ISOTOPIC SIGNATURES OF PRESOLAR MATERIALS IN INTERPLANETARY DUST

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Abstract. Interplanetary dust particles collected in the stratosphere frequently exhibit enrichments in deuterium D and ^{15}N relative to terrestrial materials. These effects are most likely due to the preservation of presolar interstellar materials. While the elevated D/H ratios probably resulted from mass fractionation during chemical reactions at very low < 100 K temperatures, the origin of the N isotopic anomalies remains unresolved. The bulk of the N-bearing material may have obtained its isotopic signatures from low temperature chemistry, but a nucleosynthetic origin is also possible.

1. Introduction

Interplanetary dust particles (IDPs) have been routinely collected in the stratosphere by NASA high-altitude research aircraft for more than two decades (Sandford, 1987). These particles are samples of both comets and asteroids, but the specific source of any given particle has not yet been determined. Nevertheless, it is clear that many IDPs are samples of *primitive* objects - parent bodies which have not been significantly affected by post-accretional alteration. Indeed, many anhydrous IDPs have escaped the hydrothermal processing that has extensively modified the matrixes of even the most primitive meteorites (Bradley *et al.*, 1988).

The view that IDPs are composed of primordial solar system materials is borne out by large, common, and highly variable excesses in deuterium D and ^{15}N relative to solar composition. The elevated D/H ratios are thought to have originated from mass fractionation during very low temperature (10 - 100 K) chemical reactions in a cold interstellar molecular cloud environment. Radio astronomical observations of the coldest clouds find some molecules with D/H ratios enriched by as much as 10^4 times the local D/H (Millar *et al.*, 1989). The origin of the N isotopic anomalies is less certain because N isotopic fractionation has not yet been observed in the interstellar

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medium (ISM). The case for nitrogen is further complicated by the possible contribution of nucleosynthetically-derived anomalous N.

While similar isotopic effects are also observed in a wide variety of primitive meteorites, the anomalies are generally smaller, especially for H. This suggests that most molecular cloud material in meteorites has been diluted, chemically evolved, and/or isotopically equilibrated since it was incorporated into the meteoritic parent bodies. The carriers of H and N isotopic anomalies in meteorites are well characterized in some cases, including a wide variety of organic compounds and water of hydration in some meteorites (Messenger and Walker, 1997; Deloule and Robert, 1995). In contrast, the coordinated chemical and isotopic characterization of IDPs is still at an early stage, though significant strides have been made in recent years (Keller *et al.*, 2002).

While it remains a considerable technical challenge, the molecule-specific isotopic analysis of molecular cloud material in IDPs would provide a direct probe of some poorly constrained interstellar chemical processes, such as grain surface chemistry and photolysis of condensed materials in the ISM. Furthermore, this would offer a direct test of models of the origin of meteoritic organic compounds, and provide insight into the relative importance of chemical processes in the solar nebula. Here we review the H, C, and N isotopic measurements performed on IDPs over the past 20 years. We concentrate on presenting a comprehensive review of H, C, and N isotopic data, as this has not been previously compiled. More detailed discussions of the origin and chemical characterization of molecular cloud materials in IDPs are reviewed elsewhere (Messenger and Walker, 1997; Keller *et al.*, 2002; Messenger, 2000).

2. Experimental Techniques

Interplanetary dust particles are collected by NASA high altitude research aircraft by inertial impact onto silicone oil-coated pylons. The particles are picked from the collectors using a micromanipulator and washed of the oil in a hexane rinse. Most particles on the collectors are well separated from any other debris, but some IDPs are found as dense clusters, or sprays of material (cluster IDPs), which must have been fragile particles that disrupted upon impact.

Virtually all IDPs discussed here have been subjected to the following protocol. Each particle picked from the collector is measured for its elemental abundances by energy dispersive X-ray analysis in a scanning electron microscope in order to distinguish extraterrestrial (approximately chondritic elemental abundances) particles from terrestrial contaminants. IDPs of interest are transferred to an ultrapure Au substrate into which they are pressed with a spectroscopic grade quartz or sapphire disc for subsequent isotopic measurements.

