

Theoretical Predictions of Deuterium Abundances in the Jovian Planets

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Using current concepts for the origin of the Jovian planets and current constraints on their interior structure, we argue that the presence of large amounts of "ice" (H_2O , CH_4 , and NH_3) in Uranus and Neptune indicates temperatures low enough to condense these species at the time Uranus and Neptune formed. Yet such low temperatures imply orders-of-magnitude fractionation effects for deuterium into the "ice" component if isotopic equilibration can occur. Our models thus imply that Uranus and Neptune should have a D/H ratio at least four times primordial, contrary to observation for Uranus. We find that the Jovian and Saturnian D/H should be close to primordial regardless of formation scenario. The Uranus anomaly could indicate that there was a strong initial radial gradient in D/H in the primordial solar nebula, or that Uranus is so inactive that no significant mixing of its interior has occurred over the age of the solar system. Observation of Neptune's atmospheric D/H may help to resolve the problem.

INTRODUCTION

Almost all of the hydrogen remaining in the planetary system is incorporated in the four Jovian planets. The hydrogen isotope deuterium is a convenient tracer of formation processes for these bodies since deuterium is believed to have been produced in the initial moments of the universe, and it is uncertain whether there are significant production mechanisms for subsequent times (Wagoner *et al.*, 1967). Thus, according to conventional concepts, the deuterium observed in planets is primordial material which is not significantly renewed by any nuclear reaction. Assuming initial hydrogen isotopic homogeneity of the solar nebula, variations of the observed deuterium to hydrogen ratio (D/H) from one planet to another must reflect processes of fractionation of deuterium during planetary formation, as well as possible subsequent fractionation between the surface layers and the interior. In the following, we will express D/H as a number ratio of deuterons to hydrogen atoms, in parts per million

(ppm). Thus 1 deuteron in 10^6 hydrogen atoms = 1 ppm.

For deuterium, the most significant fractionation process in Jovian planets will involve the formation of deuterated species of H_2O , CH_4 , and NH_3 , owing to the high cosmic abundances of O, C, and N. The substitution of a deuteron for a proton in a molecule such as H_2O leads to a decrease in the vibrational energy and therefore an increase in the molecular binding energy. At low temperatures ($T < 500^\circ\text{K}$), differences in binding energy become comparable to or exceed the thermal energy per molecule, and deuterium tends to become strongly concentrated in molecules such as HDO , CH_3D , and NH_2D , relative to HD (Richet *et al.*, 1977).

Since water, methane, and ammonia are present in variable amounts relative to hydrogen in the Jovian planets, fractionation effects are expected to be likewise variable, depending on the temperature at which chemical and isotopic equilibration occurred. Using current concepts about the origin of the Jovian planets, this paper

arrives at theoretical predictions for the expected atmospheric D/H in each planet. We then compare these predictions with observational data which are now available for Jupiter, Saturn, and Uranus. The results indicate a strong discrepancy between theory and observation in the case of Uranus.

FORMATION OF THE JOVIAN PLANETS

Currently, two different scenarios are proposed for the origin of the Jovian planets. The first of these, the *nucleation* model (Mizuno *et al.*, 1978), hypothesizes the initial formation of a core $\sim 10\text{--}20M_E$ (M_E = Earth mass) by condensation and aggregation of material from the primordial solar nebula. The composition of the core depends upon temperature and pressure conditions in the nebula. According to the model nebula assumed by Barshay and Lewis (1976), temperatures were less than $\sim 200^\circ\text{K}$ in the Jovian planet zone and may have been less than $\sim 100^\circ\text{K}$ in the outer part of this zone. Thus the initial core would include not only refractory materials such as iron and magnesium silicates, but also solid H_2O ice and, in the outer parts of the zone, possibly NH_3 and CH_4 ice as well. Formation of the core may be quite complex, since its growth to $\sim 10\text{--}20M_E$ will be accompanied by accretional heating, which could partially revaporize the ices. The ices would then recondense as grains in the outer region of the hydrogen-helium atmosphere which is gravitationally attracted to the nucleus. According to Mizuno *et al.* (1978), and Mizuno (1980), the hydrogen-helium atmosphere detaches from the general nebula and becomes gravitationally bound to the nucleus when the nucleus has grown by accretion to a critical mass. The critical mass depends upon the opacity in the envelope but is typically $\sim 10M_E$. The amount of hydrogen and helium collapsed onto the nucleus is small, $\sim 5M_E$. These results are essentially independent of the region of the nebula where collapse takes place.

