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, and the recent discovery that some IDPs contain abundant grains of silicate stardust (Messenger *et al.*, 2002). The stardust is marked by extreme variations in oxygen isotopic ratios, reflecting its recent nucleosynthetic origin in the parent stars. Here we will focus on the evidence for preserved molecular cloud material, which obtained its isotopic signatures from chemical processes, not nucleosynthetic processes. 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

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anomalies is less certain because N isotopic fractionation has not yet been observed in the interstellar 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 clean spectroscopic grade quartz or sapphire disc for subsequent isotopic measurements.

Isotopic measurements are performed by SIMS (secondary ion mass spectrometry). 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 $< 1\ \mu$m, but high precision (1 ‰) isotopic measurements are difficult to achieve because of matrix-dependant instrumental mass fractionation. The degree of instrumental mass fractionation is corrected for by measuring standards of similar composition under the same conditions, immediately prior to and following the sample analysis. The typical precision for hydrogen isotopic measurements is of order 10–100 ‰. However, for the samples discussed here, sensitivity is usually more important than precision. Bulk isotopic measurements of IDPs reported here 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; Aléon *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 I (cluster IDPs) and II (individual IDPs). 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 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 that significant variations in D/H often occur on a micrometer scale (Messenger, 2000; McKeegan *et al.*, 1987; Nittler and Messenger, 1998; Aléon *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 nucleosynthetic fuel in

TABLE I
Isotopic mesurements in cluster IDPs.

Ref.	**Nichname**	**Particle ID**	**C1#**	δD	$\sigma(\delta\text{D})$	δ^{13}C	$\sigma(\delta^{13}\text{C})$	δ^{15}N	$\sigma(\delta^{15}\text{N})$
8	Dragonfly	L2005 A2a	31	603	76	−4	23	479	40
8		L2005 A2b	31	675	44				
8		L2005 F	31	20000	1400	−26	14	390	28
8		L2005 4	31	24800	1500	−49	15	338	78
8		L2005 3	31	8000	500	−31	13	261	24
8		L2005 *A3	31	−417	24	−1	20	396	41
8	Penelope	L2006 A1a	4	211	96				
8		L2006 A2a	4	118	29				
8		L2006 A2b	4	613	77				
8	Speedy	L2006 A9	14	3503	276				
8		L2006 A10	14	110	46				
8	Gossamer	L2006 A8	10	−14	51				
8	Claude	L2006 A4a	6	748	52				
8		L2006 A3	6	−69	49				
8		L2006 A6	6	−89	85				
8	Tweety	L2008 B2a	4	1147	92	−45	11	237	15
8		L2008 B1	4	970	56				
8	Elmer	L2008 310x	5	71	75	−4	7	89	27
8		L2008 310d	5	66	75	−11	7	41	29
8		L2008 310e	5	17	79	−33	9	63	37
8		L2008 310f	5	−14	72				
8		L2008 310g	5	−35	6	−7	6	73	23
8		L2008 310i	5	−55	18	−23	27	139	43
8		L2008 313	5	322	67				
8		L2008 19a	5	664	84	−16	26	260	34
8		L2008 19b	5	424	71	−33	5	202	16
8		L2008 110	5	822	91	−18	10	180	18
8		L2008 37a	5	−24	17				
8		L2008 37b	5	25	22				
8		L2008 37c	5	−14	36				
8	Marvin	L2009 D1	3	2145	120	−52	11	320	33
8		L2009 D2a	3	1906	80				
8		L2009 D2b	3	−34	11	140	13		
8	Pepe	L2009 D4	4	3	50				
8	Roadrunner	L2009 D5	7	11035	969				
8		L2009 D6	7	1155	115	−43	17	142	23
8		L2009 E2	7	392	117				
8	Foghorn	L2009 D7	8	1174	203	−1	20	149	27

TABLE I

Isotopic mesurements in cluster IDPs (continued).

