

Isotopic ratios D/H and $^{15}\text{N}/^{14}\text{N}$ in giant planets

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ABSTRACT

The determination of isotopic ratios in planets is important since it allows us to investigate the origins and initial composition of materials. The present work aims to determine the possible range of values for isotopic ratios D/H and $^{15}\text{N}/^{14}\text{N}$ in giant planets. The main objective is to provide valuable theoretical assumptions on the isotopic composition of giant planets, their internal structure, and the main reservoirs of species. We use models of ice formation and planet formation that compute the composition of ices and gas accreted in the core and the envelope of planets. Assuming a single initial value for isotopic ratios in volatile species, and disruption of planetesimals in the envelope of gaseous planets, we obtain a wide variety of D/H and $^{15}\text{N}/^{14}\text{N}$ ratios in low-mass planets ($\leq 100 M_{\text{earth}}$) due to the migration pathway of planets, the accretion time of gas species whose relative abundance evolves with time, and isotope exchanges among species. If giant planets with mass greater than $100 M_{\text{earth}}$ have solar isotopic ratios such as Jupiter and Saturn due to their higher envelope mass, Neptune-type planets present values ranging between one and three times the solar value. It seems therefore difficult to use isotopic ratios in the envelope of these planets to get information about their formation in the disc. For giant planets, the ratios allow us to constrain the mass fraction of volatile species in the envelope needed to reproduce the observational data by assuming initial values for isotopic ratios in volatile species.

Key words: planets and satellites: atmospheres – planets and satellites: composition – planets and satellites: formation.

1 INTRODUCTION

The measurement and comparison of isotopic ratios in small bodies and planets is one of the methods used to investigate the origin of materials (Pontoppidan et al. 2014). Their determination in planets and their comparison with models are crucial in order to constrain the processes of planetary system formation, the internal structure, and thermal evolution of planets. The deuterium to hydrogen (D/H) fraction and the ratio of the two stable nitrogen isotopes ^{15}N and ^{14}N are important since these elements show large isotopic heterogeneity in various Solar system reservoirs (Hartogh et al. 2011; Fletcher et al. 2014; Pontoppidan et al. 2014). Their study in the context of planet formation should allow us to explore the origins of material accreted by giant planets in the Solar system and to constrain the chemical and physical processes which occur in the atmospheres of planets (Owen & Encrenaz 2003). In both Jupiter and Saturn, the abundance of nitrogen is supersolar (de Pater & Massie 1985; Niemann et al. 1998; Owen et al. 1999; Wong et al. 2004; Fletcher et al. 2009), suggesting an enrichment due to accretion of icy

planetesimals during the formation process. In addition, other constraints on the abundance of species provided by the Galileo Probe Mass Spectrometer (Niemann et al. 1998; Atreya et al. 1999; Mahaffy et al. 2000; Wong et al. 2004) show that Jupiter's elements are uniformly higher by a factor of 4 ± 2 than protosolar values.

Recent studies on the $^{15}\text{N}/^{14}\text{N}$ ratio suggested that Jupiter and Saturn accreted primordial N_2 (expected to be less enriched in ^{15}N), either in the gas phase from the solar nebula, as ices formed at very low temperatures, or exclusively in the form of trapped species in clathrates (Mousis et al. 2009, 2014; Fletcher et al. 2014). Moreover, following Mousis et al. (2014) and Fletcher et al. (2014), the accretion of nitrogen in the gas phase alone cannot produce these supersolar enrichments without some contributions of nitrogen species trapped in water ice.

In the Solar system, the D/H ratio varies up to one order of magnitude depending on the bodies (Hartogh et al. 2011; Altwegg et al. 2015). H-bearing volatile species in comets present the highest D/H ratio values, up to three times the protosolar value. The D/H ratio in the envelope of giant planets (mainly composed of H_2) should be close to the protosolar value as observed for Jupiter and Saturn (Lellouch et al. 2001). The enrichment in deuterium of the envelope of gas giant planets through ices should then be minor. However, for Neptune-like planets, in which the mass of the core is assumed to be similar to the mass of the envelope, the envelope

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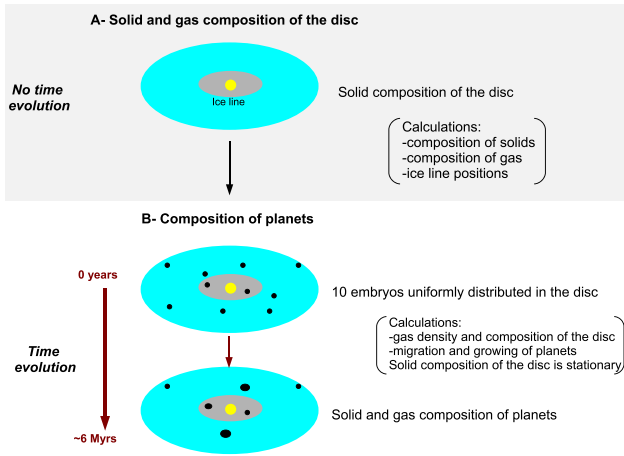


Figure 1. Schema presenting the different steps allowing the calculation of the composition of planets.

is expected to be enriched in deuterium as observed for Uranus and Neptune (Feuchtgruber et al. 2013), which exhibit D/H ratios significantly higher than in Jupiter and Saturn.

In the frame of all these hypotheses, a study of the different scenarios of ice formation and incorporation in planets, and their implication on the isotopic ratios $^{15}\text{N}/^{14}\text{N}$ and D/H in planets, seems to be of great interest to constrain models of planet formation and interiors of planets, and the origins of material. This article is organized as follows: in a first step (Section 2), we briefly present the models (both the planetary formation model and the composition model) and describe the assumptions considered. Physical assumptions are discussed in Section 3. In a third step (Section 4), we discuss the $^{15}\text{N}/^{14}\text{N}$ and D/H ratios in giant planets using different assumptions and compare our results with data from Jupiter, Saturn, Uranus, and Neptune. The last section (Section 5) is devoted to the discussion and conclusion.

2 MODELS

The models described hereafter are fully explained in Thiabaud et al. (2014, 2015) and Marboeuf et al. (2014a,b). We give in this section a short description and the assumptions made.

