Organic and volatile elements in the solar system

L. Remusat

*Laboratoire de Minéralogie et Cosmochimie du Muséum, UMR CNRS 7202,
Muséum National d'Histoire Naturelle, CP 52, 57 rue Cuvier, 75231 Paris Cedex 05, France*

Abstract. Chondrites and comets have accreted primitive materials from the early solar system. Those materials include organics, water and other volatile components. The most primitive chondrites and comets have undergone few modifications on their respective parent bodies and can deliver to laboratories components that were present at the origin of the protosolar nebula. Here I present a review of the organic material and volatile components that have been studied in the most primitive chondrites, and the last data from the stardust mission about the cometary record. This paper focuses on materials that can be studied in laboratories, by mass spectrometry, ion probes or organic chemistry techniques.

1. INTRODUCTION

Several kinds of extraterrestrial samples can be collected and studied in laboratories to assess the composition of the matter in the solar system when it formed 4.56 Gy ago. They include meteorites, micrometeorites, interplanetary dust particles (IDPs) and cometary grains. The meteorites constitutes by far the largest mass of samples available for study, and among them chondrites are the most valuable to get information about the origin of the solar system.

Chondrites are undifferentiated meteorites and are considered as primitive objects in the solar system, along with comets. They come from small bodies that did not undergo differentiation, i.e. internal heating was not enough to result in the formation of layers of different mineralogical and chemical composition by melting/crystallisation, because they did not contain enough amounts of short lived radionuclides, like for instance ^{26}Al . They contain the first solids that condensed in the early solar system (chondrules, calcium aluminium rich inclusions: CAIs) mixed with few presolar components (including nanodiamonds, graphite, silicon carbide or oxides) with an abundance up to 1000 ppm in some primitive meteorites [1, 2]. They are thus believed to have accreted and preserved the primitive components of our solar system.

Their main constituents are chondrules included in a fine grain matrix [2]. The accretion process gathered minerals, presolar grains but also organic matter and water on the chondrites parent bodies. Some have then evolved due to hydrothermal (aqueous) alteration or thermal metamorphism on the parent body [3]. For instance, water ice melted, releasing fluids that have altered the composition of the constituents in the chondrites [4]. Extends of these modifications are variable among meteorites and is at the basis of the classification of these objects [5]. Moreover, several classes of chondrites are defined depending on their chemical and mineralogical composition. Carbonaceous chondrites are rich in carbon and organic matter, and they contain a high amount of volatile elements (with condensation temperatures below 640 K) like H, noble gases, halogens, Pb or Hg [6]. They are the oldest meteorites in the solar system [7] and their elemental composition is close to the composition of the Sun, except for the most volatile elements as H, He, C, O and N [8]. They are considered as the closest objects to the molecular cloud that gave birth to the solar system that are available for study in laboratory [9]. As they have the

highest content in organic matter, water and noble gases, the present paper will describe these three components mainly in carbonaceous chondrites, which represent 4% on the meteorites found on Earth. Carbonaceous chondrites are divided into several groups [5]. CI are the most hydrated carbonaceous chondrites. They contain up to 15 wt% of water, they are the richest in organics and noble gases. They are constituted only by matrix, without chondrules or CAIs in contrast to CM, which are less hydrated meteorites. CR are often considered as the least modified carbonaceous chondrites on their parent bodies, with the less processed materials. They are supposed to have been subjected to mild metamorphism and hydrothermalism. CO and CV are the metamorphosed counter parts of the CM. They differ from their content in refractory elements and the size of their chondrules (both being larger in CV) [10]. They have been subjected to temperatures higher than 350°C, and contain much less organics and water.

Organic matter in chondrites can be divided in two fractions. The main fraction, in mass, is the insoluble one, hereafter called the insoluble organic matter (IOM). It represents between 75% and 95% of the mass of organics in carbonaceous chondrites. This fraction is not soluble in water and any other organic solvent and is also often named macromolecular carbon. The other organic fraction is constituted by soluble compounds, ranging from carboxylic acids to hydrocarbons, including amino acids and other moieties of biological interest. These compounds have been mixed with water during the hydrothermal alteration and have likely migrated throughout the parent body. They may also have reacted leading to the synthesis of new compounds. Soluble organic compounds have been extensively studied in Murchison (CM), but the knowledge on other meteorites has recently been extended to other meteorites of CI and CR class. An overview of the chondrites content in soluble compounds, water and noble gases will be presented in part 2. The IOM has been studied for the last 30 years, allowing us to have precise knowledge of its molecular and textural properties and variations over classes of carbonaceous chondrites, this will be described in part 3. Stable isotopes are often used to determine the origin of volatile components in meteorites. The isotopic properties of water and the IOM will be presented in section 4 in relation with the processes that may have ruled their evolution in the solar system. The NASA stardust mission has recently brought comet samples to laboratories [11]. Moreover, IDPs and micrometeorites recovered from Antarctica may also be comet samples and could bring information on cometary materials as presented in part 5.

The goal of this paper is not to provide a detailed report of the content in volatile components in carbonaceous chondrites and comets, but rather to shed light on a few questions arisen from the study of those objects that could be assessed by combining advances in cosmochemistry and astrophysics.

In the following, the isotopic compositions may be expressed in delta units, defined by the Relation (1):

$$\delta(\text{‰}) = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000 \quad (1)$$

with R_{sample} being the sample isotopic ratio and R_{standard} the ratio of a terrestrial standard. Commonly used standards are: Standard Mean Ocean Water (SMOW: $D/H = 155.76 \times 10^{-6}$) for H isotopes, Pee Dee Belemnite (PDB: $^{13}\text{C}/^{12}\text{C} = 0.011237$) for C isotopes, and Air for N ($^{15}\text{N}/^{14}\text{N} = 3.67 \times 10^{-3}$).

2. FLUIDS (WATER AND SOLUBLE ORGANIC COMPOUNDS) AND GASES IN CARBONACEOUS CHONDRITES

Carbonaceous chondrites, in particular type 1 and 2 meteorites (see below), contain a lot of volatile components. They include soluble organic compounds, water and noble gases. The heated objects (the types 4 to 6) lack these constituents, which may have been lost to space due to internal heating during the parent body evolution or by chemical reactions. These constituents are described in the following sections.

Figure 1. SEM images of two CM chondrites showing different level of aqueous alteration. On the left, in the case of the CM3 chondrite, the chondrule (ch) is not altered, and the contact with the matrix (m) is sharp. On the right, the meteorite is more altered (CM 2.3), and there is a rim around the chondrule (white arrow). This rim is due to the alteration of the chondrule, and contains altered phase, like the matrix. The matrices are different; the CM 2.3 contains more carbonates, magnetite and phyllosilicates than the CM3.