8	Wiley	L2009 D9	10	12007	653	−52	17	241	31
8		L2009 D10	10	1080	133	−42	11	191	15
8	Taz	L2009 D11	13	5585	770				
8		L2009 D12	13	4122	571	−117	42	105	35
12		L2009 I3	13	−84	76	70	65	62	17
12*	Russell	L2011 AD2	3	3593	495	0	22	75	21
12		L2011 AD2	3	385	254				
8	Leghorn	L2011 2	5	708	72				
8		L2011 4	5	−345	25				
12		L2011 AD6	5	−173	69	0	6	−4	7
12		L2011 AD6	5	−106	52				
12		L2011 AD6	5	120	66				
12		L2011 AD7	5	87	59				
12		L2011 AD7	5	−70	63				
8	Yosemite	L2011 A1	6	1236	126	−38	15	176	12
8		L2011 A2	6	1376	154	−14	87	103	32
12		L2011 AD8	6	862	107	−10	1	600	38
12		L2011 AD8	6	220	93			295	37
8	Porky	L2011 A3	7	5570	222	−53	2	−93	4
8		L2011 A4	7	929	89	−55	60	−10	48
12*	Pasternak	L2011 AD13	8	−253	160	10	46	−7	25
12	-Mauriac	L2011 AD13	8	−64	211				
12*		L2011 AD14	8	535	336	0	11	19	11
8	Daffy	L2011 A5	11	2865	226	−27	14	94	17
8		L2011 A6	11	2914	654	33	26	290	90
8		L2011 B5	11	−100					
8	Petunia	L2011 A7	15	127	129	−76	23	17	35
8		L2011 A8	15	3579	367	−67	21	47	24
12*	Hemingway	L2011 AD19			17	−30	10	70	2
12*	-Jimenez	L2011 AD20	17	192	84	−10	11	470	159
8	Bugs	L2011 A9	22	80	80				
8		L2011 A10	22	678	61	−41	15	18	16
11		L2021 *C4	4	365	60	−40	6	445	30
11		L2021 *C4	4	780	97			334	55
11		L2021 *C6	5	100	66	−54	12	445	30
11		L2021 *C6	5	423	206			267	83
11		L2021 *C6	5	−120	152			−128	85
9		L2021 A6	5	1880	40				
9		L2021 A6	5	840	25				

TABLE I
Isotopic mesurements in cluster IDPs (continued).

11		L2036 *C10	2	984	82	−20	5	472	23
11		L2036 *C10	2	2590	200			377	107
11		L2036 *C10	2	565	124			543	129
11		L2036 *C10	2	1360	150			828	130
12*	Sienkiewicz	L2036 D3	9	278	100	−40	51	34	20
12		L2036 D3	9	58	80				
12*	Carducci	L2036 G3	14	−7	96			15	11
12*	Eucken	L2036 E2	17	−512	39			42	24
12		L2036 E2	17	−58	79				
11		L2036 *C7	19	572	85	5	50	334	95
11		L2036 *C7	19	1380	274			590	300
11		L2036 *C7	19	1670	175			363	146
2,4*	SP-56E	u2-24sp56		−340	50	−53	34	104	24
2,4		u2-24sp56		252	28				
2,4		u2-24sp56		−125	32				
2,4*	SP-88a	u2-19c3a		1345	126	−21	34	406	32
2,4		u2-19c3a		713	54				
1,4*	Calrissian	W7021 r21-m1-9a		373	107	−18	14	54	9
1,4*		W7021 r21-m1-9a		428	112	−28	39	63	16
1,4*		W7021 r21-m1-9a		776	149	−23	18	57	10
1,4*		W7021 r21-m1-9a		2191	272	−43	14	44	11
1,4*		W7021 r21-m1-9a		1078	170	2	20	42	14
1,4		W7021 r21-m1-9a		1633	224				
1,4		W7021 r21-m1-9a		515	120				
2,5*	Essex	W7021 r21-m4-3a		−242	35	−20	13	10	10
2,5*		W7021 r21-m4-3a		−269	44	−20	7	15	8
2,5*		W7021 r21-m4-3a		−225	43	−33	6	14	6
2,5*		W7021 r21-m4-3a		−235	52	−23	13	15	11
2,5*		W7021 r21-m4-3a		−256	52	−25	11	−2	8
2,5*	Ptaar/Tyson	W7021 r21-m3-4a		−169	80	−25	9	14	7
2,5*	Tyson	W7021 r21-m3-4b		−299	25				
1,5*	Skywalker-Solo	W7021 r21-m3-5a		696	96	−7	7	47	6
1,5*		W7021 r21-m3-5a		487	86	−36	7	54	9
1,5*		W7021 r21-m3-5a		297	71	−32	8	52	5
1,5*		W7021 r21-m3-5a		393	75	−41	7	46	5
1,5*		W7021 r21-m3-5a		58	59	−35	7	66	5
1,5		W7021 r21-m3-5a		56	56				
1,5		W7021 r21-m3-5a		659	89				
1,5		W7021 r21-m3-5a		266	71				
1,5		W7021 r21-m3-5a		393	84				