Isotopic measurements are performed by secondary ion mass spectrometry (SIMS). In this technique, ions are generated from the sample by bombardment with a high energy ion beam, most commonly Cs^+, but occasionally O^- or Ga^+. These instruments are extremely sensitive, enabling isotopic measurements on samples < 1 μm, but high precision (1 ‰) is difficult to achieve. However, for the samples discussed here, sensitivity is usually more important than precision. Bulk isotopic measurements of IDPs have closely followed the techniques developed by McKeegan *et al.* (1985).

As discussed below, many particles have strongly heterogeneous H and N isotopic compositions on a μm scale. Two isotopic imaging techniques have been employed to investigate isotopic variations on this scale. The first takes advantage of the fact that the spatial distribution of secondary (sample-derived) ions is retained, and the SIMS instrument is used as an ion *microscope* where ion images are detected with a multichannel plate coupled to a fluorescent screen and CCD camera (McKeegan *et al.*, 1987; Messenger, 2000). Alternatively, the primary ion beam is rastered across the sample and secondary ions are synchronously detected with one or more electron multipliers (Nittler and Messenger, 1998; Aleon *et al.*, 2001; Floss and Stadermann, 2002). In the latter technique, isotopic images are more easily quantified.

3. Hydrogen Isotopic Measurements

The H isotopic measurements of IDPs are summarized in Tables 1 and 2. H isotopic anomalies in IDPs are common, occurring most often as enhanced D/H ratios relative to terrestrial samples. As shown in Figure 1, D enrichments are far larger, more common, and are more highly variable among cluster IDPs than individual IDPs. In some cases the D/H ratios observed in cluster IDPs exceed those measured in any other solar system materials, reaching 50 times the terrestrial value (1.5576×10^{-4}) in the cluster IDP Dragonfly. This exceeds the maximum D/H ratio observed in meteorites by nearly an order of magnitude. It is remarkable that this IDP also has fragments strongly depleted in D, resulting in nearly two orders of magnitude variation in D/H within this one dust particle. Most other cluster IDPs also have strong H isotopic variations among different fragments. Isotopic imaging studies have shown significant variations in D/H often occur on a micrometer scale (Messenger, 2000; McKeegan *et al.*, 1987; Nittler and Messenger, 1998; Aleon *et al.*, 2001).

There is strong support for an interstellar origin of the high D/H ratios observed in IDPs and meteorites. Deuterium is quickly consumed as

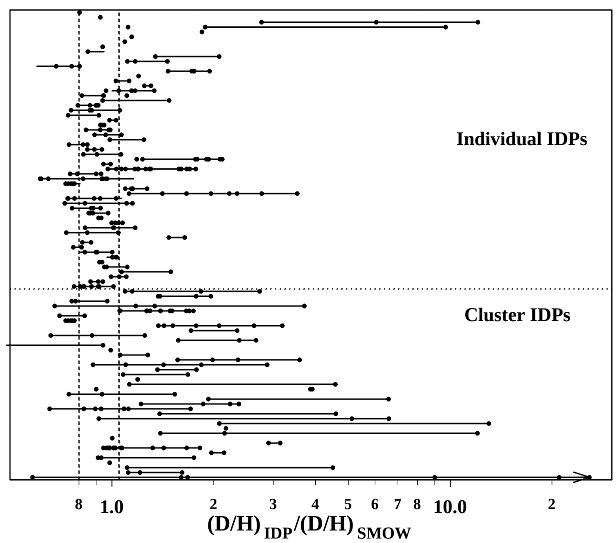

Figure 1. Comparison of D/H ratios of cluster and individual IDPs relative to the terrestrial standard mean ocean water (SMOW). The D/H ratios of different fragments of each IDP are shown as points, where the lines denote the range of values observed in each particle. The range of D/H values observed among terrestrial rocks is shown by the vertical dashed lines. Messenger (2000).

nucleosynthetic fuel in stars and its spallogenic generation is not significant. The only known process capable of producing significant deuterium enrichments is chemical fractionation. This process is known to be efficient at very low temperatures, but a completely different fractionation process in strong radiation fields may also play a role. Extremely high D/H ratios are directly observed for a variety of simple gas phase molecules in molecular clouds, reaching the highest values (D/H > 0.1) in the coldest regions. The D-rich molecules observed by radio astronomy demonstrate the efficacy of gas-phase deuteration, but grain surface reactions may be far more significant in deuterating the bulk of the solid materials in the ISM (Tielens, 1997). Sandford (2001) has also argued that selective 'unimolecular photodissociation' of PAH molecules could lead to very high D/H ratios in the diffuse ISM. While this has not yet been observationally confirmed, such a process would leave a unique fingerprint in its size-dependent effect on the D/H ratios of different PAH molecules.