2.1 Models of disc and planet formation

To compute the chemical composition of planets, we first compute the composition of planetesimals at any distance to the central star (Step A in Fig. 1), for a population of protoplanetary discs, whose initial density profiles, masses, and lifetimes are different, and follows, as closely as possible, observational characteristics (see Mordasini, Alibert & Benz 2009; Mordasini et al. 2012; Alibert et al. 2013; Marboeuf et al. 2014a).¹ In the computation, we consider both the volatile species (see Marboeuf et al. 2014a,b; Thiabaud et al. 2015), and refractory ones (see Thiabaud et al. 2014). We combine these results with the planet formation model of Alibert et al. (2005, 2013), which provides the amount of planetesimals

and gas accreted by every planet as a function of the distance to the star, to derive the final composition of planets (see step B in Fig. 1). Solid accretion depends on the planetary mass (which provides the excitation of planetesimals, important to compute the gravitational focusing factor), on the planetary capture radius (the effective collision cross-section is enhanced by the presence of a gas envelope.), and on the surface density of planetesimals at the location of the planet. The structure of the gas envelope is computed by solving the internal structure equations for planetary interiors, the luminosity being given by the accretion of planetesimals, and the outer boundary conditions (temperature and structure) by the local condition in the disc, at the planet’s location. Migration is included and depends on the structure of the disc and the planetary mass. We use the formulas of Dittkrist et al. (2014) for type 1 migration, and for higher planets, which migrate in type 2, the migration rate is given by the viscous velocity in the disc (Alibert et al. 2013). In addition, planet–planet interactions are computed using a NBODY code. The model reproduces the mass function of extrasolar planets (at least for planets more massive than a few Earth masses). The model reproduces the structure of Jupiter and Saturn independently (see Alibert et al. 2005).

In this study, planetesimals are believed to form from the coagulation of small grains (icy and/or rocky), whose chemical composition is described in Section 2.2 and Marboeuf et al. (2014a). The scenarios of the different thermodynamic conditions of ice formation in the disc provide us the composition of grains, which is further assumed to be identical to the one in planetesimals formed at the same location in the disc since we do not include the radial drift of both small icy grains and planetesimals (see Marboeuf et al. 2014a for the chemical composition of grains in the disc and ice line positions in the disc as a function of the surface density.).

At the beginning of the simulations, the model of planet formation considers 10 planetary embryos of lunar mass (mass of about $10^{-2} M_{\text{earth}}$) which are randomly placed in the disc and grow by accretion of planetesimals during their migration. Embryos and planetesimals have initially the same chemical composition at that location, assuming there are no chemical fractionations during their growing. With time, embryos migrate in the disc and accrete planetesimals of different chemical compositions. The migration is the result of angular momentum exchange with the disc (Alibert et al. 2013; Dittkrist et al. 2014). The migration tracks are presented in Dittkrist et al. (2014). The migration pathways are the sum of a migration that is generally towards the star, but are perturbed by interactions with other planets. As a result, planets are enriched or depleted in volatile species compared to initial protoplanets. We note that planets and gas are the only ones to move and allow the mixing of solid materials and gas at different epochs depending on the migration pathway of planets and their final position in the disc. The drift of the gas in the evolving disc is taken into account and changes the composition of the gas accreted by planets depending on the time and distance to the star such as described in Thiabaud et al. (2015).

The process of accretion of planetesimals on to planets² is assumed to retain the original mass of species initially incorporated in bodies. Once they are accreted, heavy elements are incorporated in

¹ Disc characteristics that are included in the models, and taken from observations, are mass, lifetime, and composition (= metallicity). The mass range is of the order of $1.e-3$ to $0.1 \times M_{\text{sun}}$; the lifetime is taken from the observations of Mamajek (2009), i.e. a few Myr, and metallicity is derived from the CORALIE survey.

² The time-scale for the accretion of planetesimals is of the order of Myr, and is per construction similar to the planetary formation time-scale, as the formation models end when the protoplanetary disc has disappeared, which signals the end of gas accretion. Planetesimals accretion can continue after the disc has disappeared, but, at least for the formation of giant planets, the majority of the solid mass is accreted when the gas disc is still present.

the core if the mass of the envelope is lower than $10^{-4} M_{\text{earth}}$.³ For higher masses, heavy elements are assumed to be only incorporated in the envelope.

It results that the envelope/core of gaseous planets, where the mass of the envelope is higher than $10^{-4} M_{\text{earth}}$, is enriched/depleted in heavy elements compared to previous results (Marboeuf et al. 2014a,b; Thiabaud et al. 2015). The abundance of volatile species initially contained in planetesimals does not undergo chemical changes during the melting, the sublimation, break up of bodies on to planets (in the core or in the envelope): only the change of phase and exchanges of isotopes D and ^{15}N among volatile species are taken into account. Moreover, the migration of planets towards the star which could induce chemical reactions due to an increase in the surface temperature and temperature-pressure of planetary atmospheres is assumed not to change the abundances and phases (ice, gas, or liquid) of species in planets.

2.2 Model of ice formation

The chemical composition of volatile molecules incorporated in icy grains, i.e. icy planetesimals, and later in planets by accretion, is determined by both the process of condensation (pure crystalline structure) and the process of gas trapping in water ice (clathrate hydrates) on the surface of grains during the cooling of the disc. This gas trapping process assumes that the disc is initially warm enough ($T \geq 150\text{--}170\text{ K}$) to sublimate all the ices originally formed in the nebula.

The crystalline arrangement of water molecules can take mainly two forms:

(i) The pure crystalline structure (called crystalline model) assumes that molecules form a pure crystalline structure around refractory grains during the condensation of species, following the model of Greenberg (1982), and depending on the temperature and pressure conditions in the disc's environment.

(ii) The clathrate hypothesis (called clathrate model) assumes the formation of a structure of water ice which traps volatile species ($\neq \text{H}_2\text{O}$) during the cooling of the disc by water ice–gas interaction, assuming kinetic conditions of its formation, is favourable. This structure is organized in the form of cages which contain a single gas molecule trapped due to van der Waals interactions. During the cooling of the disc, species will be condensed and/or trapped in water ice depending on the thermodynamic conditions encountered by grains and distance to the Sun.

The final composition of grains is given by the condensation/trapping sequence of the gas (see Fig. 2) which stops at a temperature which is the one at the initial time of the planet formation model and which depends on the distance to the star (see Fig. 3). The reader is directed to Marboeuf et al. (2014a,b) for more details. Refractory components are calculated following the method described in Thiabaud et al. (2014).