TABLE I

Isotopic mesurements in cluster IDPs (continued).

1,5	Solo	W7021 r21-m3-5a	742	105				
1,5		W7021 r21-m3-5a	506	65				
1,5		W7021 r21-m3-5a	270	46				
2	Butterfly	W7021 r21-m4-8a	340	54				
2		W7021 r21-m4-8a	177	88				
2		W7021 r21-m4-8a	2705	170				
2		W7021 r21-m4-8a	−322	34				
2	Viburnum	r72-m2-3a	−218					
2		r72-m2-3a	−238					
2		r72-m2-3a	−30					
1	Spray-2	u23-m4-4b	389	90				
1		u23-m4-4b	961	130				
1		u23-m4-4b	370	116				
1		u23-m4-4b	775	115				
7	Dood	W9019-3	1734	119	N/A	N/A	−15	30
7		W9019-3	95	77	N/A	N/A	−58	62
7		W9019-3	149	95	N/A	N/A	−131	70
7		W9019-3	833	73	N/A	N/A	25	26

* For these measurements H and C/N data for fragments are not correlated.

References: 1. McKeegan *et al.* (1985); 2. McKeegan *et al.* (1987); 3. McKeegan (1987); 4. Stadermann *et al.* (1989); 5. Stadermann (1991); 6. Keller and Messenger (1997); 7. Nittler and Messenger (1998); 8. Messenger (2000); 9. Aléon *et al.* (2001); 10. Floss and Stadermann (2002); 11. Nittler *et al.*, unpublished; 12. Floss and Stadermann, unpublished.

stars and its spallogenic generation is not significant. Only chemical fractionation is capable of producing significant deuterium enrichments. This process is known to be efficient at very low temperatures, but selective photodissociation 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.

TABLE II

Isotopic mesurements in individual IDPs.