In principle, there were regions of the solar nebula that had low enough temperatures to enable significant H isotopic fractionation during chemical reactions. However, Geiss and Reeves (1981) first argued that ion molecule chemistry was required at such low temperatures, and the highly opaque solar nebula probably inhibited sufficient radiation to support such processes.

Recently, Aikawa and Herbst (1999,2001) have shown that D/H fractionation can occur in outer regions of protoplanetary disks where ionization by cosmic rays and interstellar UV and x-ray fields can drive ion molecule reactions. The resulting chemistry would be equivalent to the analogous processes in molecular clouds.

4. Nitrogen Isotopic Measurements

The N isotopic measurements of IDPs are summarized in Tables 1 and 2. Nitrogen isotopic anomalies are somewhat more common among cluster IDPs than individual IDPs, though the distinction is not as strong as that observed for D/H ratios. Subfragments of both types of particles often show significant variations in their N isotopic ratios. While H and N anomalies are equally common, the N isotopic anomalies observed in IDPs are typically much smaller. However this is not unexpected if the ^{15}N excesses originated from chemical fractionation because the relative difference in the masses of ^{15}N and ^{14}N is much smaller than the difference between D and H.

The enrichments in ^{15}N have been attributed to chemical fractionation because: (1) they are usually associated with materials enriched in D (including meteorites), (2) as described below, there are no accompanying anomalies in C, excluding any known nucleosynthetic source, and (3) spallation reactions have negligible effects compared to the sizes of these anomalies (Geiss and Reeves, 1983). While a correlation between the D/H and ^{15}N/^{14}N ratios in IDPs would constitute clear support for the chemical fractionation origin, no such correspondence is observed (see Fig. 2). However, there is no reason to expect correlated anomalies in interstellar molecules as the isotopic composition of a given species is determined by a complex interplay of the reaction pathways and isotopic compositions of the precursor species (e.g. Millar *et al.* (1989)). Unfortunately, unlike the case for deuterium, low temperature N isotopic fractionation has not been definitively observed in the ISM. In fact, until recently there was little direct theoretical support for significant N isotopic fractionation in the ISM, although Adams and Smith (1981) suggested that proton exchange with N_2H could result in 1,000 ‰ enhancement in ^{15}N at 10 K. Two recent models have offered new insight into this issue. Terzieva and Herbst (2000) calculated the N isotopic fractionation in a variety of relevant gas phase reactions, finding a maximum of 250 ‰ enhancement. More recently, Charnley and Rodgers (2002) have proposed that ^{15}N-rich NH_3 is efficiently formed in the late stages of cold molecular cloud evolution, reaching 800 ‰ fractionation. For comparison, the largest fractionation observed in an IDP to date is 1,250 ‰ (Floss and Stadermann, 2002). It is not yet clear whether abundant ^{15}N-rich ammonia could pass on

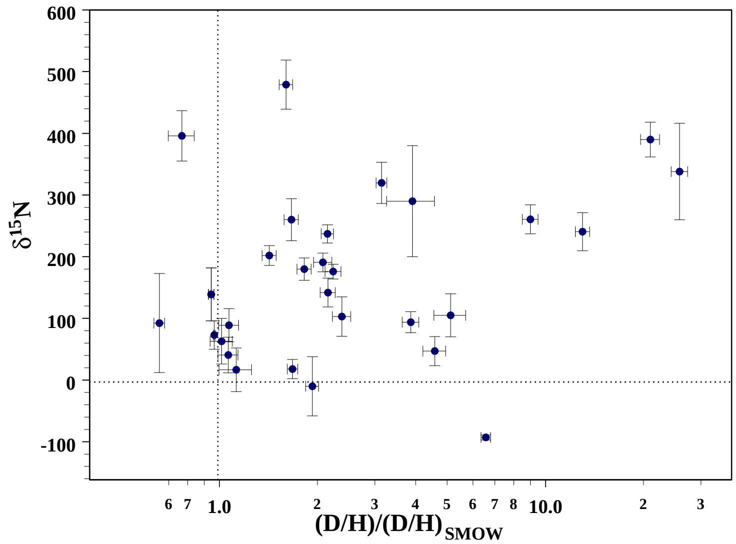

Figure 2. Comparison of H and N isotopic measurements of cluster IDPs. Despite the fact that H and N isotopic anomalies are both common and large in these particles, no clear correlation is observed. The data are taken from Messenger (2000).

its anomalous nitrogen to the abundant organic hosts that have been found in meteorites and IDPs.