3 PHYSICAL ASSUMPTIONS AND PARAMETERS

The chemical composition of planets is determined by taking into account both refractory (minerals and organics) and volatile

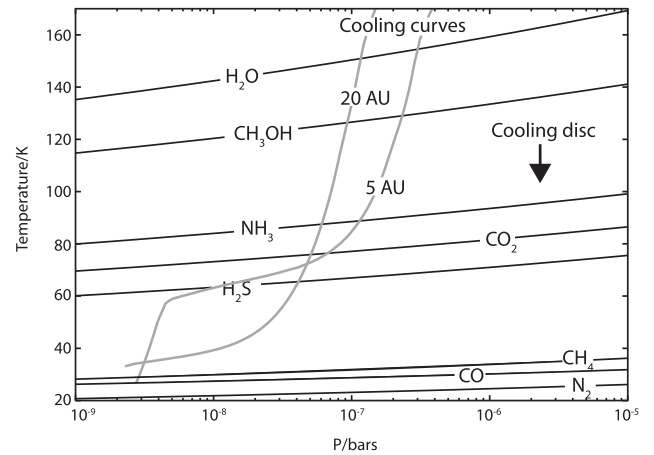


Figure 2. Stability curves of pure condensates (horizontal lines) and cooling curves of the protoplanetary disc model (vertical lines) at two given distances to the star: 5 and 20 au (the evolution of the disc proceeds from high to low temperatures), for irradiated discs. Species remain in the gas phase above the stability curves. Below, they condense as pure ices. Model with CO:CO₂ = 1:1. Adapted from Marboeuf et al. (2014a).

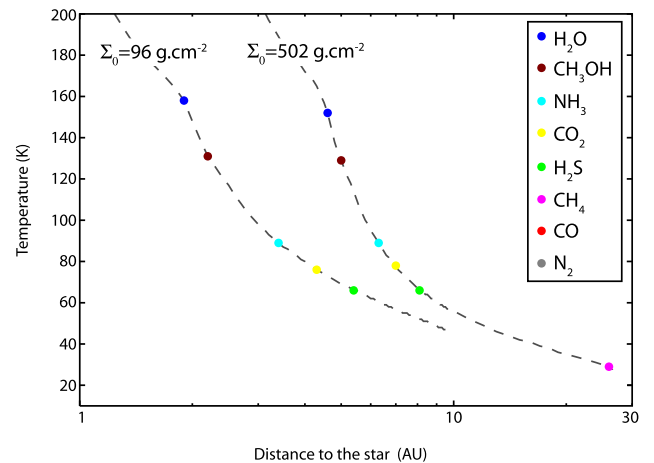


Figure 3. Final temperature profile of irradiated discs at the beginning of the time evolution model (step B of Fig. 1) for two particular simulations ($\Sigma_0 = 95.844\text{ g cm}^{-2}$ and $\Sigma_0 = 502.52\text{ g cm}^{-2}$) as a function of the distance to the star. Coloured dots represent the ice line positions of H_2O , CH_3OH , NH_3 , CO_2 , H_2S , CH_4 , CO , and N_2 . Models without clathrates. Adapted from Marboeuf et al. (2014a).

components. All volatile species are composed of H, O, C, N, and S atoms in solar nebula abundances (Lodders 2003) in the following proportions: 26 per cent of the total oxygen in the disc is devoted to minerals (Lodders 2003). The relative abundance of O, C, and N in organics compounds is taken respectively at 15 per cent, 60 per cent, and 26 per cent (Jessberger, Christoforidis & Kissel 1988; Pollack et al. 1994; Sekine et al. 2005; see Marboeuf et al. 2014a for more descriptions). The remaining is devoted to volatile molecules which are only composed of H_2O , CO_2 , CO , CH_3OH , CH_4 , NH_3 , N_2 , H_2S whose abundances are given in Marboeuf et al. (2014a,b) for model with CO:H₂O = 1:1.⁴ Except N_2 , these molecules are the major abundant volatile

³ Private communication from Mordasini C. and Venturini J. A sensitivity test on the envelope mass has been done and the results do not change in the range $10^{-5}\text{--}10^{-3} M_{\text{earth}}$.

⁴ A sensitivity test has been made with the abundance of volatile species by using the CO-poor model (CO:H₂O = 20:100) and results were similar.

species observed in the ISM (Gibb et al. 2000, 2004; van Dishoeck 2004; Whittet et al. 2007; Boogert et al. 2011; Mumma & Charnley 2011) and in comets (Bockelée-Morvan et al. 2004; Crovisier 2006; Mumma & Charnley 2011). Based on the previous studies (Marboeuf et al. 2014a,b), we aim to analyse the effect of the structure of water ice (pure crystalline, clathrate) on the isotopic ratios in giant planets for irradiated discs.⁵

The chemical processes which could change abundances of volatile species in warm surface layers of the protoplanetary disc and the dynamical evolution of icy grains are not taken into account in this study. All the volatile molecules (H₂O, CO₂, CH₃OH, CH₄, NH₃, and H₂S), except CO and N₂, are easily destroyed in the gas phase of the surface layers of the disc (see Visser, Doty & van Dishoeck 2011) by reactions with UV and X-ray photons from the central star as well as UV photons and cosmic rays originating from the interstellar medium. They do Volatile species not keep high abundances once they are evaporated from grains (Doty et al. 2002; Nomura & Millar 2004). However, grain surface reactions in the disc will recover the loss, and the abundances of volatile molecules in ice may not be very different from those adopted in planetesimals for this study (see Marboeuf et al. 2014a for more explanations).

We analyse the chemical composition of planets formed in the different synthetic planetary systems presented in Alibert et al. (2013) using different initial chemical compositions of planetesimals (the chemical composition of planetesimals changes with the distance to the star; see Marboeuf et al. 2014a) and different initial surface densities at 5.2 au (varying from 3 g cm⁻² to about 700 g cm⁻²), density slopes (varying from 0.4 to 1.1), and characteristic scaling radius (varying from 14 to 198 au) of the disc (see Alibert et al. 2013, and section 3.3 of Thiabaud et al. 2014). The different initial physical conditions of discs induce different initial thermodynamic conditions of ice formation (see Marboeuf et al. 2014a) and planetary evolution (see fig. 7 in Marboeuf et al. 2014b), providing a diversity of composition.

4 ISOTOPIC RATIOS IN PLANETS

We discuss in this section the different values of isotopic ratios ¹⁵N/¹⁴N and D/H in the envelope of giant planets with the planet formation model, and compare our results with data in giant planets of the Solar system (see Table 1). The following study suggests that giant planets have a homogeneous distribution of isotopes ¹⁵N and D in their envelope among the N-bearing volatile species and H-bearing volatile species, respectively. The envelope of giant planets incorporates volatile species originally from icy planetesimals⁶ and gas accreted during their growing and migration pathway.