Ref.	**IDP**	**IDP ID**	**C1#**	δD	$\sigma(\delta D)$	$\delta^{13}C$	$\sigma(\delta^{13}C)$	$\delta^{15}N$	$\sigma(\delta^{15}N)$
8	Dragonfly	L2005 A2a	31	603	76	−4	23	479	40
1	Attila	r21-m2-8	−171	49					
1		r21-m2-8	−176	50					
1		r21-m2-8	−82	47					
1		r21-m2-8	−129	54					
1		r21-m2-8	−193	45					
1		r21-m2-8	−226	50					
1		r21-m2-8	12	72					
1		r21-m2-8	−88	54					
2,5*	Cannonball	u23-m4-9	−59	35	−73	32	−11	39	
2,5*		u23-m4-9	−88	47	−2	31	−63	25	
2,5		u23-m4-9	−134	67					
2	Pb-1	u14-m2-8	52	38					
2		u14-m2-8	104	17					
2		u14-m2-8	−5	14					
2,4*	Cedarcreek	u014-m1-9	69	39			94	32	
2,4		u014-m1-9	494	56			10	21	
2,5*	Chicago-2	r29-j10	−49	34	−40	15	79	28	
2,5		r29-j10	−34	40					
2,5		r29-j10	111	35					
2	Chicago-3	u2001-c6	−81	35					
2		u2001-c6	−64	67					
2,5*	Chicago-5	u2015-c25	33	42	−51		46	31	
2,5		u2015-c25	4	43					
2,5		u2015-c25	29	41					
2,5*	Jefferson City	u23-m7-8	−102	61	−19	24	24	17	
2,5*		u23-m7-8	3	66	−38	31	17	28	
2,5		u23-m7-8	−168	40	−4	34	−4	17	
2,5		u23-m7-8	−96	39					
3	Nugget	u23-m1-6	−230	35					
3		u23-m1-6	−186	32					
2,5*	Pattonsburg	u014-m3-3	−132	38	−64	38	6	28	
2,5		u014-m3-3	−182	60					
2,5	Rocheport	r18-m7-16	643	52			−16	29	
2,5		r18-m7-16	474	237					
2,5*	Speckles	u21-m4-8	−154	41	−39	40	3	29	
2,5		u21-m4-8	45	60					
2,5		u21-m4-8	−266	52					

TABLE II

Isotopic mesurements in individual IDPs (continued).

2,5*	St. Elizabeth	u014-m2-2	15	47	−62	31	25	15
3,5*		u014-m2-2	173	54			185	23
3,5		u014-m2-2	11	54				
3,5		u014-m2-2	−166	77				
2,5*	Summersville	u014-m2-11	24	39	−35	23	8	7
2,5*		u014-m2-11	76	45	−21	37	28	32
2,5		u014-m2-11	47	48	13	26	13	30
2,5		u014-m2-11	−1	38				
2,5	Pb-2	u014-m2-9	−86	28				
2,5		u014-m2-9	−69	28				
2,5*	The Clown	u21-m9-4	−135	44			66	35
2,5*		u21-m9-4	−24	42			55	36
2,5		u21-m9-4	−121	42				
2,5		u21-m9-4	−145	106				
2,5*	Verona	u014-m4-7a	−237	118	−27	20	26	16
2,5*		u014-m4-7a	−131	34	2	25	−34	34
2,5*		u014-m4-7a	−74	35	−16	19	−18	13
2,5		u014-m4-7a	−119	60				
2,5*	Xavier	r21-m4-1	151	59			−85	25
2,5		r21-m4-1	−274	111				
2,5		r21-m4-1	−167	138				
2,5		r21-m4-1	106	92				
2,5*	Yoda	r21-m3-6	−224	72	−90	31	39	16
2,5*		r21-m3-6	−257	219	−18	12	25	11
2,5		r21-m3-6	−76	41				
2,5		r21-m3-6	30	34				
2,5		r21-m3-6	−113	41				
2,5		r21-m3-6	−259	35				
1	Mosquito	r21-m4-7	411	110				
1		r21-m4-7	125	85				
1		r21-m4-7	1346	170				
1		r21-m4-7	1774	207				
1		r21-m4-7	1224	160				
1		r21-m4-7	2534	260				
1		r21-m4-7	663	138				
1		r21-m4-7	963	146				
5*	Augustus	u44-m1-2	96	77	−16	31	22	14
5*		u44-m1-2	272	71	−80	34	119	60
5		u44-m1-2	152	68				
5		u44-m1-2	143	68				

TABLE II
Isotopic mesurements in individual IDPs (continued).

