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A POSSIBLE DEUTERIUM ANOMALY: IMPLICATIONS OF THE $\text{CH}_3\text{D}/\text{CH}_4$ MIXING RATIOS
IN THE ATMOSPHERES OF JUPITER, SATURN, AND URANUS

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Observations of CH_3D in the atmospheres of the outer planets provide a test of the theory of deuterium fractionation equilibrium in the formation and evolution of these planets. Recent measurements of the $\text{CH}_3\text{D}/\text{CH}_4$ mixing ratios made for Saturn and Uranus are presented and intercompared with current values for Jupiter, illustrating large differences between the planets. Their implied D/H ratios are compared to D/H ratios derived from measurements of HD/H_2 ; and, in the cases of Jupiter and Saturn, they may be incompatible. Implications of these comparisons are discussed in terms of the deuterium fractionation chemistry and possible enrichments of deuterium in the core ices of the planets.

INTRODUCTION

Hubbard and MacFarlane (1980) have suggested that equilibrium partitioning of deuterium among various molecular species in the cold protosolar nebula would yield a significant enrichment of it in the icy cores of the giant planets. For Uranus and Neptune, this primordial isotopic fractionation could lead to observable enrichments in the bulk D/H ratios in their present-day atmospheres if a substantial fraction of these atmospheres is derived from the icy cores and thoroughly mixed with subsequently accreted envelopes of hydrogen-rich, nebular composition, and if equilibrium repartitioning of the deuterium is re-established in the atmosphere.

The level of primordial fractionation that may have occurred in the protosolar nebula is uncertain. Under low-temperature conditions, such as those associated with the canonical solar system formation scenario, the time scale for neutral gas-phase equilibrium partitioning exceeds the age of the universe (Beer and Taylor, 1973). However, catalysis on solid grain surfaces present in the nebular material (Black, 1973) or ion-molecule reactions in the antecedent interstellar cloud (Solomon and Woolf, 1973) can avoid this problem and provide a substantial enhancement of deuterium in the condensible volatiles. Such *ad hoc* processes are sometimes invoked to explain the enhancement of deuterium in certain meteorites as well as in the terrestrial waters.

Whether or not equilibrium repartitioning of the ice-trapped deuterium occurs between the enriched volatiles which outgas from a planet's icy core and any hydrogen envelope which may have accreted subsequent to the core formation is also uncertain. Since there is insufficient time for gas-phase equilibrium to be established at temperatures below about 450 K, an internal heat source is required to drive convective mixing of the hydrogen-rich envelope with the hot interior gases where deuterium exchange can proceed.

If this repartitioning occurs, its effect is to dilute the primordial deuterium enhancement in the outgassed volatiles while increasing the bulk D/H ratio in the overall atmosphere. Based on this scenario and an assumed primordial enrichment by at least a factor of 10, Hubbard and MacFarlane predicted lower limits of about 10^{-4} for the D/H ratios in the atmospheres of Uranus and Neptune.

THE D/H RATIO IN THE OUTER SOLAR SYSTEM

Methane is the most abundant volatile in the atmospheres of the outer planets. Its singly substituted deuteride, CH_3D , is a well-suited tracer of deuterium, and its relative abundance is a test of fractionation equilibrium. Figure 1 shows how D/H ratios are derived from the methane isotopes and from H_2 and HD measurements and gives the relationship between these two ratios if deuterium fractionation has reached equilibrium through chemical exchange reactions of the type shown.

THE MOLECULAR EXCHANGE REACTION
WHICH CONTROLS THE DISTRIBUTION OF
DEUTERIUM IN A MIXTURE
OF H_2 AND CH_4 IS:



THE $\left[\frac{\text{D}}{\text{H}}\right]$ RATIOS IN EACH
COMPONENT GAS ARE:

$$\left[\frac{\text{D}}{\text{H}}\right]_{\text{H}_2} = \frac{1}{2} \frac{|\text{HD}|}{|\text{H}_2|}$$

$$\left[\frac{\text{D}}{\text{H}}\right]_{\text{CH}_4} = \frac{1}{4} \frac{|\text{CH}_3\text{D}|}{|\text{CH}_4|}$$

IN EQUILIBRIUM, THE COMPONENT $\left[\frac{\text{D}}{\text{H}}\right]$
RATIOS ARE RELATED BY:

$$\left[\frac{\text{D}}{\text{H}}\right]_{\text{H}_2} = \frac{1}{f} \left[\frac{\text{D}}{\text{H}}\right]_{\text{CH}_4} = \frac{1}{4f} \frac{|\text{CH}_3\text{D}|}{|\text{CH}_4|}$$

Figure 1. Schematic representation of deuterium fractionation in CH_4 and H_2 .