4.1 The ¹⁵N/¹⁴N ratio

The degree of ¹⁵N enrichment in N-bearing species varies with temperature and formation time, and the value changes from one species to another due to escape and fractionation processes (Fletcher et al. 2014). Following Fletcher et al. (2014), the lowest primitive ¹⁵N enrichment is expected in the highly volatile species N₂ which condenses or could be efficiently trapped in water ice at low temper-

atures. However, the major observable N-bearing species in Solar system bodies remains NH₃ (Bockelée-Morvan et al. 2004; Marboeuf et al. 2014a,b) which exhibits large variations of the isotopic ratio ¹⁵N/¹⁴N up to a factor of 5 among different Solar system bodies (Briani et al. 2009). Yet, in giant planets, this molecule is thermo-chemically converted from N₂ in the hot deep interiors in a gas dominated by H₂ (Lewis & Prinn 1980; Fegley & Lodders 1994):



In the interstellar medium, ¹⁵N/¹⁴N is just above 2.5×10^{-3} with little variation (Aléon 2010, and references therein). Fletcher et al. (2014) have determined that the Jovian value in NH₃ varies from 1.4×10^{-3} to 2.5×10^{-3} , consistent with previous studies ($2.3 \pm 0.3 \times 10^{-3}$; Owen et al. 2001; Wong et al. 2004). Similarly, the Saturnian ratio is inferior to 2.8×10^{-3} (Fletcher et al. 2014). The ¹⁵N/¹⁴N value in a meteorite inclusion (Meibom et al. 2007), assumed to be representative of the primitive solar nebula value, is $2.36 \pm 0.02 \times 10^{-3}$, value consistent with the Sun value derived from solar wind samples ($2.27 \pm 0.03 \times 10^{-3}$; Marty et al. 2011). Finally, the highest ¹⁵N/¹⁴N ratios are those in comets with values greater than those in giant planets ($7.9_{-2.6}^{+4.6} \times 10^{-3}$ from NH₃ molecules and from an average of 12 comets; see Rousselot et al. 2014), implying that ¹⁵N-enriched cometary NH₃ ices could not have been the main contributor to the bulk nitrogen inventory of giant planets (Fletcher et al. 2014).

The low ¹⁵N enrichment in Saturn and Jupiter ($< 2.8 \times 10^{-3}$, Wong et al. 2004, Fletcher et al. 2014) compared to the bulk Sun value ($2.27 \pm 0.03 \times 10^{-3}$, Marty et al. 2011) favours therefore the accretion of primordial N₂ (expected to be poorly enriched in ¹⁵N) in both planets, either in the gas phase of the solar nebula or as ices formed at very low temperatures in the disc or trapped in icy planetesimals. However, Fletcher et al. (2014) suggested that the accretion of nitrogen in the gas phase alone cannot produce the supersolar N-enrichments without some contribution of nitrogen species trapped in solids.

In our study, we investigate the possible values of ¹⁵N/¹⁴N ratio in gas giants by the following relation in the envelope of planets:

$$\left(\frac{^{15}\text{N}}{^{14}\text{N}}\right)_{\text{planets}} = \frac{N_{\text{NH}_3} \left(\frac{^{15}\text{N}}{^{14}\text{N}}\right)_{\text{NH}_3} + 2.N_{\text{N}_2} \left(\frac{^{15}\text{N}}{^{14}\text{N}}\right)_{\text{N}_2}}{N_{\text{NH}_3} + 2.N_{\text{N}_2}} \quad (2)$$

where $\left(\frac{^{15}\text{N}}{^{14}\text{N}}\right)_{\text{NH}_3}$ and $\left(\frac{^{15}\text{N}}{^{14}\text{N}}\right)_{\text{N}_2}$ are the ¹⁵N/¹⁴N ratios in NH₃ and N₂, respectively, and N_{NH_3} and N_{N_2} the corresponding number of molecules in planets. We adopt the ¹⁵N/¹⁴N ratio observed in comets ($7.9_{-2.6}^{+4.6} \times 10^{-3}$; Rousselot et al. 2014) for NH₃ and the bulk Sun value ($2.27 \pm 0.03 \times 10^{-3}$; Marty et al. 2011) for N₂. This relation supposes that NH₃ (observed in the envelope of gas giants) is produced from N₂ by equation (1) and that ¹⁵N atoms are homogeneously distributed among N-bearing volatile molecules (NH₃ and N₂ in this study) in the envelope of planets.

Fig. 4 presents the wide variety of ¹⁵N/¹⁴N ratios in the envelope of planets using the relation (2) for models using N₂:NH₃ = 1:10, N₂:NH₃ = 1:1, and N₂:NH₃ = 10:1. Values in giant planets range from 1 to 3.5 times the solar value. The lower value 1 in planets is explained by an envelope mainly composed of N-bearing species coming originally from N₂ and accreted as gas or ice in the envelope of planets. Inversely, planetary envelopes with higher isotopic ratios (3.5 times the solar value) as shown in Fig. 4 have incorporated much higher NH₃ as gas and ices, i.e. ices whose N is exclusively provided by NH₃. We note that an initial high N₂:NH₃ in the disc ratio allows us to significantly reduce the ¹⁵N/¹⁴N ratio in the envelope of gas giant planets. Inversely, by taking the value N₂:NH₃ = 1:10 given in

⁵ Ice line positions in the irradiated disc are in good agreement with those in models of chemical composition of protoplanetary discs (Drozdovskaya et al. 2016).

⁶ Assumed to be disrupted for mass of envelope higher than $10^{-4} M_{\text{earth}}$.

Table 1. Isotopic ratios in the proto-sun, giant planets, and comets.

Isotopic ratios	Sun	Jupiter	Saturn	Uranus	Neptune	Comets
$^{15}\text{N}/^{14}\text{N}$	$2.27 \pm 0.03 \times 10^{-3(g)}$	$2.3 \pm 0.3 \times 10^{-3 (a)}$	$<2.8 \times 10^{-3(b)}$	-	-	$7.9^{+4.6}_{-2.6} \times 10^{-3(e)}$
D/H	$2.1 \pm 0.4 \times 10^{-5(h)}$	$2.25 \pm 0.35 \times 10^{-5(c)}$	$1.7^{+0.75}_{-0.45} \times 10^{-5(c)}$	$4.4 \pm 0.4 \times 10^{-5(d)}$	$4.1 \pm 0.4 \times 10^{-5(d)}$	$1.6\text{-}5.3 \pm 0.7 \times 10^{-4(f)}$

^aWong et al. (2004); ^bFletcher et al. (2014); ^cLellouch et al. (2001); ^dFeuchtgruber et al. (2013); ^eRousselot et al. (2014); ^fHartogh et al. (2011), Altwegg et al. (2015); ^gMarty et al. (2011); ^hLinsky et al. (2006).