2.1 Water on chondrites

In contrast to comets, meteorites do not contain any ice or liquid water. Water has reacted with minerals and produced phyllosilicates and other secondary phases (see Fig. 1), in type 1, 2 and 3 carbonaceous chondrites and LL3 ordinary chondrites [12]. All the other meteorites are free of water, either because it did not accrete, or because it was lost by post accretional heating. There is still a debate if this alteration took place on the parent body [4, 13] or if this is a pre-accretion process [14].

The type 1 chondrites, mainly CI, are only constituted by a hydrated matrix [13, 15]. In the type 2 and 3 carbonaceous chondrites, alteration is evidenced by the destabilization of chondrules (see Fig. 1) and the occurrence of low temperature hydrated phases in the matrix or in the chondrules rim [4]. Only the least metamorphosed ordinary chondrites LL3 exhibit traces of water: Semarkona and Bishunpur [16, 17]. Nevertheless, in these objects, water is not only found in phyllosilicates, but also diffused in the chondrules [18].

The precise determination of the water content of these meteorites is difficult because since their fall on earth, most of them have been contaminated by terrestrial atmosphere. Moreover, it may not represent the amount initially accreted on the parent bodies as they have been open systems during the alteration process [12]. Alexander et al. [19] have calculated water contents from the bulk and organic matter hydrogen content in various objects. They determined that CI are the richest in water, with contents up to 15 wt%. The water content in type 2 carbonaceous chondrites (CM and CR) goes from 3 to 14 wt%. Semarkona contains less than 1 wt%, and ion probe measurements [18] have determined abundance of water up to 4000 ppm in its chondrules and also traces of water in nominally anhydrous minerals (1300 ppm in olivine and 2400 ppm in pyroxene). This water could have accreted as ice mixed with silicates grains or was trapped in phyllosilicates. The use of isotopes and in particular H isotopes can help to determine the history of water in chondrites. This will be discussed in section 4.

2.2 Soluble organic compounds

As shown in table 1, carbonaceous chondrites contain a diverse suite of soluble organic compounds [20]. Murchison has been extensively studied for its organic matter and is therefore the best documented case. The most abundant soluble compounds in Murchison are carboxylic acids (330 ppm) [21–23].

Table 1. Soluble organic compounds detected in Murchison and Tagish Lake, from [20].

Class	Murchison		Tagish Lake	
	Concentration (ppm)	Compounds identified	Concentration (ppm)	Compounds identified
Aliphatic hydrocarbons	>35	140	5	12
Aromatic hydrocarbons	15–28	87	>1	13
Polar hydrocarbons	<120	10	n.d.	2
Carboxylic acids	>300	48	40	7
Amino acids	60	74	< 0.1	4
Hydroxy acids	15	7	n.d.	n.d.
Dicarboxylic acids	>30	17	17.5	18
Dicarboximides	>50	2	5.5	9
Pyridine carboxylic acids	>7	7	7.5	7
Sulfonic acids	67	4	>20	1
Phosphonic acids	2	4	n.d.	n.d.
N-heterocycles	7	31	n.d.	n.d.
Amines	13	20	<0.1	3
Amides	n.d.	27	<0.1	1
Polyols	30	19	n.d.	n.d.
Imino acids	n.d.	10	n.d.	n.d.

Murchison contains 60 ppm of amino acids, compounds of biological interest which will be described in more detail in the following section. Other oxidized compounds have been detected: alcohols, polyols, aldehydes, ketones for a total of 600 ppm. Aromatic and aliphatic hydrocarbons occur in Murchison, although long chains normal alkanes have been shown to be contaminants [24]. These soluble compounds share several molecular properties [20]: 1- they have a complete structural diversity (for each formula, every isomer is detected), 2- the abundance decreases when the carbon number increases and in general 3- branched chains are more abundant.

Apart from amino acids, Murchison contains other compounds of biological interest: sugar [25], carboxamides [26] and N-heterocycles [27]. The latest are of primary interest for the origin of life on Earth and in the solar system, but no isotopic data has ruled out terrestrial contamination, and their low content (less than 1 ppm) makes them to be considered with caution.

Relationships have been looked for between some soluble compounds and the IOM. To date, only aromatic hydrocarbons could be related to the macromolecular carbon. Pyrolysis of the IOM releases aromatic moieties similar to those detected as free soluble compounds, and carbon isotopes are consistent with an origin of this fraction by hydrolysis or pyrolysis of the macromolecule [28].

Distribution of soluble compounds varies between meteorites (see table 1 and the comparison Murchison/Tagish Lake). The soluble fraction hence appears to be a complex mixing between moieties that could have been formed on the parent body, from the reaction of precursors that could have been accreted in ices or from the hydrolysis of the IOM, and compounds that could have been synthesized prior to accretion and preserved trapped in the matrix of the carbonaceous chondrites. The complex isotopic distribution (an example is given in the following section for amino acids) clearly point to various origin for soluble compounds (see [29] for a compilation of isotopic composition of soluble compounds).

2.3 Soluble organic compounds: Amino acids

Amino acids are emblematic organic compounds in meteorites. They are often cited as possible prebiotic molecules for the origin of life and are known to be indigenous in meteorites since the 70's [30, 31]. To date, about 80 amino acids have been detected in CI, CM and CR chondrites; many of them have no

terrestrial counterparts. Their abundance varies between meteorites from less than 1 ppm in some CI up to 250 ppm in some CR2 [32]. Amino acids in meteorites have from 2 to 8 carbon atoms; all the possible isomers are present. The distribution of amino acids differs from one meteorite to the other. For instance, in Murchison, glycine > α -aminoisobutyric acid > alanine, whereas in Orgueil β -alanine > glycine > γ -aminobutyric acid. Branched chains are in general more abundant than straight ones. Moreover, α , β and γ amino acids can be detected, with abundance order $\alpha > \gamma > \beta$.

Amino acids in meteorites have been found to be racemic, leading to the unambiguous interpretation of their indiginity [30]. Nevertheless, the progress in GC-MS and protocols for analysis of enantiomeric excess in the 80's allowed the report of small excess of the L-form of some amino acids in Murchison [33], though doubts about contaminations raised [34]. But compound specific isotopic measurements of ^{13}C and ^{15}N show that these excesses are not due to contamination [35, 36]. This was further confirmed by the discovery of L-excess in non-protein chiral amino acids and in other meteorites [37, 38]. Enantiomeric excesses are variable among meteorites [39], and also inside the same objects [40] but never exceed 18%. The hydrated meteorites exhibit higher excess, pointing to a possible amplification during aqueous alteration [39]. Nevertheless, the effect of UV circularly polarized light has been suggested to explain the excesses observed [41]. This hypothesis is being tested by laboratory experiments [42–47] but the source of the CPL at the vicinity of the early solar system still needs to be assessed.