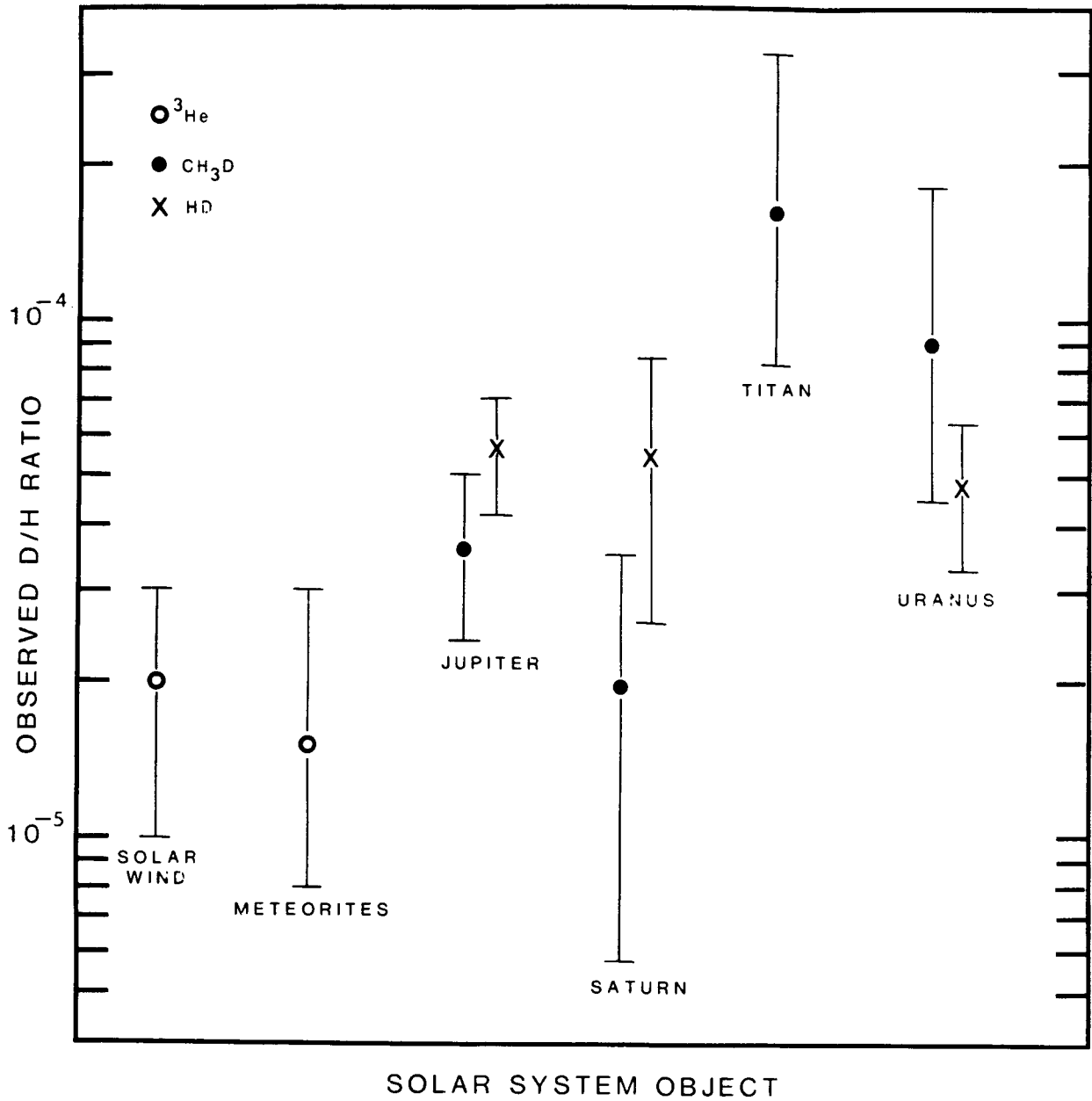


Figure 2. Comparison of the D/H ratios represented in the hydrogen and methane components of outer solar system atmospheres and as deduced from observations of ^3He .

Figure 2 summarizes the current estimates of the D/H ratios in the outer solar system for both the methane and the molecular hydrogen components and compares them with the protosolar values deduced from mass spectroscopic measurements of ^3He in the solar wind and in meteorites (Geiss and Reeves, 1981). The ratios derived from methane in the atmospheres of Uranus and Titan are taken from our own simultaneous study of CH_3D and CH_4 absorption in the spectra at $1.6 \mu\text{m}$ (de Bergh et al., 1985a, 1985b); Saturn's methane ratio is a mean of our ground-based value (de Bergh et al., 1985c) and the recently published Voyager estimate (Courtin et al., 1984); and for Jupiter, the methane ratio is a weighted mean of published ground-based (Beer and Taylor, 1973, 1978; Knacke et al., 1982) and Voyager results (Drossart et al., 1982; Kunde et al., 1982). These values represent the D/H ratios in methane; that is, the D/H ratios are taken as the stoichiometric values $1/4 [\text{CH}_3\text{D}/\text{CH}_4]$, which, if in equilibrium, would be related to the D/H ratio in hydrogen gas by the fractionation factor f , illustrated in Fig. 1. The ratios for molecular hydrogen are derived from a spectroscopic study of H_2 and HD absorption in the visible spectra of the planets and are taken directly from the literature (Trafton and Ramsay, 1980; Macy and Smith, 1978; Trauger et al., 1977; McKellar et al., 1976).