The resulting protoplanet has approxi-

mately the correct parameters for Uranus and Neptune, but is clearly too small for Jupiter and Saturn. Perri and Cameron (1974) have proposed a version of the nucleation model in which the critical mass of the nucleus is $\sim 70M_E$ and the total planetary mass produced by collapse is on the order of a Jovian mass. The large difference between the model of Mizuno and the model of Perri and Cameron arises because the latter assume a completely adiabatic hydrogen-helium envelope while the former allows for the existence of an isothermal, optically thin outer layer. In the Mizuno model, formation of Jupiter and Saturn requires further accretion of hydrogen and helium after the initial collapse of the nebula onto the nucleus, while the accumulation of Uranus and Neptune progresses no further because of the low nebular density in their vicinity.

In the *homogeneous-collapse* model, discussed, e.g., by DeCampi and Cameron (1979), the giant planets originated as distended gaseous protoplanets. As such a protoplanet contracts by radiating energy, internal temperatures rise to the point of hydrogen molecular dissociation, leading to collapse of the object to densities $\sim 1\text{ g/cm}^3$. In this model, no provision is made for an initial central core. Rather, formation of a core occurs through a process of sedimentation of refractory compounds such as iron and silicates. Thus, in contrast with the nucleation model, an enhancement of volatiles such as H_2O , CH_4 , and NH_3 is not particularly to be expected. The homogeneous-collapse model does lead to a natural and attractive explanation of the intrinsic luminosity of Jupiter and, with additional mechanisms, that of Saturn (Hubbard 1977, Pollack *et al.*, 1977).

Explanation of the observed features of the Jovian planets may well require a combination of the two types of origin models. Static models of Uranus and Neptune (Hubbard and MacFarlane, 1980) and of Jupiter and Saturn (Hubbard *et al.*, 1980) indicate that a good fit to constraints such

as radius, mean density, gravitational moments, and starting temperature for adiabats is obtained for models with fairly massive cores. In the case of Jupiter, a core of $\sim 25\text{--}30M_E$ is required if the core is composed of both "ice" and "rock" in solar proportions. For a pure "rock" core, the core mass is about a factor of 2 smaller (Slattery, 1977). For Saturn, the "rock-ice" core is $\sim 15\text{--}20M_E$. Neither Jupiter nor Saturn shows strong indication of enhancement of NH_3 , CH_4 , or H_2O over solar proportions relative to H_2 in the envelope. Indeed, in the case of Jupiter, spectroscopic observations show a possible depletion of H_2O by a factor $\sim 10^3$ (Larson *et al.*, 1975). These results suggest that the "ices," H_2O in particular, may be present in large quantity but trapped in the vicinity of the core in Jupiter and Saturn. The large cores in Jupiter and Saturn are probably difficult to explain on the homogeneous collapse model. This model would likewise not predict substantial bulk enrichment of H_2O , CH_4 , or NH_3 relative to H_2 in Jupiter or Saturn. On the other hand, no quantitative modeling has been performed to determine whether the postcollapse accretion of hydrogen in the nucleation model is able to supply enough energy to Jupiter, for example, to explain its present luminosity.