Amino acids in carbonaceous chondrites have been shown to be enriched in ^{15}N , ^{13}C and D relative to terrestrial amino acids. In Murchison [48], N isotopic composition seems homogeneous with $\delta^{15}\text{N} \approx 60\text{‰}$ (compared to around 1‰ in terrestrial proteins), whereas in the two CR2 LAP02342 and GRA95229, it is more heterogeneous and $\delta^{15}\text{N}$ is comprised between 70 and 130 ‰ [49]. $\delta^{13}\text{C}$ are variable [50], with values ranging from -6 to $+50\text{‰}$ (terrestrial value from -35 to -25‰). Amino acids are usually enriched in ^{13}C by 40‰ compared to the other extraterrestrial soluble organic compounds except the carboxylic acids [29]. For C isotopes in α -amino acids, it must be noted that branched chained have higher ^{13}C content than straight ones. Moreover, $\delta^{13}\text{C}$ decreases with the carbon number. Amino acids have high δD , usually higher than the isotopic enrichment observed in the IOM of the corresponding meteorite (see section 4.1). Indeed, in Murchison, δD reaches 3500 ‰ (i.e. $\text{D}/\text{H} = 701 \times 10^{-6}$) [51] and the highest value ever reported for an amino acid is $\delta\text{D} = 7245\text{‰}$ for GRA95229 ($\text{D}/\text{H} = 1284 \times 10^{-6}$) [49] (compare with values in Fig. 7). Like for C isotopes, D distribution is heterogeneous among amino acids. There is no clear trend or correlation with any molecular parameter, indicating a complex origin for the extraterrestrial amino acids fraction. It must be noted that the 2-methyl amino acids and branched chains tend to have higher δD than 2-H amino acids and straight chains.

The correlation between the distribution of amino acids and hydroxy acids has lead to the suggestion that amino acids were synthesized by Strecker-cyanohydrin synthesis [52]. Indeed, this reaction can form, from aldehydes or ketone precursors, α -amino acids and α -hydroxy acids that will have parallel distribution. This reaction requires HCN and water as co-reactants. But this reaction can not produce the non α -amino acids and other mechanisms like hydrolysis of lactams and Michael addition has been proposed to account for the β and γ amino acids [53]. Molecular properties and isotopic ratios of both the IOM and the amino acids fraction rule out an origin from the hydrolysis of the macromolecule [54]. Molecular and isotopic data on extraterrestrial amino acids thus indicate a complex origin for this fraction. They also show that the synthetic pathway and evolution depends on the parent body. A lot of questions then remain open on the origin and evolution of extraterrestrial amino acids.

2.4 Noble gases in carbonaceous chondrites

Noble gases occur as very low concentration in meteorites. For instance, an abundance of 0.6 ppt (part per trillion) of Xenon is considered as pretty high. Some noble gases may have several isotopes (for instance 9 for Xe), and some can be formed by radioactive decay (for instance ^{129}Xe is produced by radioactive decay of ^{129}I). Noble gases can also be implanted (from the solar wind), accreted in

Figure 2. Elemental (A) and isotopic (B) pattern of noble gases in several reservoirs in carbonaceous chondrites, from [55]. Abundances are normalized relative to solar value and ^{132}Xe . Earth is presented as a reference (except He that is lost from atmosphere by dynamic escape). Isotopic patterns are characteristic of the reservoir. Etching experiments could permit the identification of the carrier phase of some of the reservoir, like presolar nanodiamonds for HL and P3. Q (containing P1 gases) is not clearly identified but may be organic. Ureilite are a class of meteorites with specific noble gases signature. G and N are trapped in SiC and presolar graphite.

carrier phases and be produced by nuclear effects like spallation. Then two distinct components can be distinguished [55, 56]: the “solar” (mainly implanted) and the “planetary” noble gases (trapped in carrier phases and are often considered as “primordial”).

Elemental and isotopic pattern have been determined for noble gases as shown in Fig. 2. They both depend on the involved reservoir. Elemental patterns show subtle differences among meteorites and reservoirs. The main observation is a clear depletion in light gases. Isotopic patterns are more diverse and are usually used to trace a specific reservoir. Then, the global isotopic pattern for primordial noble gases of a specific chondrite will depend on the combination of constituents accreted. The carrier phases of noble gases were investigated by stepwise leaching [57]. Some carrier phases are presolar, like SiC and nano diamonds and the isotopic pattern can be used as a fingerprint of the origin of the carrier phase but also to determine its abundance. Some components, like HL or G are named anomalous components as they require nucleosynthetic processes (i.e. presolar phenomena) in addition to common physical and chemical processes (like diffusion or condensation) to account for the isotopic pattern observed.

One reservoir, the P1 component, also called “Q” phase (for “quintessence”) was defined by Lewis et al. [57] based on its resistance to HF/HCl leaching and disruption in HNO_3 . It seems to be a main reservoir of primordial noble gases, and it is not yet fully identified [58]. Some striking observations have been made on Q noble gases. Q seems to release most of its noble gases at 1000°C , and this temperature is the same for all the noble gases [59]. Moreover, the relative abundance of each noble gas is the same in all the chondrites [58]. Nevertheless, its properties likely relate it to the IOM. The exact process that trapped the noble gases in Q is also unknown. It was suggested that the texture of the IOM (see later in section 3) could trap noble gases atoms in holes in the aromatic and aliphatic network of the IOM [60]. A lot of questions remain opened about the accretion and origin of noble gases in chondrites; the framework is complicated by the superimposition of signatures of presolar and solar components in addition to parent body processes.

3. THE INSOLUBLE ORGANIC MATTER: THE MAIN ORGANIC RESERVOIR IN CHONDRITES

Carbonaceous chondrites contain up to 4 wt% of organic matter, mainly as an insoluble macromolecule. IOM can be isolated by solvent extractions and acid demineralisation. Although it concentrates the residue in the insoluble macromolecule, this treatment has the drawback to remove all the fingerprints

of interactions of the IOM with inorganic matrix, and might also induce slight laboratory modifications of the molecular structure and isotopic composition of the IOM. Nevertheless, several studies have been performed to determine the distribution of the organics and their textural relations with the inorganic component.