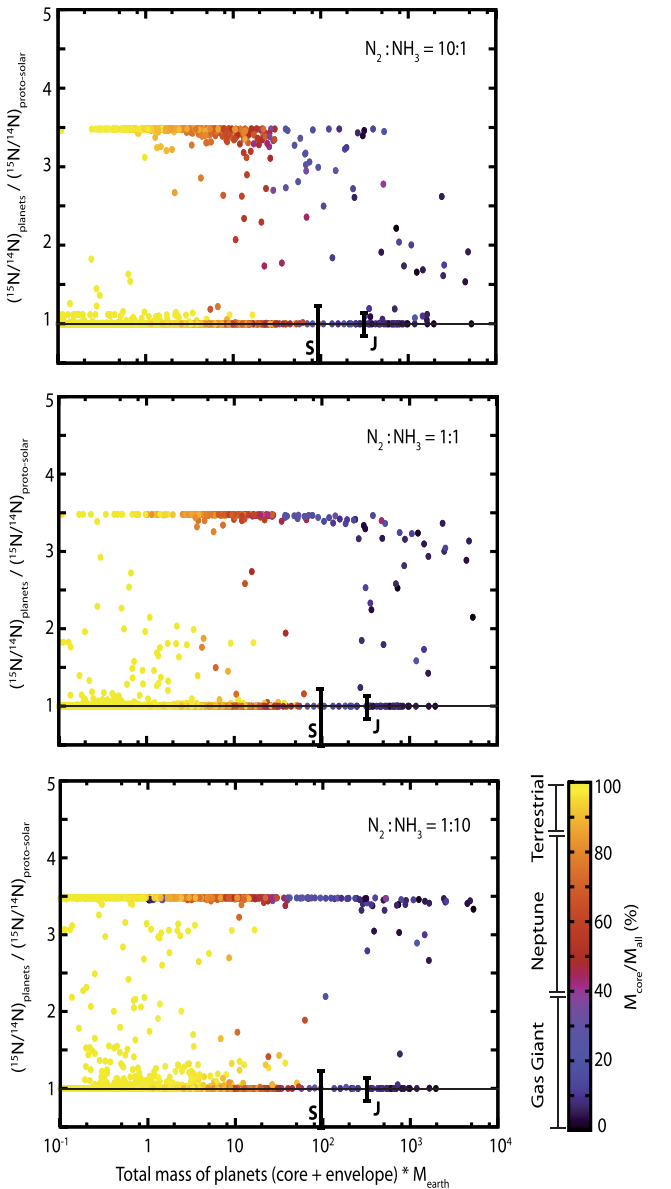


Figure 4. $^{15}\text{N}/^{14}\text{N}$ ratio in the envelope of planets relative to the $^{15}\text{N}/^{14}\text{N}$ ratio in the Sun as a function of the total mass of planets $M_{\text{pl}}^{\text{all}}$ (core + envelope) and mass ratio of solids M_{pl}^{s} relative to total planetary mass $M_{\text{pl}}^{\text{all}}$. We assumed $^{15}\text{N}/^{14}\text{N}$ ratio from comets ($7.9^{+4.6}_{-2.6} \times 10^{-3}$; see Rousselot et al. 2014) for NH_3 and the bulk solar value for N_2 ($2.27 \pm 0.03 \times 10^{-3}$; Marty et al. 2011). Horizontal grey lines represent the Sun value (1). Error bars J and S represent the values for Jupiter and Saturn, respectively. Data for Jupiter and Saturn are provided by Fletcher et al. (2014). $\text{N}_2:\text{NH}_3 = 1:10$ (bottom panel), $\text{N}_2:\text{NH}_3 = 1:1$ (middle panel), and $\text{N}_2:\text{NH}_3 = 10:1$ (top panel). The 3.5 times the solar value is an upper limit imposed by our assumption of the cometary $^{15}\text{N}/^{14}\text{N}$ ratio which is the central value of the Rousselot’s survey (Rousselot et al. 2014).

Lewis & Prinn (1980), the $^{15}\text{N}/^{14}\text{N}$ ratios in the envelope of planets are mainly either equal to 3.5 times the solar value or equal to one times the solar value. We note also that results remain similar whatever the structure of water ice because N_2 is poorly trapped in clathrates because no more water molecules are free after trapping of CO. Moreover, the low trapping efficiency of N_2 in the clathrate structure does not allow us to reduce the $^{15}\text{N}/^{14}\text{N}$ in the envelope of planets and this assumption is not necessary to explain low $^{15}\text{N}/^{14}\text{N}$ ratios in the envelope of planets.

In addition, the accretion of N_2 gas, which can provide more than 80 per cent of N atoms in the envelope of some gas giants, and expected to be poorly enriched in ^{15}N , can lower the $^{15}\text{N}/^{14}\text{N}$ ratio to values similar to those observed in Jupiter and Saturn. The time evolution of the relative N_2 (to H_2) abundance of volatile species in the disc as shown in figs 4 to 7 in Thiabaud et al. (2015) can allow their enrichment in the envelope of planets. However, this is not always necessary to explain low values of $^{15}\text{N}/^{14}\text{N}$ in the envelope of planets since it depends also on the pathway of planets in the disc and time-scale of migration of planets.

Our model considers that all elements included in icy planetesimals accreted by planets are homogeneously distributed in their envelope. If it is not the case, and that late accreted planetesimals, mainly composed of NH_3 , stay in upper layers of the envelope of planets (no mixing in the envelope of planets), the upper layers of the envelope of giant planets could be enriched compared to figures presented in this work.

4.2 The deuterium-to-hydrogen ratio

The D/H ratio in the Solar system varies greatly from one body to another. If giant planets of the Solar system have values of the same order of magnitude than the protosolar value ($2.1 \pm 0.4 \times 10^{-5}$; Linsky et al. 2006), it increases up to 30 times for comets ($5.3 \pm 0.7 \times 10^{-4}$; Altwegg et al. 2015). The main parameter that governs the deuterium fractionation among species is the temperature: the lower the temperature, the larger the deuterium fractionation. The D/H ratio increases in icy grains with decreasing temperature due to ion-molecule and grain-surface interactions (Watson 1974; Brown & Millar 1989; Feuchtgruber et al. 2013). However, the D/H ratio in the Jupiter Family Comet (JFC) 103P/Hartley 2, originating from the Kuiper belt and presumably formed far away from the Sun, presents a lower value than Oort comets presumably formed closer to the Sun (Hartogh et al. 2011) and the JFC 67P/Churyumov-Gerasimenko (Altwegg et al. 2015). From this observation, the dependency of the D/H ratio in water with the distance to the Sun is not what is expected from the basis of current models (Hartogh et al. 2011). The H–D exchange in H-bearing volatile molecules occurs by interactions on the surface of grains, and chemical reactions in the gas phase dominated by H_2 . Laboratory experiments have shown that D and H atoms can be exchanged between water ice and other molecules trapped in water ice (for example CH_3OH ; Ratajczak et al. 2009; Gálvez et al. 2011). In a gas phase dominated by