Models of Uranus and Neptune (Hubbard and MacFarlane, 1980) show strong evidence for enhancement of H_2O , CH_4 , and NH_3 relative to $\text{H}_2\text{--He}$. Extreme models were calculated assuming iron-silicate cores overlain by solar-composition envelopes. Such models are in disagreement with the available constraints on the optical oblateness and gravitational quadrupole moment of Uranus and Neptune. Also, in the case of Neptune, an ice-depleted core lacks sufficient heat capacity to explain the present value of the heat flow. The most satisfactory model for both Uranus and Neptune is a three-layered one, with a central iron-silicate core $\sim 4M_E$, an "ice" layer of H_2O , CH_4 , and NH_3 in solar proportions of $\sim 10M_E$, and an atmosphere

primarily of $\text{H}_2\text{--He}$ comprising $\sim 1\text{--}2M_E$. The key conclusion which we reach from this analysis, and one which plays a major role in the discussion to follow, is that in Uranus and Neptune, the "ice"/hydrogen mass ratio has been enriched by a factor of ~ 250 relative to its value in the primordial nebula. The most plausible explanation of such an enrichment is that it is caused by temperatures in the primordial nebula which were low enough to condense a major component of "ice" from the gaseous phase. Such condensed "ice" particles were then incorporated for the most part in the cores of Uranus and Neptune.

PREDICTED D/H VALUES FOR JOVIAN PLANETS

For Uranus and Neptune, we assume the validity of the formation scenario outlined above. Consequently we assume that H_2O , NH_3 , and CH_4 condensed from the gas to the solid phase at temperatures of about 150, 110, and 60°K , respectively. A temperature at least as low as 150°K seems necessary to explain the large abundances of ice in Uranus and Neptune.

According to the theory for equilibrium partitioning of deuterium between molecular species (Richet *et al.*, 1977), there will be a substantial enrichment of deuterium in H_2O , NH_3 , and CH_4 at temperatures low enough to condense any of these species. Figure 1 shows the predicted D/H for NH_3 , H_2O , and H_2 assuming equilibrium between a gas of solar composition and its condensates. According to these results, deuterium enrichment factors can become enormous. At temperatures low enough to condense H_2O , the value of D/H in water is $\sim 15 \times$ solar, while at temperatures low enough to condense methane, the enrichment factors can be several hundred, and a significant depletion of D in the hydrogen gas can occur.

Such large fractionation effects may not be realized. At low temperatures, reactions proceed extremely slowly. Material incorporated in solid particles may not be able to

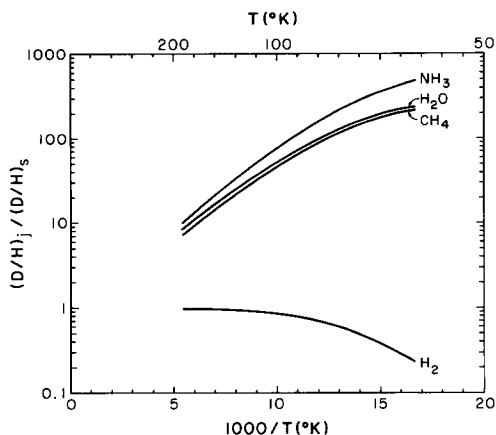


FIG. 1. The number ratio of deuterium to hydrogen in the j th molecular species $(D/H)_j$ relative to the primordial solar value $(D/H)_s$, in equilibrium as a function of temperature, calculated from the theory of Richet *et al.* (1977).

establish isotopic equilibrium with the co-existing vapor. On the other hand, very substantial enrichments of deuterium (~ 10 to $100 \times$ primordial D/H) are observed in certain meteorites (Kerridge, 1980; Robert and Merlivat, 1979; Robert *et al.*, 1980). It is not clear whether such enrichments reflect equilibrium processes, and the enrichments are observed in organic fractions rather than "ices." Enrichment factors vary greatly within a single sample, and an alternative explanation is that the extra deuterium was produced by early irradiation by intermediate energy protons in the inner, terrestrial planet region of the solar system (Robert and Merlivat, 1979).

As discussed by Black (1973), the primordial solar nebula value (s) of D/H is in the range $8 \text{ ppm} \leq (D/H)_s \leq 30 \text{ ppm}$, while the average value of D/H for terrestrial waters (SMOW = Standard Mean Ocean Water) is 156 ppm. Explanation of this enrichment by a factor of ~ 10 involves equilibration temperatures $\sim 200^\circ\text{K}$ (see Fig. 1), although other evidence indicates that some components of carbonaceous meteorites equilibrated at higher temperatures (Black, 1973).

