

Section VII

Interstellar Dust and the Solar System

INTERSTELLAR MOLECULES IN METEORITES

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ABSTRACT. Substantial enrichment of deuterium, D , in certain components of chondritic meteorites is interpreted as a record of isotopic fractionation during ion-molecule reactions at the very low temperatures characteristic of dense interstellar clouds. Whether those meteorites still contain the actual molecules that were synthesised in the presolar interstellar medium, or whether the interstellar material was recycled into a later generation of molecules within the early solar system is not known.

1. INTRODUCTION

This chapter will focus on meteoritic components that are believed to be of interstellar, as distinct from solar-nebular or circumstellar, origin. The last of those categories, i. e., material formed by condensation in outflows from a stellar object such as a supernova or red giant, is reviewed by Anders *et al.* (1989), which also includes a discussion of the criteria on which a circumstellar identification is based. The only criterion used so far to identify an origin within the interstellar medium is the presence of an anomalous excess of deuterium. This chapter will therefore begin by explaining why we use excess D as a signature for such an origin. We shall then review the salient features of the observational evidence in meteorites, briefly commenting on the nature of the meteorites themselves as probes of presolar processes. Finally, we shall discuss what the meteorites might be telling us about interstellar molecules, and how we might learn more in the future.

2. DEUTERIUM AS AN INTERSTELLAR TRACER

Because of their large relative mass difference, H and D are readily fractionated from each other in nature, and in fact yield the largest natural range of composition for a nonradiogenic isotopic system. The heaviest hydrogen found on earth is roughly 50% enriched in D relative to the lightest material. However, the range observed in meteoritic hydrogen is much greater: up to a factor of four for certain bulk samples relative to average terrestrial hydrogen, with some separated fractions enriched up to a factor of about seven. In fact, these figures underestimate the actual D enrichment experienced by the meteoritic material, because the earth itself is enriched in D by a factor of about seven with respect to the galactic hydrogen from which the solar system was formed (Geiss and Reeves, 1981). Consequently, production of some meteoritic components involved enrichment of D by a factor in excess of 40.

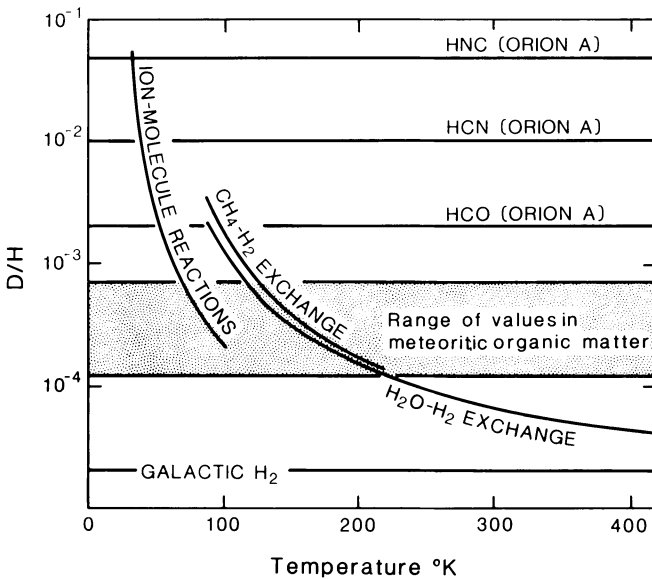


Fig. 1. Deuterium fractionation, relative to galactic H_2 , caused by exchange reactions and ion-molecule reactions, compared with D/H values observed in meteoritic components and in the Orion interstellar cloud. After Geiss and Reeves (1981)

Equilibrium partitioning of the hydrogen isotopes between H_2 gas and a molecule such as CH_4 , which we may take as representative of organic matter, concentrates D in the latter by a factor that increases with decreasing temperature, achieving a value of about 40 at 120 K, Figure 1. However, at such a low temperature, equilibrium would not be attained within the age of the universe, ruling out any such chemical or isotope-exchange reaction as the cause of the meteorite data. Similarly, we may rule out kinetic isotope enrichment of the kind that generates the largest D enrichments observed on earth. Such kinetic fractionation, e.g., by the isotopically selective loss of gas *via* diffusion, can achieve essentially unlimited degrees of D enrichment, but only by massive depletion of the residual gas. Thus, enrichment to the levels seen in meteoritic organic matter entails loss of all but 10^{-7} of the initial complement of hydrogen, whereas the actual hydrogen depletion, though difficult to calculate accurately, is of the order of 10^{-4} .