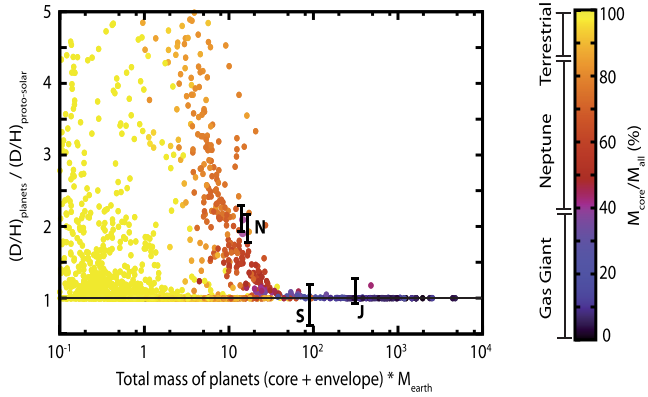


Figure 5. D/H ratio in planets relative to the D/H ratio in the protosolar disc as a function of the total mass of planets $M_{\text{pl}}^{\text{all}}$ (core + envelope) and mass ratio of solids M_{pl}^{s} relative to total planetary mass $M_{\text{pl}}^{\text{all}}$. We assumed D/H ratio from Oort comets (about 2.5×10^{-4} ; see Bockelée-Morvan et al. 2012) for volatile species. Horizontal grey lines represent the protosolar value (1). Error bars J, S, U, and N represent the values for Jupiter, Saturn, Uranus, and Neptune, respectively. Data for Jupiter and Saturn are provided by Lellouch et al. (2001). Data for Uranus and Neptune are provided by Feuchgruber et al. (2013).

H_2 , H–D exchange occurs through reactions with H_2 and HD in the solar nebula or in the envelope of planets following the reaction:



where X is a radical such as HO (for water).

We investigate the possible value for the D/H ratio in giant planets by assuming that D atoms are homogeneously distributed among H-bearing species in the envelope of planets (see equation 3) and by using the following relation:

$$(\text{D}/\text{H})_{\text{planets}} = \frac{N_{\text{H}_2}(\text{D}/\text{H})_{\text{H}_2} + N_{\text{H-b.species}}(\text{D}/\text{H})_{\text{H-b.species}}}{N_{\text{H}_2} + N_{\text{H-b.species}}}, \quad (4)$$

where $(\text{D}/\text{H})_{\text{H}_2}$ and $(\text{D}/\text{H})_{\text{H-b.species}}$ are the D/H ratios in H_2 and in H-bearing volatile species (water, ammonia, methanol, methane, and hydrogen sulphide), respectively, and N_{H_2} and $N_{\text{H-b.species}}$ the corresponding number of atoms H or D in molecules. We consider that $(\text{D}/\text{H})_{\text{H}_2}$ in the envelope of gas giants is initially similar to the protosolar nebula value ($2.1 \pm 0.4 \times 10^{-5}$; Linsky et al. 2006). $(\text{D}/\text{H})_{\text{H-b.species}}$ is assumed to be similar to the water cometary value, believed to be representative of planetesimals. As this ratio varies with comets (Hartogh et al. 2011; Bockelée-Morvan et al. 2012; Altwegg et al. 2015), we have tested several values: the Oort value (about 2.5×10^{-4} ; see Bockelée-Morvan et al. 2012), the 103P/Hartley 2 value (about 1.6×10^{-4} ; Hartogh et al. 2011), and the 67P/Churyumov-Gerasimenko value ($5.3 \pm 0.7 \times 10^{-4}$; Altwegg et al. 2015).

Using relation (4), we obtain Fig. 5, which shows the wide variety of possible values for the D/H ratio in the envelope as a function of the total mass of planets $M_{\text{pl}}^{\text{all}}$ (core + envelope) and mass ratio of solids M_{pl}^{s} relative to total planetary mass $M_{\text{pl}}^{\text{all}}$. We note that calculations have been performed by using the Oort comet D/H ratio value for H-bearing volatile species. The D/H ratio in planets ranges from one to more than five times the solar value. D/H decreases with the total mass of planets and the increasing relative (to total mass) mass fraction of the envelope (mainly H_2). If for terrestrial (icy and/or rocky) planets, the D/H ratio presents the larger range, gas giant planets (total mass $\geq 100 M_{\text{earth}}$) show lower values close to the solar value as observed for Jupiter and Saturn. This is mainly due

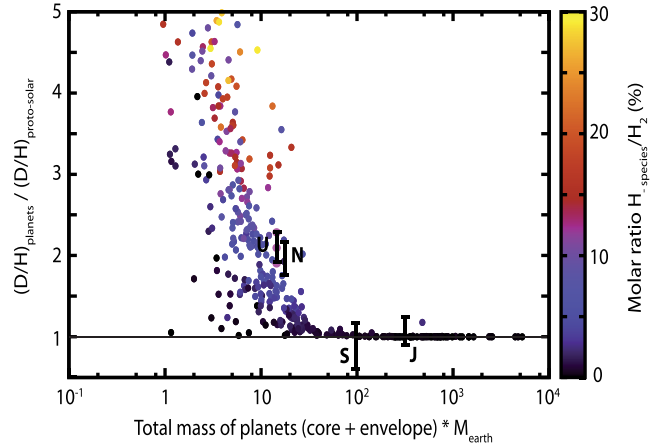


Figure 6. Same as in Fig. 5 but with the molar fraction of H-bearing species relative to H_2 in the envelope of planets.

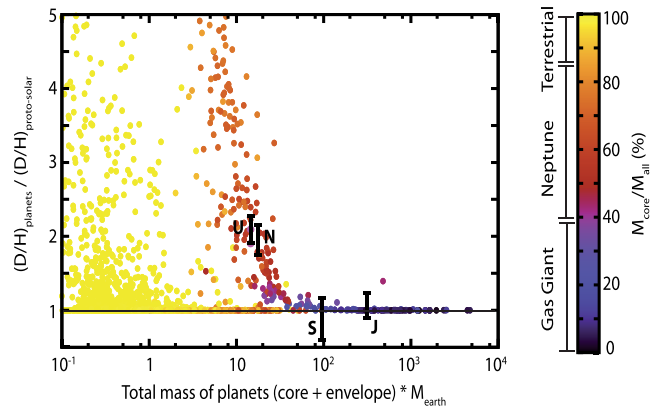


Figure 7. Same as in Fig. 5 but by using D/H ratio from the 67P/Churyumov-Gerasimenko comet (about 5.3×10^{-4} ; Altwegg et al. 2015) for volatile species.

to the low fraction of heavy elements in the envelope of gaseous giant planets: the molar fraction of volatile species relative to H_2 is inferior to 2 percent in gaseous giants (see Fig. 6). The result is that the D/H ratio in the envelope of massive giant planets does not change whatever the D/H cometary value adopted in H-bearing volatile species (103P/Hartley 2, 67P/Churyumov-Gerasimenko, or Oort D/H ratios; see Figs 5 and 7). Inversely, the lower mass envelope in Neptune-type planets and the resulting higher molar fraction of volatile species in the envelope (≤ 20 per cent) induce D/H values ranging between one and about three times the solar value. We note that some terrestrial planets, without a massive gas envelope (rocky planets, yellow dots), show also values close to the solar value, mainly because they are dry. In this case, the envelope is only composed by H_2 . Because planetesimals are destroyed in the envelope of giant planets, the core of giant planets is rocky-dominated and composed in most cases by less than 5 wt per cent of volatile species.