3.1 Molecular structure of the IOM: A peculiar macromolecule

Elemental analysis of the IOM of the CI and CM chondrites reveals that it is made of C, H, O, N and S. Typical formula has been calculated to be $C_{100}H_{70}O_{22}N_3S_7$ for Murchison IOM. The molecular structure of the IOM of CI and CM has been studied by the combination of destructive and non destructive techniques. Two approaches can be used to study the molecular structure of an insoluble macromolecule: we can destroy its structure by thermal process (pyrolysis) or chemical reagents (mainly oxidants), or use spectroscopic techniques that will preserve the structure (like infrared spectrometry or solid state NMR). The first ones release small fragments that can be identified by gas chromatography or liquid chromatography leading to a very precise molecular identification. The main drawback is that the degradation processes used have usually yields that are far from 100% and we have to assume that the products obtained are representative of the starting material. Moreover, pyrolytic processes may lead to artefacts by recombination or aromatisation of the products. This is overwhelmed by the spectroscopic techniques, which give bulk information more robust in term of statistic distribution for the whole macromolecule. But, the molecular identification is much less precise. It is then very useful to combine all those techniques together to correct for potential analytical artefacts and to understand the initial molecular structure from puzzle pieces obtained from the different set of data.

Table 2. Summary and compilation of molecular parameters for Orgueil and Murchison IOM from data collected over the last 20 years.

Relative Molecular abundances		Analytical Techniques	Reference
Aromatic-linked C as CH ₃ / Total C	0.01	¹³ C NMR	[61–63]
C as CH ₂ Aliphatic / C as CH ₃ Aliphatic	2	¹³ C NMR, IRTF	[61–63]
Non Protonated Aromatic C /			
Aromatic Protonated C	2.8	¹³ C NMR	[61–63]
Aromatic C / Total C	0.75	¹³ C NMR	[61–63]
Acids C / Total C	0.07	¹³ C NMR	[61–63]
S as Thiophenes / S as Aliphatic S	3.12	Xanes S, Pyrolysis GC-MS	[54, 72, 78]
N as pyrroles / Total N	0.85	15N NMR, Pyrolysis GC-MS	[54]
Relative Bulk Chemical Composition		compilation from:	[54, 63, 67]
H/C	0.70		
N/C	0.03		
O/C	0.22		
S/C	0.045		
Structural informations			
Small aromatic units		EPR, ¹³ C NMR, TEM	[61–63, 76, 79]
Short Chains		Oxidative GC-MS, ¹³ C NMR	[63, 67]
Highly branched aliphatics		Pyrolysis and oxidative GC-MS, Infrared	[54, 63, 67, 80]
Highly substituted aromatics		Pyrolysis GC-MS	[54, 66, 80]

Solid state ¹³C NMR and infrared spectroscopy [61–64] reveal that most of the carbon is involved in aromatic structures. Only 20 to 30 % of the carbon constitutes aliphatic bonds. This is confirmed by pyrolysis [54, 65, 66] which releases rather small aromatic units: up to coronene (7 rings aromatic unit).

Figure 3. Summary of molecular information on the chemical structure of IOM of Murchison. R means an organic moiety. This picture was established thanks to data collected from 20 years and summarized in table 2. (This figure is modified from Derenne and Robert (2010), « Model of molecular structure of the insoluble organic matter isolated from Murchison meteorite », *Meteoritics and Planetary Science*, doi: 10.1111/j.1945-5100.2010.01122.x).

Pyrolysis does not reveal any long aliphatic chains in the chondritic IOM. Though it could be due to an artefact of aromatization upon the flash heating during the experiment, it indicates that IOM is free of long aliphatic moieties. This is consistent with solid state NMR [62, 63], which indicates that aliphatic moieties are short and branched. Ruthenium tetroxide oxidation was performed on IOM [67, 68] and confirmed NMR conclusions. The maximum length is 7 carbon atoms for aliphatic bridges between aromatic units, and 4 carbon atoms for the side chains with a free end. Those aliphatic moieties exhibit a lot of branching with methyl and ethyl groups, and they often link more than 2 aromatic units together. This is consistent with recent FTIR data on the IOM of CI and CM chondrites [69]. Such carbon skeleton results in a high degree of cross linking that may explain the chemical resistance of the IOM.

Oxygen is involved in ether and ester groups as revealed by pyrolysis and chemical oxidation [54, 67, 70]. So far, no insight of occurrence of oxygen in aromatic units has been determined. Almost no compound containing N is detected by pyrolysis and chemical oxidation [54]. ^{15}N solid state NMR on Orgueil IOM has shown that N mainly occurs as pyrroles, i.e. in five atoms aromatic moieties [54]. Nevertheless, the occurrence of minute amount of nitriles may occur. Upon pyrolysis, sulphur is released as thiophenes, i.e. five atoms aromatic units [54, 71, 72]. More recent S K-Edge XANES has shown that the occurrence of S in chondritic IOM may be more complex than this simple picture. Hydrated meteorites exhibit also sulfoxide and sulfone in the aliphatic chains [73].

All these molecular information can be summarized in Fig. 3. This model is not the exact representation of the molecular structure of the IOM but it rather shows the main characteristics of the C skeleton and the O-, N- and S-containing groups. The principal statistical parameters determined for the molecular structure of the IOM in the case of Orgueil and Murchison are reported in table 2.

The organic radicals contained in the IOM of Orgueil (CI), Murchison (CM), Tagish Lake (C1) and Kainsaz (CO3) have been studied by electron paramagnetic resonance (EPR) [74–77]. The IOM

of non heated chondrites exhibit two peculiar properties: 1- their organic radicals are heterogeneously distributed, leading to the occurrence of radical rich clusters; 2- they contain abundant diradicaloids (unpaired radicals), that are not detected in any other natural organic matter. In contrast, heated IOM does not have diradicaloids and have very few radicals, showing that organic radicals are sensitive to thermal stress and thus occur only in primitive (least modified) IOMs. Their occurrence may likely indicate the radical chemistry plays a key role in the synthesis of chondritic IOM.

3.2 Distribution of the IOM: Understanding the accretion process

To understand the origin and evolution of organic compounds in chondrites, it is necessary to study the textural and petrographic relationships of organics and minerals (Fig. 4). This can be done at several scales. At the macroscopic scale, it appears that the organic matter is located in the matrix of chondrites, associated with phyllosilicates [81]. Osmium tetroxide vapour impregnation [84] labels specifically organic compounds in rocks and reveals that chondrules and CAIs are free of organic matter. At this scale, no specific pattern is observed, leading to the conclusion that organics accreted with other volatile components in the matrix. This is confirmed by fluorescence microscopy [82, 85], which uses the fluorescence of organic matter under UV light. This technique also shows that organic matter occurs as circular particles, with a diameter around a couple of microns.