To formulate a theoretical prediction of D/H for the Jovian planets, we adopt the

assumption that the terrestrial D/H does reflect an equilibration at $\sim 200^\circ\text{K}$, and that an enrichment factor of at least 10 will therefore occur for the ice component in planets which accumulated from condensed ices. As mentioned above, this enrichment factor is a lower limit in the case where equilibration and condensation occurs at still lower temperatures. Our picture of the formation of the Jovian planets and establishment of D/H is then as follows. As the solar nebula cools, refractory materials condense and form planetesimals. With further cooling, H_2O and possibly NH_3 and CH_4 condense also. At this time, the D/H value in the ices is established. The planetesimals aggregate to form a nucleus of ~ 10 – $15 M_E$. Some of the ices may be lost due to revaporization, but most remain, enriched in deuterium. Finally, as the nucleus reaches the critical mass, the planet acquires a hydrogen-rich envelope by collapse from the surrounding nebula. In the case of Uranus and Neptune, no further material is added, while Jupiter and Saturn continue to acquire hydrogen-rich material until reaching their present mass. We then assume that the hydrogen-rich envelope is able to equilibrate deuterium with the icy core. For adiabatic interior models, the H_2O – CH_4 – NH_3 core is in fact liquid and at a temperature $> 6000^\circ\text{K}$ (Hubbard and MacFarlane, 1980), so that the excess deuterium in the core will be redistributed in the hydrogen-rich envelope. In the case of Jupiter and Saturn, the possible existence of a phase transition between metallic and molecular hydrogen will cause fractionation of deuterium between the metallic and molecular zone, but this effect is small, of the order of 15% or less (Hubbard, 1974) and can be neglected for our purposes.

Under the above assumptions, the value of D/H for the planet (pl) as a whole is

$$(D/H)_{\text{pl}} = (D/H)_s \frac{X_e M_e + f X_i M_i}{X_e M_e + X_i M_i}, \quad (1)$$

where X_e is the mass fraction of hydrogen

in the outer envelope of the planet, assumed to be solar and therefore 0.78, M_e is the mass of the outer envelope, X_i is the mass fraction of hydrogen in the ice layer (composed of H_2O , CH_4 , and NH_3), M_i is the mass of the ice layer, and f is the average enrichment factor relative to solar D/H in the ice layer at the time of its equilibration during initial condensation and removal from the gas phase. It is assumed that f is in the range 10–20 so that depletion of deuterium in the hydrogen gas at this time is negligible.

Formula (1) was evaluated using a recent model of each Jovian planet (Hubbard and MacFarlane, 1980; Hubbard *et al.*, 1980). The value of f was taken to be 10, i.e., essentially the enrichment factor for SMOW relative to primordial D/H. If equilibration temperatures were lower than $\sim 200^\circ K$, then f could be much larger and the predicted $(D/H)_{pl}$ would also be larger. For Uranus and Neptune, $M_i \approx 10 M_e$ and $M_e \approx 1 M_e$, while for Jupiter and Saturn, $M_i \approx 14 M_e$ and $M_e \approx 300$ and $75 M_e$, respectively. The resulting planetary average D/H is plotted in Fig. 2. This figure shows the primordial value, $(D/H)_s$, the range of values for carbonaceous meteorites, and predicted values for the Jovian planets. Although for clarity error bars are not shown for the predicted values of D/H, note that the asterisks actually represent lower limits for models with equilibration at "ice" condensation, followed by isotopic redistribution in the compressed and heated planet.