Finally, whatever the value adopted in cometary ices (Oort or JFC values), we obtain results in good agreement with the four giant planets of the Solar system. The range of possible values for Neptune-type planets (one to three times the solar value) is due to (1) the lower mass fraction of the envelope in planets (between 20 and 60 wt per cent), and (2) different relative (to H_2) mass fractions of H-bearing volatile species in the envelope due itself to the

migration pathway of planets which determines the accretion rate of planetesimals and gas at different epochs.

We note that models using Oort values or higher (67P/Churyumov-Gerasimenko) agree better (see Fig. 7) than those with the 103P/Hartley 2 value,⁷ and this assumption is in good agreement with the Saturn’s moon Enceladus value ($2.5_{-0.7}^{+1.5} \times 10^{-4}$; Waite et al. 2009). Moreover, results are roughly similar whatever the structure of water ice considered because water remains by far the major volatile species that exchanges H–D atoms with H_2 in the envelope of planets. The possible trapping of H-bearing volatile species in water ice does not significantly change the results because their relative (to H_2O) abundance is significantly lower.

5 SUMMARY AND DISCUSSION

We have shown that the model of planet formation is able to produce a wide variety of D/H and $^{15}\text{N}/^{14}\text{N}$ in the envelope of planets by considering only a single initial value for both ratios in volatile species. D/H and $^{15}\text{N}/^{14}\text{N}$ ratios in giant planets both range between one and three times the solar value. The range of possible isotopic values is mainly due to the mass fraction of elements in the envelope of planets whose abundances depend on (1) the migration pathway of planets in the disc allowing us to have access to different material reservoirs at different epochs, and (2) the availability of H-bearing and N-bearing volatile species (gas and ices) in the disc at accretion time. Remember that ices are condensed after ice line positions (see Marboeuf et al. 2014a) and that abundances of gas species in the disc evolve with time due to migration through the disc (see Thiabaud et al. 2015), allowing us to change relative (to H_2) abundances in the envelope of planets. Finally, it seems difficult to use isotopic ratios observed in the envelope of giant planets to get information about the origin of formation of materials in the disc and about the associated thermodynamic conditions. However, it allows us to constrain approximately the mass fraction of volatile species in the envelope needed to reproduce the observational data by assuming initial values for isotopic ratios in volatile species. By taking into account all major volatile species, and disruption of planetesimals in the envelope of gaseous giants, we obtain rocky-dominated cores of giant planets made in most cases by less than 5 wt per cent of ices. Inversely, the envelope of planets is enriched in volatile species with relative (to H_2) molar ratios lower than 2 per cent for gaseous giant (total mass $\geq 100 M_{\text{earth}}$) and inferior in most cases to 20 per cent for Neptune-type planets.

Our assumption on the disruption of planetesimals in the envelope of gaseous planets is in good agreement with observations of the isotopic ratios of giant planets in the Solar system. However, even if the variety of isotopic ratios determined in planets is wide in our simulations, it is impossible in our simulations to get both a low $^{15}\text{N}/^{14}\text{N}$ and supersolar N/H in the same planet as observed in the Solar system. The disruption of planetesimals in the envelope is consistent with the assumption of a gradual increase of the heavier elements deeper in their interiors (Helled et al. 2011). For gaseous giants such as Jupiter and Saturn, where the core is a small fraction of the total mass, the envelope is of solar composition as shown in our results but a gradual increase of heavy elements with the depth could occur as suggested by Helled et al. (2011). For lower mass giant planets such as Neptune-type planets, where the envelope mass is smaller, a similar situation might occur but the enrichment

in heavy elements of the envelope due to infalling planetesimals and gas accreted, and the convection of materials between the core and the surface of the envelope, could induce a non-solar abundance of materials as observed in Neptune and Uranus.

Interestingly, our results on the D/H ratio in Neptune-type planets are inconsistent with those in Feuchtgruber et al. (2013). To reproduce the observations, the authors determined a D/H ratio in water ice in the range $5.75\text{--}7.0 \times 10^{-5}$ and $5.1\text{--}7.7 \times 10^{-5}$ for Uranus and Neptune, respectively, values four to six times lower than those in Oort comets. These values were found by adopting extreme compositions of interior models, mainly made of water, H_2 , and He. This assumption increases the amount of H-bearing volatile species in planets and reduces therefore the D/H ratio in ices required to reproduce the one in Uranus and Neptune. Conversely, they constrained the mass fraction of ices in these planets to be in the range 14–32 wt per cent by taking a cometary D/H ratio for ices (1.5 to 3×10^{-4}), values in good agreement with the planet formation model by considering both gas and ice phases of volatile species in the planet. Considering the disruption of infalling planetesimals in the envelope of giant planets and refractory elements as in our study, where water represents less than 15 wt per cent of the total mass of planets in most cases (and less than 5 wt per cent in the core), would increase the D/H ratio in volatile species (four to six times lower than comets in their study) following the method used in Feuchtgruber et al. (2013).

We note that results are similar whatever the structure of water ice. This is mainly due to the low trapping efficiency of H-bearing and N-bearing volatile species in clathrate hydrates. The trapping of N_2 in water ice as a unique solution to explain the $^{15}\text{N}/^{14}\text{N}$ ratio observed in Jupiter and Saturn is not viable. It is also consolidated by the low abundance of N_2 in the comet 67P/C-G (Rubin et al. 2015). Our results show that the accretion of N_2 gas and ice in the envelope of planets allows us to obtain similar $^{15}\text{N}/^{14}\text{N}$ values to those observed in Jupiter and Saturn, assuming that N_2 is poorly enriched compared to the solar value, and mainly accreted originally as gas in the envelope. This result is consistent with the findings of Fletcher et al. (2014) but we are unable to reproduce both the low $^{15}\text{N}/^{14}\text{N}$ ratio and the supersolar nitrogen enrichment as Mousis et al. (2014). However, as discussed in this paper, we made the assumption that all heavy elements incorporated in the envelope of planets were homogeneously distributed in the atmosphere (good mixing of species). If this assumption is not valid, it could create some changes in the abundances of volatile species and isotopic ratios in the upper layers of the envelope of giant planets, depending on the chemical composition of the last gas components and icy planetesimals accreted.