1,5	Essex	r21-m4-3a	−242	35				
1,5		r21-m4-3a	−269	44				
1,5		r21-m4-3a	−225	43				
1,5		r21-m4-3a	−235	52				
1,5		r21-m4-3a	−256	38				
1,5*	Lea	r21-m2-4	−386	54	−27	12	2	7
1,5*		r21-m2-4	−381	38	−23	18	0	15
1,5*		r21-m2-4	−31	37	−20	26	−1	12
1,5		r21-m2-4	−350	29				
1,5		r21-m2-4	−60	43				
1,5		r21-m2-4	−66	40				
1,5		r21-m2-4	−177	42				
1,5		r21-m2-4	−39	50				
3	Shannondale-B	u014-m2-13	−209	76				
3		u014-m2-13	−101	79				
3		u014-m2-13	−247	152				
3		u014-m2-13	−70	135				
5*	Aurelian	u47-m1-2a	700	73	−20	12	39	27
5*		u47-m1-2a	170	91			813	25
5		u47-m1-2a	604	78				
5		u47-m1-2a	580	66				
5		u47-m1-2a	667	67				
5		u47-m1-2a	69	62				
5		u47-m1-2a	−26	44				
5		u47-m1-2a	31	55				
5		u47-m1-2a	291	59				
5		u47-m1-2a	259	56				
5		u47-m1-2a	304	67				
5		u47-m1-2a	199	76				
5		u47-m1-2a	196	82				
5		u47-m1-2a	98	69				
5		u47-m1-2a	771	85				
2	Carrollton A	u014-m2-12a	−8	50				
2		u014-m2-12a	−55	52				
5*	Florianus	u47-m1-3a	927	88	−34	11	411	20
5*		u47-m1-3a 904	76	−23	14	409	11	
5*		u47-m1-3a	185	70	−22	20	−373	21
5		u47-m1-3a	1120	101				
5		u47-m1-3a	1085	103				
5		u47-m1-3a	233	89				

TABLE II
Isotopic mesurements in individual IDPs (continued).

5		u47-m1-3a	766	81				
5		u47-m1-3a	788	109				
5		u47-m1-3a	933	74				
5	Galba	u44-m1-1	−176	54				
5		u44-m1-1	65	73				
5		u44-m1-1	−97	49				
5*	Gratian	u44-m4-1c	−153	35	−20	7	39	20
5		u44-m4-1c	−65	40				
5		u44-m4-1c	−112	124				
5*	Jovian	u44-m4-9a	−177	39	−43	18	28	14
5		u44-m4-9a	−252	36				
5		u44-m4-9a	−153	35				
5*	Nero	u44-m1-7	244	68	−43	13	22	9
5		u44-m1-7	−13	125				
5*	Petronius	u47-m2-12	−111	46	−15	10	7	15
5		u47-m2-12	−40	45				
5		u47-m2-12	68	64				
5*	Romulus	u44-m2-3b	−10	90	−4	22	22	96
5		u44-m2-3b	−76	54				
5		u44-m2-3b	−161	66				
5		u44-m2-3b	−20	58				
5*	Tacitus	u44-m1-11a	−64	36	−28	15	−1	20
5*	u44-m1-11a	−50	45	−37	8	42	12	
5		u44-m1-11a	−75	41				
5		u44-m1-11a	−72	39				
5*	Tiberius	u44-m1-5	−15	50	−41	12	53	6
5		u44-m1-5	30	54				
5	Titus	u44-m1-12	−84	63				
5		u44-m1-12	−257	76				
5*	Trajan	u47-m2-5	−242	31	−30	31	120	17
5		u47-m2-5	−128	45				
5		u47-m2-5	−139	66				
5		u47-m2-5	56	82				
5*	Vespasian	u47-m3-5a	−206	46	−34	8	10	7
5		u47-m3-5a	−88	27				
5		u47-m3-5a	−138	34				
5		u47-m3-5a	−97	44				
5		u47-m3-5a	−102	40				
4*	Santa Fe	u33-m3-11	−60	48	−52	10	233	11
4*		u33-m3-11	477	71	−48	15	61	11
4*		u33-m3-11			−50	32	442	29
5*	Majorian	u44-m6-1a	108	50	−23	20	53	6

TABLE II

Isotopic mesurements in individual IDPs (continued).