The comparison of the D/H ratios in methane with the protosolar values derived from the ^3He content of the solar wind and of meteorites provides a number of results which, exclusive of the D/H ratios in the atmospheric molecular hydrogen, bear on the Hubbard and MacFarlane deuterium fractionation theory.

1. Deuterium in methane in the atmosphere of Uranus is enhanced relative to the protosolar values derived from the solar wind and meteorites, nominally by a factor of nearly 5. Such an enhancement is consistent with the Hubbard-MacFarlane postulates that, in contrast to Jupiter and Saturn, the present-day atmosphere of Uranus has a significant contribution of volatiles that out-gassed from the icy core of Uranus and that those ices are enhanced in deuterium by fractionation.
2. A similar enhancement of deuterium in methane occurs in the atmosphere of Titan, nominally by a factor of 10 over the solar wind and meteoritic values. This enrichment is further supportive of the Hubbard-MacFarlane proposal of core-ice enrichment since Titan's atmosphere is thought to be derived entirely from its interior.
3. The average deuterium content in the methane component of the atmospheres of Jupiter and Saturn is only slightly enhanced over the protosolar values derived from the solar wind and meteorites. Such a marginal enhancement suggests that any deuterium-enriched, interior ices in the cores of these planets have had little or no effect on the isotopic composition of the atmospheric methane. This conclusion is also consistent with the Hubbard-MacFarlane model.

The analogous comparison of the D/H ratios in hydrogen component of the planetary atmospheres with solar wind and meteoritic values is somewhat chancy since the D/H ratios derived from HD and H_2 observations is very uncertain. In addition, recent remeasurements of the molecular parameters needed for analysis of planetary observations (Cochran and Smith, 1983) suggest that the published values of D/H derived from HD and H_2 observations may require an upward

revision by as much as a factor of 2. However, there are trends present in these data which relate to deuterium fractionation, and since they may imply a possible deuterium anomaly in the molecular hydrogen component of the protosolar nebula, they are deserving of speculation.

1. The planetary ratios in molecular hydrogen do not exhibit the differentiation that Hubbard and MacFarlane predicted. This observation appears to contradict the methane results, which show significant differences among the planets, and suggests that, in some cases, the atmospheric deuterium in methane and hydrogen may not be fractionation equilibrium. In fact, for Jupiter and Saturn the D/H ratios may be smaller in methane than in molecular hydrogen, a situation which is chemically impossible if fractionation equilibrium has been reached. If the upward revisions in the hydrogen results are sustained, this discrepancy is assured.

2. For Uranus, fractionation equilibrium may have been established if the published D/H ratio in molecular hydrogen shown in Fig. 1 is accepted, but it is less certain if that ratio is a factor of 2 higher, as the new molecular parameters for hydrogen may suggest. At the level of precision of the current data complicated by the uncertain reliability of the analysis of the HD lines, it is not possible to distinguish between a fractionation equilibrium situation and a coincidental agreement. The apparent agreement among the D/H ratios in molecular hydrogen in the atmospheres in all the planets seems to argue against any significant differential enhancement; but, if the D/H ratio for Titan is indicative of the maximum level of enrichment in the primordial core ices, a measurable enhancement in molecular hydrogen by the outgassing from these ices is unlikely even if equilibrium is reached.

3. The D/H ratios in molecular hydrogen do not appear to be protosolar in any of the atmospheres of the outer planets, regardless of which set of molecular parameters is chosen to derive these ratios. The planetary values are excluded from the range of D/H estimates deduced from the solar wind and meteorite observations, and may indeed be significantly enriched over that range. However, deuterium fractionation is probably not responsible for the enhancement. Apparently high D/H ratios from molecular hydrogen observations could result if the scattering processes that affect the very weak lines of HD have been underestimated or if the possible presence of weak methane absorption in the same spectral region has contaminated the observations.

It seems that these data support the general concept of deuterium enrichment in the ices that make up the cores of the outer planets, but molecular hydrogen in the outer planet atmospheres presents us with a possible deuterium anomaly. Gaseous hydrogen appears uniformly enriched in deuterium over the protosolar value in all the outer planets, but the source of this enrichment does not appear to be the result of fractionation equilibrium with methane and in fact may be in contradiction to the methane results. What processes are needed to be invoked to explain this anomaly is not yet known, but with better observations and improved analyses the constraints needed to define them may be forthcoming.

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