Also shown are several observed values for D/H in Jovian planet atmospheres. The values for Jupiter are 52 ± 23 ppm (Beer and Taylor, 1973), 51 ± 7 ppm (Trauger *et al.*, 1977), and 23 ± 11 ppm (Combes *et al.*, 1978). Note that these values are not all mutually consistent. For Saturn we have $20 (+20, -10)$ ppm (Fink and Larson, 1978) and 55 ± 29 ppm (Macy and Smith, 1978). For Uranus, the values are 30 ± 12 ppm (Macy and Smith, 1978) and 48 ± 15 ppm (Trafton and Ramsay, 1980).

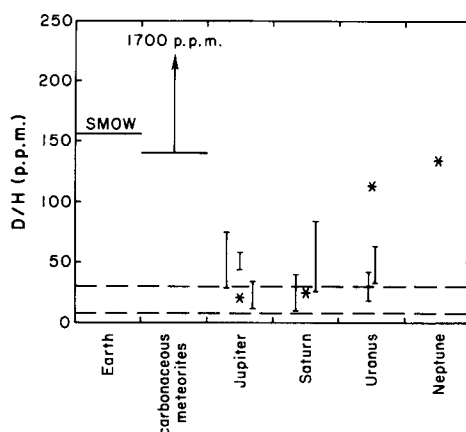


FIG. 2. Values of D/H for various solar system objects in parts per million. The value for the Earth is for ocean water (SMOW). For meteorites, the values range from ~ 140 ppm to more than ten times as much. Dashed lines show assumed range for $(D/H)_s$. Asterisks are theoretical values calculated for models discussed in the text. Sources of data are given in the text.

As expected, for Jupiter and Saturn the predicted and observed deuterium enrichment factors are not very large. For these planets, there is virtually no difference between predictions of the nucleation theory and the homogeneous-collapse theory. For homogeneous collapse, there is no low-temperature separation of the ices and therefore no opportunity for deuterium fractionation. But even in the nucleation model, the maximum mass of ice in the planet relative to hydrogen-helium is still quite small, and deuterium enrichment is not very significant for the planet as a whole. We conclude that there is no known process for substantially modifying D/H in the atmosphere of Jupiter or Saturn, and that the values observed there should be very close to $(D/H)_s$.

In the case of Uranus, there is a noteworthy discrepancy between theory and observation. To explain this discrepancy, we must postulate one of a number of special circumstances.

(a) Assume that Uranus is exceedingly inactive meteorologically, so that its hydro-

gen-helium envelope is not mixed at all with deeper layers. The isotopic composition of the atmosphere is therefore representative of primordial matter but not of the planet as a whole. A test of this concept would be to obtain a value of D/H for Neptune. Neptune has a measurable internal heat flow which may produce currents which tend to mix its internal isotopic composition with the atmosphere (Hubbard, 1978). Note that diffusive separation/mixing can only occur over scales on the order of 100 km during the age of the solar system. The observed D/H for Neptune should therefore be substantially higher than the primordial value if any mixing has occurred.

(b) Assume that the value of D/H for Neptune likewise proves to be close to $(D/H)_s$. We would then have to conclude that the exchange reactions which would lead to a concentration of deuterium in icy material are unable to proceed at the temperatures necessary to produce tenfold enrichment over $(D/H)_s$. This would necessarily cast doubt on the equilibrium fractionation theory for enrichment of deuterium in terrestrial seawater. The hypothesis of Robert and Merlivat (1979), that such enrichment is produced by proton irradiation in the inner solar system, would become more attractive. Note, however, that the low density of the primordial solar nebula at the orbits of Uranus and Neptune, in comparison with the density at the Earth's orbit, might produce important differences in the degree of equilibration for a given temperature, and this effect would also need to be considered.

(c) Interpretation of the spectroscopic data for Uranus' D/H may be affected by some large systematic error of unknown origin. This error would have to affect both of the available, independent measurements.

At the moment, assumptions (a), (b), and (c) all point in differing directions for explaining the Uranus deuterium anomaly. The decisive quantity for resolving this

dilemma is clearly a Neptune deuterium abundance. Should the Neptune value of D/H likewise turn out to be close to $(D/H)_s$, it will be clear that the processes giving rise to the deuterium distribution in the solar system are considerably more complex than is currently believed.

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