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REFERENCES

- Aléon J., 2010, *ApJ*, 722, 1342
 Alibert Y., Mordasini C., Benz W., Winisdoerffer C., 2005, *A&A*, 434, 343

⁷ Using the 103P/Hartley 2 value for H-bearing species, results are slightly shifted below compared to Fig. 5.

- Alibert Y., Carron F., Fortier A., Pfyffer S., Benz W., Mordasini C., Swoboda D., 2013, *A&A*, 558, A109
- Altwegg K. et al., 2015, *Sci*, 347, 1261952
- Atreya S. K. et al., 1999, *Planet. Space Sci.*, 47, 1243
- Bockelée-Morvan D., Crovisier J., Mumma M. J., Weaver H. A., 2004, in Festou M. C., Keller H. U., Weaver H. A., eds, *Comets II, The composition of cometary volatiles*. University of Arizona Press, Tucson, p. 391
- Bockelée-Morvan D. et al., 2012, *A&A*, 544, LL15
- Boogert A. C. A. et al., 2011, *ApJ*, 729, 92
- Briani G. et al., 2009, *Proc. Natl. Acad. Sci.*, 106, 10522
- Brown P. D., Millar T. J., 1989, *MNRAS*, 237, 661
- Crovisier J., 2006, *Asteroids, Comets, Meteors*, 229, 133
- de Pater I., Massie S. T., 1985, *Icarus*, 62, 143
- Dittkrist K.-M., Mordasini C., Klahr H., Alibert Y., Henning T., 2014, *A&A*, 567, A121
- Doty S. D., van Dishoeck E. F., van der Tak F. F. S., Boonman A. M. S., 2002, *A&A*, 389, 446
- Drozdovskaya M. N., Walsh C., van Dishoeck E. F., Furuya K., Marboeuf U., Thiabaud A., Harsono D., Visser R., 2016, *MNRAS*, 462, 977
- Fegley B., Jr, Lodders K., 1994, *Icarus*, 110, 117
- Feuchtgruber H. et al., 2013, *A&A*, 551, AA126
- Fletcher L. N., Orton G. S., Teanby N. A., Irwin P. G. J., Bjoraker G. L., 2009, *Icarus*, 199, 351
- Fletcher L. N. et al., 2014, *Icarus*, 238, 170
- Gálvez Ó., Maté B., Herrero V. J., Escribano R., 2011, *ApJ*, 738, 133
- Gibb E. L. et al., 2000, *ApJ*, 536, 347
- Gibb E. L., Whittet D. C. B., Boogert A. C. A., Tielens A. G. G. M., 2004, *ApJS*, 151, 35
- Greenberg J. M., 1982, in *Comets. (A83-13376 03-90), What are comets made of - A model based on interstellar dust*. University of Arizona Press, Tucson, p. 131
- Hartogh P. et al., 2011, *Nature*, 478, 218
- Helled R., Anderson J. D., Podolak M., Schubert G., 2011, *ApJ*, 726, 15
- Jessberger E. K., Christoforidis A., Kissel J., 1988, *Nature*, 332, 691
- Lellouch E. et al., 2001, *A&A*, 370, 610
- Lewis J. S., Prinn R. G., 1980, *ApJ*, 238, 357
- Linsky J. L. et al., 2006, *ApJ*, 647, 1106
- Lodders K., 2003, *ApJ*, 591, 1220
- Mahaffy P. R. et al., 2000, *J. Geophys. Res.*, 105, 15061
- Mamajek E. E., 2009, *AIP Conf. Ser. Vol. 1158, Exoplanets and Disks: Their Formation And Diversity: Proceedings of the International Conference*. Am. Inst. Phys., New York, p. 3
- Marboeuf U., Thiabaud A., Alibert Y., Cabral N., Benz W., 2014a, *A&A*, 570, AA35
- Marboeuf U., Thiabaud A., Alibert Y., Cabral N., Benz W., 2014b, *A&A*, 570, AA36
- Marty B., Chaussidon M., Wiens R. C., Jurewicz A. J. G., Burnett D. S., 2011, *Science*, 332, 1533
- Meibom A. et al., 2007, *ApJ*, 656, L33
- Mordasini C., Alibert Y., Benz W., 2009, *A&A*, 501, 1139
- Mordasini C., Alibert Y., Klahr H., Henning T., 2012, *A&A*, 547, A111
- Mousis O., Marboeuf U., Lunine J. I., Alibert Y., Fletcher L. N., Orton G. S., Pauzat F., Ellinger Y., 2009, *ApJ*, 696, 1348
- Mousis O., Lunine J. I., Fletcher L. N., Mandt K. E., Ali-Dib M., Gautier D., Atreya S., 2014, *ApJ*, 796, L28
- Mumma M. J., Charnley S. B., 2011, *ARA&A*, 49, 471
- Niemann H. B. et al., 1998, *J. Geophys. Res.*, 103, 22831
- Nomura H., Millar T. J., 2004, *A&A*, 414, 409
- Owen T., Encrenaz T., 2003, *Space Sci. Rev.*, 106, 121
- Owen T. et al., 1999, *Nature*, 402, 269
- Owen T., Mahaffy P. R., Niemann H. B., Atreya S., Wong M., 2001, *ApJ*, 553, L77
- Pollack J. B., Hollenbach D., Beckwith S., Simonelli D. P., Roush T., Fong W., 1994, *ApJ*, 421, 615
- Pontoppidan K. M., Salyk C., Bergin E. A., Brittain S., Marty B., Mousis O., Oberg K. I., 2014, in Beuther H., Klessen R. S., Dullemond C. P., Henning T., ed. *Protostars and Planets VI*. Univ. Arizona Press, Tucson, AZ, p. 363
- Ratajczak A., Quirico E., Faure A., Schmitt B., Ceccarelli C., 2009, *A&A*, 496, L21
- Rousselot P. et al., 2014, *ApJ*, 780, LL17
- Rubin M. et al., 2015, *Science*, 348, 232
- Sekine Y., Sugita S., Shido T., Yamamoto T., Iwasawa Y., Kadono T., Matsui T., 2005, *Icarus*, 178, 154
- Thiabaud A. et al., 2014, *A&A*, 562, A27
- Thiabaud A., Marboeuf U., Alibert Y., Leya I., Mezger K., 2015, *A&A*, 574, A138
- van Dishoeck E. F., 2004, *ARA&A*, 42, 119
- Visser R., Doty S. D., van Dishoeck E. F., 2011, *A&A*, 534, A132
- Waite J. H., Jr. et al., 2009, *Nature*, 460, 487
- Watson W. D., 1974, *ApJ*, 188, 35
- Whittet D. C. B. et al., 2007, *ApJ*, 655, 332
- Wong M. H., Bjoraker G. L., Smith M. D., Flasar F. M., Nixon C. A., 2004, *Planet. Space Sci.*, 52, 385

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