We note that two recent studies have provided evidence that the Sun might have a bulk $^{15}N/^{14}N$ ratio considerably lower than the Earth's atmosphere. First, Hashizume et al. (2000) reported isotopically light N of putative solar wind origin implanted in the outer surface of lunar soil grains. Owen *et al.* (2001) reported a new value for the solar $^{15}N/^{14}N$ ratio, based on Galileo measurements from the Jovian atmosphere, as equal to 2.3 $\pm$ 0.3 x 10^{-3}. Since the delta values reported in Tables 1 and 2 are calculated relative to the terrestrial value of 3.7 x 10^{-3}, the ^{15}N enrichments in IDPs relative to solar composition may be significantly higher, in many cases significantly greater than can be explained by even the latest theoretical isotopic fractionation models.

5. Carbon Isotopic Measurements

The large and highly variable H and N isotopic anomalies are not accompanied by any detectable anomalies in carbon. All C isotopic measurements of IDPs so far have fallen within the terrestrial range of -70 ‰ to +10 ‰ (see Tables 1 and 2). However, the average C isotopic composition of cluster IDPs (-45 ‰) is marginally distinct from that of individual IDPs (-30 ‰).

Given the significant and common anomalies in N, even larger anomalies in C might be expected from the larger relative difference in the masses of C isotopes. The lack of accompanying C isotopic fractionation may reflect the fact that the major reservoirs of H, C, and N (H_2, CO, and N_2) have different volatilities. CO is thought to condense onto grain surfaces and participate in grain chemistry, potentially erasing any significant isotopic fractionation between CO and other organic species. In contrast H_2 and N_2 are not significantly condensed onto grain surfaces, even at the lowest temperatures.

6. Summary and Conclusions

The common, large, and highly variable H and N isotopic anomalies of IDPs demonstrate that these materials have remained relatively unaltered since they accreted into parent bodies 4.5 billion years ago. The fact that the D/H ratios of IDPs are often far larger than those of meteorites implies a better preservation of presolar materials. However, the D/H ratios of IDPs are still significantly lower than those observed in interstellar molecules. It is unclear whether this means IDPs also consist of (less) altered material, or is simply due to the fact that the observable interstellar molecules represent a very small fraction of the H-bearing material in the ISM. Indeed, as the D/H ratios of solids in the ISM are generally impossible to determine spectroscopically, our only source of such information may be preserved molecular cloud materials in IDPs and their parent bodies. By better understanding the nature of the anomalous phases in IDPs, we hope to learn more about the genesis of organic compounds in meteorites and chemical processes in the interstellar medium.

There are a number of unsolved problems to be addressed in future work. First, as with most meteorites, the specific parent bodies of IDPs are unknown, although they must come from both comets and asteroids. The presently active STARDUST mission, which will collect dust from comet 81P/Wild-2 should offer important insight into which IDPs are of probable cometary origin. In regards to the present paper, most the most important issues would be clarified by identifying the specific hosts of the isotopic anomalies. For instance, some molecules (e.g. α-amino acids) in meteorites are thought to have formed during Strecker-cyanohydrin synthesis during aqueous processing of interstellar precursor molecules (Cronin and Chang, 1993). Since some D-rich IDPs have apparently escaped aqueous alteration, they should be devoid of α-amino acids, but may contain the presumed precursor species. Additionally, there is still a great deal of uncertainty regarding the origin of the ^{15}N enrichments in IDPs. Although the majority of the ^{15}N-excesses may derived from chemical fractionation, the specific processes and likely hosts of the anomalies are still poorly constrained. Further progress into these and related issues will require coordinated isotopic, chemical and petrographic studies of the same IDPs on a μm scale.

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