It turns out that to find an appropriate degree of D enrichment in nature we have to turn to interstellar molecules, such as the well-studied examples in Orion, Figure 1. At the low temperatures in a dense interstellar cloud, the ion-molecule reaction networks, believed to be responsible for production of the interstellar molecules, are characterised by D enrichments that can exceed 10^3 , consistent with D/H values measured for those molecules, Figure 1. Isotopically selective desorption of H from interstellar grain mantles could further enrich D in the molecules contained in such mantles (Tielens, 1983). Obviously, such large enrichments are more than adequate to explain the meteorite data, i.e., we conclude that the presence of a modest fraction of interstellar material constitutes the most reasonable explanation for the

D enrichment observed in meteoritic organic matter. Note that this is strictly an argument by default and the possibility exists that adequate fractionation might have been achieved by a purely solar-system process (e.g., Yung *et al.*, 1989), but at present we seem justified in taking substantial *D* enrichment as a signature of interstellar material in meteorites.

3. THE METEORITIC RECORD

Substantial *D* enrichments have now been observed in several different types of meteorite but in some cases the nature of the material carrying the apparently interstellar signature has not been identified. By far the best-studied carrier consists of organic matter found in the meteorites known as carbonaceous chondrites, and it is likely that similar organic matter is the carrier in at least some of the *D*-rich ordinary chondrites. Here we shall focus on the deuterated organic matter in carbonaceous chondrites. Note that, despite considerable work, a unique origin for meteoritic organic matter has not been identified and multiple syntheses and/or reaction conditions seem likely (e.g., Hayatsu and Anders, 1981; Cronin *et al.*, 1988). Note also that carbonaceous chondrites are not pristine nebular, or prenebular, condensates but are mixtures of lithic units many of which have experienced some geochemical processing, notably low-temperature aqueous alteration, while contained within asteroidal parent bodies (e.g., Kerridge and Bunch, 1979). Nonetheless, some trace components of such meteorites clearly escaped solar-system alteration.

Only a small fraction of the meteoritic organic matter consists of well-characterised molecules, most of it being a complex macromolecular substance resembling terrestrial kerogen. This material consists of polycyclic aromatic moieties connected in a three-dimensional array by short aliphatic bridging chains (Hayatsu and Anders, 1981). The aromatic moieties closely resemble the polycyclic aromatic hydrocarbons which have been invoked to account for the interstellar emission bands (e.g., Allamandola *et al.*, 1987), but whether there is any genetic connection is not known. It seems likely that the meteoritic kerogen-like fraction is a mixture of materials with different origins, possibly including some formed by thermal alteration of simpler, characterisable molecules.

The isotopic composition of the kerogen-like material has been quite extensively studied (e.g., Robert and Epstein, 1982; Kerridge *et al.*, 1987). As a whole, it is substantially enriched in *D* but this enrichment is not uniform throughout the material: different moieties within the macromolecular complex have markedly different *D* contents, as well as different proportions of ^{13}C and ^{15}N . Overall, the $^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$ ratios of the kerogen-like fraction are not substantially different from what we believe to be typical values for the inner solar system, though note that only for *C* is a primordial isotopic ratio well established.

Of the well-characterised molecules, none have yet been isolated in pure form for *H*-isotopic analysis, though *C*-isotopic data have been published for some of the lower-molecular-weight alkanes and monocarboxylic acids (Yuen *et al.*, 1984). Bulk fractions, rather than individual compounds, of amino and monocarboxylic acids have been analysed for *D* content by Epstein *et al.* (1987). They found that both classes of compound are substantially enriched in *D*, Figure 2. In particular, the true enrichment of the amino-acid fraction is probably even greater than that of

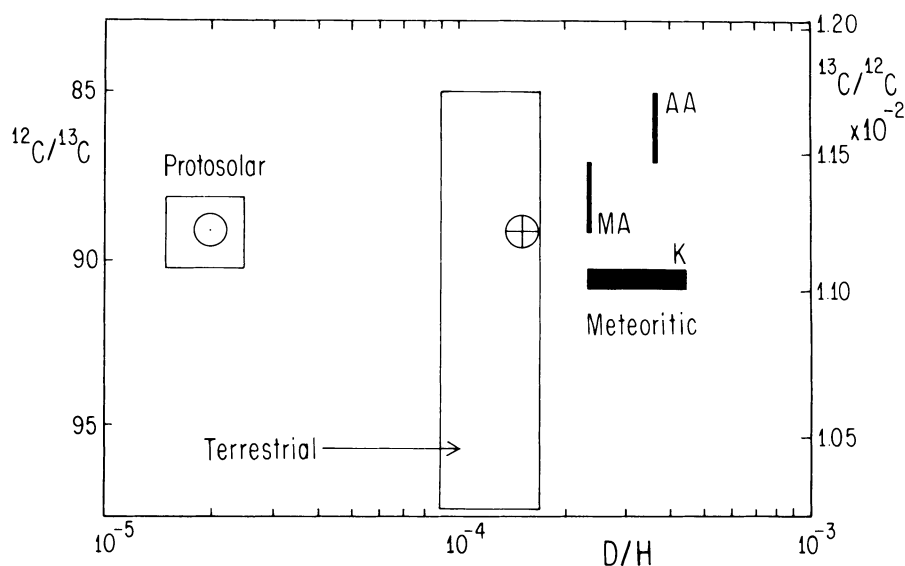


Fig. 2. Isotopic compositions of *C* and *H* in meteoritic organic components compared with mean terrestrial and protosolar values. For protosolar data, the box represents uncertainty; otherwise boxes represent observed ranges. K=kerogen-like material; MA=monocarboxylic acids; AA = amino acids.