5*		u44-m6-1a	−55	43	−54	17	36	27
5		u44-m6-1a	−184	36				
5		u44-m6-1a	−54	39				
5*	Pupienus	u47-m2-3	336	92	−40	13	306	21
5*		u47-m2-3	172	75	−43	9	214	12
5		u47-m2-3	−38	66				
5		u47-m2-3	144	79				
5		u47-m2-3	48	66				
12*	Prudhomme	L2009 N2	305	101	−22	21	415	59
12*	L2009 N2	248	90			55	29	
12	Bjornson	L2011 Q2	125	104				
12		L2011 Q2	29	89				
6	Captain Nitrano	L2011 R11	200				250	
12*	Kipling	L2011 R12	467	122	70	9	510	3
12*		L2011 R12	945	142			1090	80
12*		L2011 R12	722	126			1250	93
12		L2011 R12	752	127				
12		L2011 R12	748	140				
12*	Mistral F.	L2036 E6	−197	66	0	45	84	35
12		L2036 E6	−315	56				
12		L2036 E6	−239	55				
12*	Echegaray	L2036 F18	460	169	−50	20	34	4
12		L2036 F18	112	86				
12		L2036 F18	173	108				
7		W9019-m4-1	345	69			49	26
7		W9019-m4-1	1077	185				
7		W9019-M4-2	−150	42			34	17
7		W9019-M4-4	−60	82			−116	76
7		W9019-M4-5	93	46				
7		W9019-M4-6	145	70				
7		W9019-M4-8	848	74			195	92
7		W9019-M4-8					598	176
9		L2021 K1	888	25				
9		L2021 K1	117	50				
9		L2021 K1	8700	800				
9		L2036 E22	5050	450				
9		L2036 E22	11070	700				
9		L2036 E22	1770	300				
9		L2036 R5	−75	5				
9		L2036 R6	−197	20				

H, C, and N isotopic measurements of individual IDPs reported in ‰ deviations from terrestrial standards. For references see Table I.

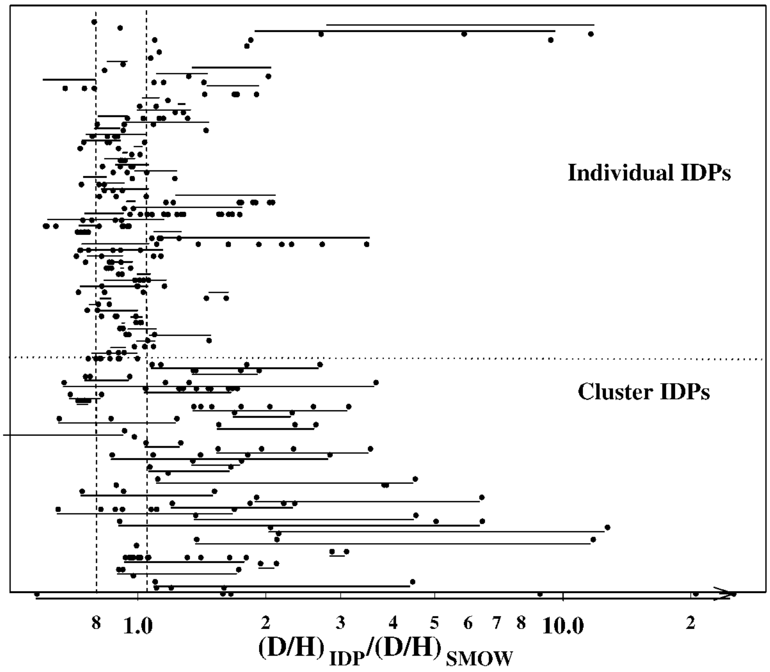

Figure 1. Comparison of D/H ratios of cluster and individual IDPs relative to the terrestrial standard mean ocean water (SMOW). The D/H ratios of different fragments of each IDP are shown as points, where the lines denote the range of values observed in each particle. The particle with the highest D/H ratio in the figure (Dragonfly) reaches a D/H ratio of 50 times solar, estimated by ion imaging (not shown). The range of D/H values observed among terrestrial rocks is shown by the vertical dashed lines.

