C. and Robert F. (1994) Hydrogen isotope exchange rates: Origin of water in the inner solar system. *Geochim. Cosmochim. Acta*, 58, 2297–2939.
- Lécluse C., Robert F., Gautier D., and Guiraud M. (1996) Deuterium enrichment in giant planet. *Planet. Space Sci.*, 44, 1579–1592.
- Lécuyer C., Gillet Ph., and Robert F. (1998) The hydrogen isotope composition of sea water and the global water cycle. *Chem. Geol.*, 145, 249–261.
- Lellouch E., Encrenaz Th., Graauw Th., Scheid S., Feuchtgruber H., Benteima D. A., Bézard B., Drossart P., Griffin M., Heras A., Kesselr M., Leech K., Morris A., Roelfsema P. R., Roos-Serote M., Salama A., Vandebussche B., Valentijn E. A., Davies G. R., and Naylor D. A. (1996) Determinations of D/H ratio on Jupiter from ISO/SWS observations. *Bull. Am. Astron. Soc.*, 28, 1148.
- Leshin L., Hutcheon I. D., Epstein S., and Stolper E. (1994) Water on Mars: Clues from deuterium/hydrogen and water contents of hydrous phases in SNC meteorites. *Science*, 265, 86–90.
- Leshin L., Epstein S., and Stolper E. (1996) Hydrogen isotope geochemistry of SNC meteorites. *Geochim. Cosmochim. Acta*, 60, 2635–2650.
- Linsky J. L. (2003) Atomic deuterium/hydrogen in the galaxy. In *Solar System History from Isotopic Signatures of Volatile Elements* (R. Kallenbach et al., eds.), pp. 49–60. ISSI Space Science Series, Vol. 16.
- Linsky J. L., Brown A., Gayley K., Diplas A., Savage B. D., Landsman T. R., Shore S. N., and Heap S. R. (1993) High-resolution spectrograph observations of the local interstellar medium and the deuterium/hydrogen ratio along the line of sight toward Capella. *Astrophys. J.*, 402, 694–709.
- Mahaffy P. R., Donahue T. M., Atreya S. K., Owen T. C., and Niemann H. B. (1998) Galileo probe measurements of D/H and  $^3\text{He}/^4\text{He}$  in Jupiter's atmosphere. *Space Science Rev.*, 84, 251–263.
- McCullough P. R. (1991) The interstellar deuterium to hydrogen ratio. A reevaluation of Lyman adsorption line measurements. *Astrophys. J.*, 390, 213–225.
- McKeegan K. D., Walker R. M., and Zinner E. (1985) Ion microprobe isotopic measurements of individual interplanetary dust particles. *Geochim. Cosmochim. Acta*, 49, 1971–1987.
- McNaughton N. J., Borthwicks S., Fallick A. K., and Pillinger C. T. (1981) D/H ratio in unequilibrated ordinary chondrites.

- Nature*, 294, 639–641.
- McNaughton N. J., Fallick A. E., and Pillinger C. T. (1982) Deuterium enrichments in type 3 ordinary chondrites. *Proc. Lunar Planet. Sci. Conf. 13th*, in *J. Geophys. Res.*, 87, A294–A302.
- Meibom A. and Clark B. E. (1999) Invited review: Evidence for the insignificance of ordinary chondritic material in the asteroid belt. *Meteoritics & Planet. Sci.*, 34, 7–24.
- Meier R., Owen T. C., Jewitt D. C., Matthews H. M., Senay M., Biver N., Bockelée-Morvan D., Crovisier J., and Gautier D. (1998a) Deuterium in Comet C/1995 O1 (Hale-Bopp). Detection of DCN. *Science*, 279, 1707–1710.
- Meier R., Owen T. C., Matthews H. E., Jewitt D. C., Bockelée-Morvan D., Biver N., Crovisier J., and Gautier D. (1998b) A determination of the HDO/H<sub>2</sub>O ratio in Comet C/1995 O1 (Hale-Bopp). *Science*, 279, 842–898.
- Messenger S. (2000) Identification of molecular cloud material in interplanetary dust. *Nature*, 404, 968–971.
- Messenger S., Stadermann F. J., Floss C., Nittler L. R., and Mukhopadhyay S. (2003) Isotopic signature of presolar materials in interplanetary dust. *Space Sci. Rev.*, 106, 155–172.
- Millar T. J. (2003) Deuterium fractionation in interstellar clouds. *Space Sci. Rev.*, 106, 73–86.
- Millar T. J., Bennett A., and Herbst E. (1989) Deuterium fractionation in dense interstellar clouds. *Astrophys. J.*, 340, 906–920.
- Morbidelli A., Chambers J., Lunine J., Petit J. M., Robert F., and Valsecchi G. B. (2000) Source regions and timescales for the delivery of water on Earth. *Meteoritics & Planet. Sci.*, 35, 1309–1320.
- Mousis O., Gautier D., Bockelée-Morvan D., Robert F., Dubrulle B., and Drouart A. (2000) Constraints on the formation of comets from D/H ratios measured in H<sub>2</sub>O and HCN. *Icarus*, 148, 513–525.
- Niemann H. B., Atreya S. K., Carignan G. R., Donahue T. M., Haberman J. A., Harpold D. N., Hartle R. E., Hunten D. M., Kasprzak W. T., Mahaffy P. R., Owen T. C., Spencer N. W., and Way S. H. (1996) The Galileo probe mass spectrometer composition of Jupiter's atmosphere. *Science*, 272, 846–849.