The recent use of the nanoSIMS allows us to map the elements constituting the organic matter in the matrices, along with the constituents of the inorganic material (Fig. 4). Micron size carbon rich particles can be observed, evenly distributed in the matrix of hydrated chondrites [86]. As they contain significant amount of H and N, they correspond to organic matter. Moreover, there is also some “diffuse” organic matter all over the phyllosilicates. No specific association with oxides, sulfides or sulfates is observed. These minerals appear free of C, and no coating is observed. These observations indicate that organics occur as isolated organic grains or organic matter intimately mixed in clay like minerals, which constitutes most of the minerals of the matrices of hydrated chondrites.

By using high resolution transmission microscopy, we can access to the nanometer scale (Fig. 4). At that scale, in Allende (CV3), organic compounds appear associated with mineral surfaces [83]. Such association leads to the conclusion that mineral surfaces may have played a role in the synthesis of organic matter. Nevertheless, it is not clear if such association is ubiquitous in meteorites. Other observations at that scale reveal that organics appear in condensed structures, with variable sizes, often in close contact with hydrated minerals.

In conclusion, organic matter occurs in association with low temperature components in chondrites. The observations point to a complex origin of the organics, one component being accreted as isolated organic particles, and the other having likely migrated throughout the matrix and being trapped into phyllosilicates.

3.3 Diversity among the different types of chondrites: Influence of parent body processes or source effect?

Comparing the molecular properties of IOM of various meteorites can reveal the effect of parent body processes on organics. Two main phenomena can occur on parent bodies: 1- thermal metamorphism due to the disintegration of short lived radionuclides that induces an increase of the temperature, or 2- a hydrothermal metamorphism due to water circulation and hydration of the constituents of the parent body. Organics will respond in different ways to these stresses.

Hydrothermal metamorphism is usually assumed to induce oxidation of the IOM, as shown by solid state NMR, S K-edge XANES and IR spectrometry [61, 69, 87, 88]. Hydrated chondrites may have accreted ice rich in H_2O_2 or it could be formed by radiolytic degradation of H_2O [61]. Then this hydrogen peroxide would have reacted with ferrous iron (Fe^{2+}) to produce OH radicals (via Fenton's reaction), much efficient oxidant than water. This oxidative agent induces the destruction of aliphatic

Figure 4. Location of organic matter in chondrites revealed by several techniques (the name of the corresponding meteorite is indicated into brackets). A and B: Osmium labelling reveals that organic matter occurs in the matrix, the chondrule being free of organic matter [81]. C: By fluorescence microscopy, organic matter (white structures) appear as isolated particles, with sizes ranging from 0.5 up to 4 microns randomly distributed in the matrix [82]. This is consistent with NanoSIMS imaging (E). Organic matter corresponds to area rich in both C and H. Organic particles are circled in green, and show no association with a big mineral rich in S, O and H (sulfate). But, at the nanometer scale [83], as what is observed by TEM (D), organic matter (called PGC: poorly graphitized carbon) forms coatings around sulfides (Pent: pentlandite). OL: Olivine grain, abundant in the matrix of this kind of chondrite.

Figure 5. Solid state ^{13}C NMR spectra of IOMs from carbonaceous chondrites of various degrees of hydrothermal alteration [61]. The least altered meteorite is on the top, the most altered is at the bottom. From the NMR spectra, it appears a clear decrease in the aliphatic C content with increasing alteration. This has been interpreted as a loss of aliphatic carbons by oxidation during the aqueous alteration.

linkages and the increase in aromatic carbon, aldehydes, ketones, ether and ester functions (Fig. 5). This is consistent with higher content of phenols produced by pyrolysis of IOMs of CI compared to CM [54, 89]. It must be noted that such process could lead to the formation of some soluble compounds [28, 90]. Nevertheless these modifications appear to be limited, as the molecular structure of CI, CM and CR IOMs seems to be broadly similar. Even in the highest altered meteorites, the oxidation process appears to be far from being fully completed [69]. It must be noted that, in detail, the differences between IOMs from different chondrites sometimes does not closely match the evolution on the parent body as determined by the mineralogical observations. For instance in Fig. 5, petrographic studies indicate that the aqueous alteration increases as $\text{CR2} < \text{CM2} < \text{Tagish Lake} < \text{CI1}$, but molecular structure evolution is interpreted as $\text{CR2} < \text{CI1} < \text{CM2} < \text{Tagish Lake}$ for the alteration extend. This likely reflects that some differences observed may be related to the organic matter accreted before parent body evolution. As shown by Raman spectrometry on low grade meteorites [91], organic macromolecules accreted on each class of parent body were broadly similar, but there is no common precursor to all the parent bodies. This is consistent with some isotopic observations described in section 4.2.

On the other hand, thermal metamorphism has more dramatic effect on the molecular structure of the IOM. As shown by Raman spectrometry, the structural order of the carbonaceous matter increases with temperature [92, 93]. There is a clear trend in losing the heteroelements, evidenced by a decrease

in H/C, N/C and O/C elemental ratios, and in increasing the size of aromatic units [77, 94]. Organic radicals seem to be more affected by thermal metamorphism than aqueous alteration. Indeed, in Kainsaz, a heated meteorite, the radical concentration is 2 orders of magnitude lower than in CI and CM, whereas organic radicals are abundant in Tagish Lake and Orgueil, which are often considered to be intensively altered [74, 75, 77].

3.4 Physical texture at the nanometer scale: HRTEM imaging

Carbonaceous matter in meteorites is heterogeneous and can occur as various textures: amorphous, graphitic and it also forms some unusual features like nanoglobules. This can be studied by High Resolution Transmission Electron Microscopy (HRTEM). Several textures of carbonaceous materials are shown in Fig. 6.

The texture of organic matter in meteorite is related to the petrographic grade of the meteorite, as indicated by Raman data [92]. Organics in low grade meteorites (hydrated objects, exposed to less than 100°C) show a disorganized structure. The size of the aromatic units is estimated at 6 cycles in diameter [79]; this is consistent with molecular data. The branching of the aliphatic linkages makes the interlayer spacing rather large. With heating, the heteroatomic groups, especially the O-containing groups, are lost, and the aliphatic linkages are progressively shorten and aromatized, leading to a decrease in the interlayer spacing and an increase of the size of the coherent domains (defined by the parts of the polyaromatic planes that are involved in the stacking of parallel planes) [77]. This aromatization process will ultimately end in the formation of graphite. Graphite is often encountered in meteorites [95] and is often associated with metal. This may be the result of catalytic effect of the metal on graphite formation, showing that temperature is not the only parameter that is required to form graphite. Moreover chondrites also contain presolar graphite [96], formed in the environment of stars or supernovae. Carbon can also occur as diamond, either presolar or solar. Nevertheless, it requires high pressure to be formed on a meteorite parent body and only shocked objects exhibit diamonds formed from organic matter that was initially accreted on the parent body (see the example of a shock chondrite in [97]). In primitive chondrites, presolar nanodiamonds, likely formed by CVD condensation, have been detected [96].