the kerogen-like material, because soluble material is more susceptible to isotopic exchange with (*D*-poor) fluids, such as laboratory reagents, than is insoluble material such as kerogen. The hydrogen in the hydrated minerals in such meteorites, and hence in the reactive water on the carbonaceous-chondrite parent asteroid, is also greatly depleted in *D* relative to the organic hydrogen. Note in Figure 2 the relatively small variations observed in $^{13}\text{C}/^{12}\text{C}$; whatever process(es) fractionated the *H* isotopes apparently left no record in those of *C*.

4. INFERENCES ABOUT METEORITIC INTERSTELLAR MOLECULES

Probably the most significant data obtained so far are those for the amino acids. Interpretation of the kerogen data in terms of specific interstellar molecules is hampered by several factors, including its inherent complexity, the ease with which very different processes can lead to production of kerogen-like material, and the probability that the meteoritic material actually does consist of a mixture of components produced by a number of such processes. For example, it is possible that the *D* enrichment in the kerogen-like material is carried by a quantitatively minor component with an "interstellar" *D/H* ratio, intimately mixed with a quantitatively dominant component with a mundane *D* content. However, studies to date have failed to isolate such hypothetical components, suggesting that, if they exist, they have similar chemical and physical properties.

For the amino acids, the situation is superficially similar: either the bulk fraction

contains a proportion of amino-acid molecules synthesised in interstellar clouds, or the amino acids as a whole were synthesised in the solar system from deuterated precursors. However, distinguishing between these alternatives should be more straightforward than in the kerogen case, as described in the next section. Note that the meteoritic amino acids are popularly thought to have been synthesised by the Strecker cyanohydrin reaction involving aldehydes, ammonia and HCN , postulated to have been formed in a prior synthesis such as the Miller-Urey reaction (e.g., Peltzer *et al.*, 1984). The Strecker reaction would have taken place during the asteroidal aqueous activity that generated the hydrated carbonaceous-chondrite lithology, but the precursors could in principle have been produced at any earlier time. In fact, aldehydes, ammonia and HCN have all been observed in molecular clouds (Irvine *et al.*, 1987).

We may summarise our findings to date as follows. Some of the most primitive meteorites contain organic compounds whose high D/H ratios are best explained by isotopic fractionation during ion-molecule reactions at very low temperatures in interstellar clouds. Whether the D -rich hydrogen entered the early solar system in the compounds in which it is now found, or in precursors (which would presumably have been those that were relatively resistant to destruction during transit in the interstellar medium) is not presently known but constitutes a major objective for research in this field. Ultimately we hope that identification of interstellar molecules in meteorites will become sufficiently detailed that their study will add to astrophysical knowledge rather than simply reflect what is already known.

5. FUTURE DIRECTIONS

This topic needs advances to be made in both theory and experiment. In the former, we need to know what isotopic and/or chemical features of interstellar molecules would accompany enrichment of D during ion-molecule reactions. This information is needed in order to test the ion-molecule hypothesis as the cause of the D enrichment. Recall that at present this hypothesis rests on an argument by default; confirmation of a specific prediction, say of a correlation between D/H ratio and some other measurable parameter, would greatly strengthen that hypothesis. In addition, we need to know just how well labile molecules such as amino acids would have survived in the interstellar medium. Would such compounds, if synthesised in molecular clouds, have survived to be incorporated into the primitive solar system?

On the experimental side, isotopic analyses are needed of carefully separated and purified samples of individual compounds extracted from uncontaminated meteorites such as Murchison. In the case of the amino acids, the results of such analyses will discriminate between a mixture of interstellar and solar-system amino acids, which would yield markedly nonuniform D/H ratios among the different amino acids, and solar-system amino acids synthesised from interstellar precursors, which would yield a relatively uniform distribution of D contents. In addition, more needs to be learned about the relationship between the meteoritic organics and the lithic matrix within which they now occur. Is there any petrographic evidence that organic synthesis involved preexisting mineral grains (e.g., Hayatsu and Anders, 1981)? Is there any trace of possible interstellar core-mantle structures (e.g., Greenberg, 1986)?

In conclusion, the probable identification of a record of interstellar molecules

surviving in meteorites is an exciting development of great potential for the future study of such molecules, but we must remember that such an identification is presently based on an argument by default and a major effort should be devoted to testing the validity of that identification.

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