- Owen T. and Encrenaz T. (2003) Element abundances and isotope ratios in the giant planets and Titan. *Space Sci. Rev.*, 106, 121–138.
- Owen T., Maillard J. P., Debergh C., and Lutz B. (1988) Deuterium on Mars: The abundance of HDO and the value of D/H. *Science*, 240, 1767–1770.
- Pizzarello S., Krisnamurthy R. V., Epstein S., and Cronin J. R. (1991) Isotopic analyses of amino acids from the Murchison meteorite. *Geochim. Cosmochim. Acta*, 55, 905–910.
- Richet P., Bottinga Y., and Javoy M. (1977) A review of hydrogen, carbon, nitrogen oxygen, sulphur, and chlorine stable isotope fractionation among gaseous molecules. *Annu. Rev. Earth Planet. Sci.*, 5, 65–110.
- Robert F. (1989) Hydrogen isotope composition of insoluble organic matter from cherts. *Geochim. Cosmochim. Acta*, 53, 453–460.
- Robert F. (2001) The origin of water on Earth. *Science*, 293, 1056–1058.
- Robert F. (2002) Water and organic matter D/H ratios in the solar system: A record of an early irradiation of the nebula? *Planet. Space Sci.*, 50, 1227–1234.
- Robert F. (2003) The D/H ratio in chondrites. *Space Sci. Rev.*, 106, 87–101.
- Robert F. and Deloule E. (2002) Using the D/H ratio to estimate the terrestrial water contamination in chondrites (abstract). In *Lunar and Planetary Science XXXIII*, Abstract #1299. Lunar and Planetary Institute, Houston (CD-ROM).
- Robert F. and Epstein S. (1982) The concentration of isotopic compositions of hydrogen carbon and nitrogen in carbonaceous chondrites. *Geochim. Cosmochim. Acta*, 16, 81–95.
- Robert F., Merlivat L., and Javoy M. (1979) Deuterium concentration in the early solar system: An hydrogen and oxygen isotopic study. *Nature*, 282, 785–789.
- Robert F. M., Javoy J., Halbout B., Dimon B., and Merlivat L. (1987) Hydrogen isotopes abundances in the solar system, Part I. Unequilibrated chondrites. *Geochim. Cosmochim. Acta*, 51, 1787–1806.
- Robert F., Gautier D., and Dubrulle B. (2000) The solar system D/H ratio: Observations and theories. *Space Sci. Rev.*, 92, 201–224.
- Rodgers S. D. and Millar T. J. (1996) The chemistry of deuterium in hot molecular cores. *Mon. Not. R. Astron. Soc.*, 280, 1046–1054.
- Sandford S. A. (2002) Interstellar processes leading to molecular deuterium enrichment and their detection. *Planet. Space Sci.*, 50, 1145–1154.
- Sandford S. A., Bernstein M. P., and Dworkin J. P. (2001) Assessment of the interstellar processes leading to deuterium enrichment in meteoritic organics. *Meteoritics & Planet. Sci.*, 36, 1117–1133.
- Schilke P., Walmsley C. M., Pineau des Forêts G., Roueff E., Flower D. R., and Guilloteau S. (1992) A study of HCN, HNC and their isotopomers in OMC-1. I. Abundances and chemistry. *Astron. Astrophys.*, 256, 595–612.
- Schramm D. D. (1998) Big-Bang nucleosynthesis and the density of baryons in the universe. *Space Sci. Rev.*, 84, 3–14.
- Sears D. W. G., Morse A. D., Hutchison R., Guimon K. R., Kie L., Alexander C. M. O'D., Benoit P. H., Wright I., Pilinger C., Kie T., and Lipschutz M. E. (1995) Metamorphism and aqueous alteration in low petrographic type ordinary chondrites. *Meteoritics*, 30, 169–181.
- Smith M. D., Schempp W. V., Simon J., and Baines K. H. (1989a) The D/H ratio for Uranus and Neptune. *Astrophys. J.*, 336, 962–966.
- Smith M. D., Schempp W. V., and Baines K. H. (1989b) The D/H ratio for Jupiter. *Astrophys. J.*, 336, 967–970.
- Vidal-Madjar A., Laurent C., Gry C., Bruston P., Ferlet R., and York D. G. (1983) The ratio of deuterium to hydrogen in interstellar space. V. The line of sight to Epsilon Persei. *Astron. Astrophys.*, 120, 58–65.
- Vokrouhlický D. and Farinella P. (2000) Efficient delivery of meteorites to the Earth from a wide range of asteroid parent bodies. *Nature*, 407, 606–608.
- Watson W. D. (1976) Interstellar molecule reactions. *Rev. Mod. Phys.*, 48, 513–552.
- Willacy K. and Millar T. J. (1998) Adsorption processes and the deuterium fractionation in molecular clouds. *Mon. Not. R. Astron. Soc.*, 228, 562–568.
- Yang J. and Epstein S. (1983) Interstellar organic matter in meteorites. *Geochim. Cosmochim. Acta*, 47, 2199–2216.
- Yung Y., Friedl R., Pinto J. P., Bayes K. D., and Wen J. S. (1988) Kinetic isotopic fractionation and the origin of HDO and CH<sub>3</sub>D in the solar system. *Icarus*, 74, 121–132.
- Zinner E., McKeegan K. D., and Walker R. M. (1983) Laboratory measurements of D/H ratios in interplanetary dust. *Nature*, 305, 119–121.