IOM is usually porous (see Fig. 6C), with voids like holes or tubes up to a few tens of nanometers. IOM studied by HRTEM is usually extracted by acid dissolution of silicates and these voids might be the result of the loss of the minerals. This would be consistent with the suggestion of organic coating around minerals.

IOM from low petrographic grade meteorites contains unusual features: nanoglobules (see Fig. 6E and F) [98]. They can occur as isolated grains, coalesced spheres or clusters [99]. Their sizes range from 20 up to 1700 nm, with a typical void in the centre not attributed to the chemical treatment used to isolate the IOM; the size of the internal void is variable, so is the wall thickness [98–100]. In some cases, there is no central cavity; the globules then appear as solid nanospheres [99, 100]. Though the wall is composed of several layers, the carbonaceous component is amorphous as revealed by Raman spectrometry [100]. Chemical composition, determined by EELS (Electron Energy-Loss Spectroscopy), shows minor variation among meteorites, but particle to particle differences are significant [98]. Some molecular features have been studied by FTIR, EELS and STXM (Scanned Transmission X-rays Microscopy) and indicate variations among particles [99–101]. Both aromatic and aliphatic components are detected; C=O and C—O features are also detected, indicating the occurrence of ether and ester functions. Despite the particle-to-particle heterogeneities, the overall chemical and molecular properties of nanoglobules are close to those of the IOM [99–101]. Nanoglobules often exhibit enrichments in D and/or ¹⁵N [101, 102], comparable to enrichments observed for the D and ¹⁵N rich hot spots found in IOM (see section 4.1), but some nanoglobules have isotopic composition similar to the bulk IOM. These enrichments have been interpreted as the influence of interstellar-like processes during the formation of the nanoglobules or the organic matter precursor [101, 102]. The exact process that leads to their

Figure 6. HRTEM images of various textures of carbonaceous material in chondrites. IOM usually shows a disorganized structure (A: Murchison, B: Kainsaz). Aromatic layers are curved and do not defined large coherent domains. With temperature increase, the organization improves slightly (compare A and B), with an increase in the size of aromatic layers, and a reducing of the interlayer spacing. In reduced conditions or/and under pressure, the organic matter will end to graphite (D, in Kansaz). In general, the structure exhibits important porosity (C: Kainsaz). In a lot of CM, CR and CI, nanoglobules have been observed (E in Tagish Lake and F in Mighei; from [98]).

formation is still a matter of debate, between a parent body origin during hydrothermal alteration and an interstellar origin [99–102].

4. STABLE ISOTOPES IN INSOLUBLE ORGANIC MATTER AND CHONDRITIC WATER

Isotopic compositions are often used to determine the history of the volatile components in meteorites. The following section describes the isotopic properties of the IOM and the water in chondrites, in relation with their origin.

Figure 7. Isotopic compositions vs the relevant elemental ratio in the IOM of chondrites of various classes, from [17, 93]. Correlations may be observed for some groups for H isotopes (b) (like for instance an increase in δD with a decrease in H/C in the case of ordinary chondrites), or C isotopes (c) (see the increase of $\delta^{13}C$ with decreasing H/C). For N isotopes (a), no clear trend is observed. O isotopes (d) do not show any pattern, and the values are in the range of solar system objects.

4.1 Isotopic compositions of chondritic IOM

As shown in Fig. 7, organic molecules in meteorites are systematically enriched in deuterium [103, 104] relative to molecular hydrogen in the ProtoSolar Nebula (referred to as PSN; $(D/H)_{PSN} = 25 \times 10^{-6}$ i.e. $\delta D = -840\text{‰}$ [105]). In chondritic IOMs, these enrichments range from -100‰ in enstatite chondrites up to 11000‰ in some ordinary chondrites [103]. Several groups can be distinguished based on the D/H

Figure 8. NanoSIMS image of the IOM of Orgueil. The image covers an area of $20 \times 20 \mu\text{m}^2$. At this scale, D appears heterogeneously distributed, with the occurrence of D-rich hot spots (black arrows) but also small areas depleted in D (white arrows). These hot spots cover ca 25% of the surface imaged.

and H/C ratios; H/C is usually a fingerprint of thermal or aqueous evolution of the organic matter [103]. CI and CM (except Bells CM chondrite) exhibit similar ratios, and they are the most aqueously altered carbonaceous chondrites. CR chondrites, believed to be the less modified carbonaceous chondrites have a D/H ratio twice as large. CO and oxidized CV, heated carbonaceous chondrites, have D/H ratio around the terrestrial ratio; they are depleted compare to CI, CM and CR (2 times less compared to CM and 4 times less than CR). In these groups, the D/H ratio does not correlate with an evolution in the H/C ratio. Ordinary chondrites exhibit a negative trend in the diagram, with the samples with the lowest H/C having the highest D-enrichment. The reduced CV also exhibit the same trend, though the range of D/H ratio is much smaller (a few hundred of permil compared to several thousands of permil in delta units). Enstatite chondrites have D/H ratio lower than all the other chondrites, and there is not correlation between H/C and D/H ratios. It must be noted that the lowest isotopic enrichment was measured in Abee enstatite chondrite ($\delta\text{D} = -480\text{‰}$; $\text{D}/\text{H} = 80 \times 10^{-6}$ [106]).

CR and Bells (CM) carbonaceous chondrites contain IOM enriched in ^{15}N compare to terrestrial organic matter (on Earth, $\delta^{15}\text{N} \approx 0\text{‰}$, in these meteorites is can go up to 400‰). It must be noted that the picture for ^{15}N is pretty different than the case of D (see Fig. 7), as only few IOMs show large fractionations, whereas the others are almost around the terrestrial value; moreover larger variations in N isotopic compositions are observed in presolar grains (several orders of magnitude for $^{14}\text{N}/^{15}\text{N}$ ratio), and are attributed to nucleosynthetic processes [1]. There is no large fractionation for C and O isotopes in contrast to what can be observed in presolar grains for instance [1]. O isotopes seem controlled by parent body alteration. C isotopes seem to correlate with the parent body temperature, pointing to a thermal control of the $^{13}\text{C}/^{12}\text{C}$ ratio: under thermal stress, a distillation process leads to enrichment in ^{13}C by preferential loss of the light isotope upon breaking C-C linkages.