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) 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. Recent models by Aikawa and Herbst (1999, 2001) suggest that some regions of the outer solar nebula may have experienced sufficient ionization by cosmic rays and interstellar UV and X-ray fields to drive ion molecule reactions. In any event, the physical conditions and resulting chemistry of these models are similar to the analogous processes in molecular clouds.

4. Nitrogen Isotopic Measurements

The N isotopic measurements of IDPs are summarized in Tables I and II. 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 Bochsler, 1982). 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 Figure 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 NH_3, enriched in ^{15}N by 800 ‰, can be efficiently produced in the late stages of cold molecular cloud evolution. 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 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 $2.3 \pm 0.3 \times 10^{-3}$. Since the delta values reported in Tables I and II are calculated relative to the terrestrial value of 3.7×10^{-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.

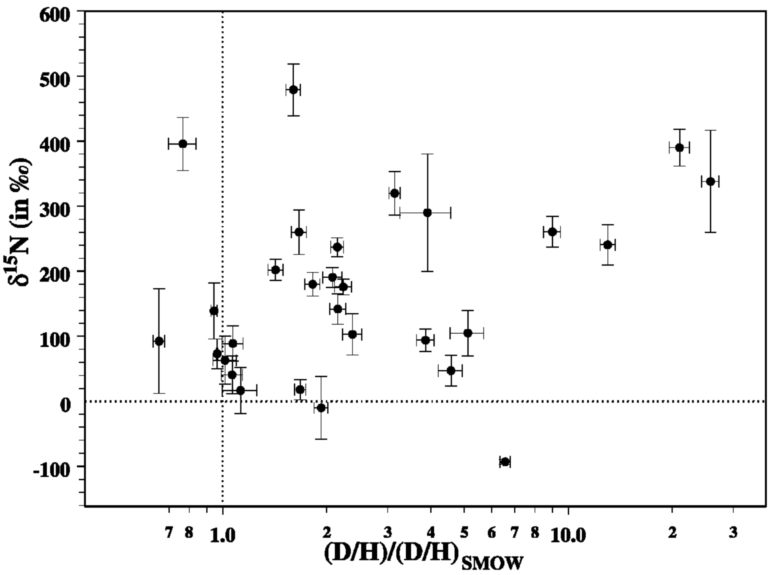

Figure 2. Comparison of H and N isotopic measurements of cluster IDPs. Despite the fact that H and N isotopic anomalies are both common and large in these particles, no clear correlation is observed. The data are taken from Messenger (2000).

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 I and II). 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 IDPs often have D/H ratios far larger than those of meteorites suggests that they contain a better preserved record of presolar low-temperature chemistry. 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. It may also be possible to collect dust from specific comets in the stratosphere with appropriately timed collections (Messenger, 2002). Most of the important issues about the origins of the isotopic anomalies would be clarified by identifying their specific hosts. 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 have been derived from chemical fractionation, the specific processes and likely hosts of the anomalies are still poorly constrained. The fact that both H and N isotopic ratios strongly vary within most IDPs implies that there are multiple, isotopically distinct phases in IDPs. Recently, Aléon *et al.* (2001) have used ion imaging to infer characteristics of these carriers, proposing distinct D/H values of water of hydration, macromolecular material, and chained aliphatics. Analytical advances now enable the direct measurement of specific aromatic hydrocarbons (Clemett *et al.*, 1993), the spectroscopic detection of aliphatic hydrocarbons (Keller *et al.*, 2002), and the detection of amino acids by fluorescent tagging (Clemett *et al.*, 2002). Ultimately, the coordinated isotopic, chemical and petrographic studies of the same IDPs on a μm scale may provide new insight into chemical processes in molecular clouds and the solar nebula.

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