The recent use of NanoSIMS ion probe provides new information on the distribution of the isotopic ratios in chondritic IOMs [102, 107, 108] with a spatial resolution of ca 100 nm. Images of the IOM of CI, CM and CR chondrites reveal the occurrence of micron size areas with large positive D- and ^{15}N -anomalies, which could go up to $\delta\text{D} = 8000\text{‰}$ ($\text{D}/\text{H} = 1402 \times 10^{-6}$ see Fig. 8). These hot spots are distributed all over the samples, without any specific pattern. No clear trend is observed between the D/H or the $^{15}\text{N}/^{14}\text{N}$ in these hot spots and the classical molecular parameters (for instance C/H or C/N), moreover no association with inorganic acid resistant minerals is observed. In contrast, no D or ^{15}N rich

Figure 9. D/H isotopic ratio versus C-H bond energy among different molecular components in Orgueil IOM. The observed trend can be interpreted as the result of an isotopic exchange reaction between D-poor organic solids and D-rich gaseous molecules (H_2D^+ , HD_2^+ ...), most likely taking place in the outer and relatively cold regions of the protoplanetary disk.

hot spots are observed in IOM of heated chondrites, i.e. CO, CV and ordinary chondrites [108, 109]. This should point out to the thermal sensitivity of these entities.

The distribution of the D has been studied at the molecular scale [68, 110, 111]. It has been shown in Orgueil IOM that three types of organic groups (Fig. 9) hold most of the H in IOM [111]. *Type 1* is benzylic H, i.e. H bound to the first C atom linked to an aromatic ring (C atom in α position). *Type 2* is non benzylic aliphatic H. *Type 3* is aromatic H. Although aromatic moieties in chondritic IOM are known to be easily released by pyrolysis [54, 110], the aliphatic linkages are recovered by ruthenium tetroxide oxidation [67, 68]. Compound specific D/H isotope measurements can be performed by GC-irMS (Gas Chromatography-isotope ratio Mass Spectrometry) and allow us to determine the isotopic ratios of each type of H [111]. The C-H bond dissociation energy differs for the three types: the higher this energy, the stronger the bond. Fig. 9 shows that any exchange between the hydrogen in these molecules and an external reservoir is affected by the binding energy. For Orgueil IOM, $\delta\text{D} = 1250\text{‰}$, 550‰ and 150‰ (i.e. $\text{D}/\text{H} = 350 \times 10^{-6}$, 240×10^{-6} , 180×10^{-6}) can be calculated for hydrogen of Type 1, 2 and 3 respectively, whereas for the bulk $\delta\text{D} = 980\text{‰}$ [103].

Pulsed Electron Paramagnetic Resonance has been used to determine the isotopic composition of radicals in IOM of Orgueil meteorite [112]. As shown in Fig 9, these radicals, which are heterogeneously distributed in the IOM, contain a very high deuterium concentration ($\text{D}/\text{H} = 15000 \pm 5000 \times 10^{-6}$; $\delta\text{D} = 95300\text{‰}$), much larger than the average bulk value $\text{D}/\text{H} = 350 \times 10^{-6}$ for this meteorite. This D-enrichment is comparable to the maximum enrichments observed in some organics in the ISM (45000 to 60000×10^{-6} [113]).

These isotopic signatures have been interpreted as fingerprints of synthetic environments of the IOM. The H isotopes are in this respect a matter of intense debate. Starting from the 80's, an interstellar origin was considered for IOM based on its systematic enrichment in deuterium [103, 104, 106]. Several processes believed to occur in cold dense clouds, like ion/molecule, gas grain or photodissociation

reactions, have been suggested to account for D enrichment [114]. However, the D/H ratio in IOM remains much lower than those measured in deuterated organic molecules commonly observed in the dense interstellar medium (ISM; $\delta D > 63000\text{‰}$; $D/H > 10000 \times 10^{-6}$) [115]. Several qualitative interpretations have been proposed to account for the isotopic difference between the chondritic IOM and the organic molecules in the ISM. The interstellar organic matter would have been diluted in solar components much less enriched in D, or would have exchanged with a solar reservoir either in the gas phase or the meteorite parent body [103, 106, 116]. The last possibility is that the IOM would have been formed at temperatures much higher (120 K) than canonical ISM temperatures (10–20 K) [115]. Indeed, at the first order (and as observed in Hot Cores [117, 118]) the enrichment in deuterium is expected to decrease with increasing formation temperature of IOM. Nevertheless, an interstellar origin implies that the D/H ratio of an interstellar precursor would have survived and escaped isotopic exchange during its travel in the ISM before and during the very early stages of the formation of the solar system. From laboratory experiments on organic matter of IDPs (that could be considered not so different than the chondritic IOM of CR, CI and CM), it has been shown that irradiations that would occur in the ISM would likely erase a D rich signature and lower to D/H ratio due to exchange with the molecular H_2 gas (with a D/H ratio close to 16×10^{-6}) [119]. Then, reactions during the formation of the solar system have to be considered to explain the D enrichment of the organics in meteorites. In irradiated and cold areas of proto planetary disks, ion/molecule reactions inducing the formation of H_2D^+ or CH_2D^+ may lead to the isotopic enrichment of organic molecules [120, 121]. In that case, the trend observed in Fig. 9 would indicate that the strength of the C-H bond influences the isotopic exchange between the organics and the D rich ionised gas [111]. Moreover, it would indicate that radicals are very efficient to grab the D from the gas [108].

Two different hypotheses have been proposed to account for the D-rich hot spots: (1) these hot spots are remnants grains of interstellar D-rich organic material [102, 107] or (2) they are related to organic radicals occurring in IOM [108, 112], as radicals are known to be highly enriched in D and are heterogeneously distributed in the IOM. By combining data from NanoSIMS and pulsed EPR, it is possible to show that all the D-excess is borne by organic radicals: as these radicals are concentrated in small areas, they define small regions in the IOM which could constitute D-rich hot spots [108].

^{15}N enrichments are usually attributed to cold chemistry in interstellar clouds similar to that of the D enrichments, even though much less modelling has been done for this isotopic ratio. Aléon suggested that for most of the chondritic IOMs, D and ^{15}N -enrichments are correlated due to ion/molecule reactions. For some anomalous organic moieties, which exhibits the highest ^{15}N -enrichments, there is an additional self shielding of N_2 that induces the production of ^{15}N -rich material that would be mixed with the previously mentioned organic matter [122]. This would happen during an evolved stage of the protoplanetary disk. Aléon also suggested that ordinary chondrites may contain up to 1% of interstellar organic matter, being highly enriched in D and depleted in ^{15}N [122].

4.2 Isotopic compositions and parent body evolution

As shown in Fig. 7, parent body processes are suspected to have different effects on the isotopic compositions, if a common precursor is assumed. For carbonaceous chondrites, heating induces a decrease in δD and $\delta^{15}N$, as shown by the evolution from CR to CO and CV. This is consistent with laboratory experiments showing that heating over 270°C decreases of the D content of Murchison IOM [94]. The same process also destroys the D-rich hot spots in Murchison IOM [108]. For ordinary chondrites, δD increases with heating; the interpretation of this different behaviour is unclear. It might be due to different redox conditions on parent bodies [103] or different organic precursors accreted on the parent bodies of carbonaceous and ordinary chondrites. The effect of thermal metamorphism on carbon isotopes is less enigmatic. It is well known that during heating processes, distillation of C will lead to an increase of the $\delta^{13}C$.

The effects of aqueous alteration on the isotopic ratios are a matter of great debates. It has been suggested that during alteration, D-depleted water would exchange with organic matter, leading to a

Figure 10. NanoSIMS ratio images of the matrix of Orgueil meteorite (A) reveals the location of C rich particles, from the C/Si image. The corresponding D/H image shows a D-rich hot spot, inside which we can make profiles (B) along the blue bar. H/Si and C/Si profiles indicate that C and H are intimately associated, consistent with organic matter constituting this particle. C/H and D/H profiles show that there is no diffusion of D from the D-enriched organic matter to the surrounding phyllosilicates, as the D/H curve matches pretty well with the C/H one. Isotopic exchange would have resulted in broadening of the D/H curve.

decrease in the δD with the alteration increasing [103]. This would be consistent with the higher δD in CR than in CI and CM (Fig. 7, the CR being less altered than CM and CI). Nevertheless, in situ nanoSIMS imaging (Fig. 10) of organic particles in the matrices of CR, CI and CM indicates that no isotopic exchange occurred between the most D-enriched organic particles and the surrounding phyllosilicates depleted in D relative to the organic matter [86]. This seems to indicate that organic matter constituting the D-rich “hot spots” does not exchange with water or phyllosilicates during the hydrothermal event on the parent body. This is in contrast to what is observed for terrestrial organic matter in sedimentary basins where aqueous alteration induces an evolution in the isotopic ratio of both the kerogen and the water [123]. In such environments, minerals may have catalytic effects [124–126], leading to significant D-exchange at the timescale of 50,000 to 100,000 years. Another explanation is that the time window for an efficient exchange is too short. Indeed, it has been suggested that aqueous alteration may have happened by pulses [86, 127] and then, the total time of actual water circulation on the parent body may have been much shorter than the 5–10 millions years usually assumed for the duration of this event [128]. Then the D-exchange water/organic matter could be too slow to be efficient at the conditions of the parent body hydrothermalism. The question remains opened and ongoing laboratory experiments are under progress to assess to which extends the hydrothermal alteration influences the D-enrichment on the organic matter in carbonaceous chondrites. It must be noted that in all the hydrated chondrites, water is always depleted in D compared to organic matter, whereas the equilibrium requires the opposite, whatever the location of the H in the molecule [86, 126]. This indicates that isotopic disequilibrium has been preserved during 4.5 billion years on the parent

body of these carbonaceous chondrites and that organic matter did not acquire its high D-enrichment on the parent body.

The effect of chemical reactions has to be considered in the interpretation of the D/H ratio of IOMs. D/H isotopic composition of an organic sample may vary by several processes, and one has to distinguish between pure isotopic exchange and chemical reactions or molecular rearrangements [126]. It has been shown that the molecular structure of the IOM evolves with the alteration/metamorphism on the parent body (see section 3.3). To this respect, thermal metamorphism seems to have a larger effect on the molecular structure of the IOM. So, even if pure isotopic exchange between organic matter and water is limited in the condition of the chondritic parent bodies, chemical reaction may lead to the evolution of the D/H ratio by addition or depletion of H (and D). Then, chemical processes, rather than isotopic exchange, may explain the variations between the different classes of chondrites. The example of CV chondrite may be consistent with this hypothesis. IOM in oxidized CV exhibits a lower D/H than reduced CV. They differ by the traces of water for CV_{ox}, while the CV_{red} are believed to have been water free during all their evolution. So, one possible explanation is that IOM in CV_{ox} exchanged its D with water while not in CV_{red}. But the H/C of the IOM is also different between CV_{ox} and red; the oxidized CV have a higher H/C. It clearly shows that the chemical reactions occurring on CV_{ox} and CV_{red} parent bodies had different effects on their IOM. We can then assume that the difference in their D content is due to chemical reactions rather than pure exchange.

4.3 D/H in water

Isotopic composition is a powerful tool to determine the origin of water in meteorites. The oxygen isotopic composition of the water that circulated on the meteorite parent body is impossible to determine as it has reacted with the minerals, the other large O-reservoir (and whose initial isotopic composition is a matter of debate). On the other hand, H isotopes of water can be determined by measuring them in the phyllosilicates. Moreover H in phyllosilicates can be distinguished easily from organic matter, the other large H-reservoir in chondrites. D/H isotopic ratio of the phyllosilicates can be estimated by mass balance considering the organic matter, as it has been done for carbonaceous chondrites [19, 104], and by in situ measurements using an ion probe [18, 129]. The variations of H isotopes in phyllosilicates in chondrites are reported in Fig. 11. One of the main difficulties comes from the contamination by terrestrial water (from the atmosphere). Nevertheless, it appears that meteoritic water has an average value around the terrestrial ratio, but with some high enrichment in some cases. It must be noted that D-isotopic fractionation (i.e. the difference between the isotopic composition of the two phases that exchange their D) at equilibrium between water and phyllosilicates is predicted to be lower than 100‰ [130].

Water in CI and CM is depleted in D compared to organics (see 4.1), with $-180‰ < \delta D < +30‰$ (i.e. $128 \times 10^{-6} < D/H < 160 \times 10^{-6}$ [17, 94]). This clearly indicates that organics and water are far from isotopic equilibrium. Indeed, at equilibrium between water and organic matter, organic matter is supposed to be depleted in D compared to water [86]. Nevertheless, it must be noted that the water is heavier in CR chondrites, which also have heavier organic matter ($\delta D = 680‰$; $D/H = 262 \times 10^{-6}$ in Renazzo phyllosilicates). As isotopic exchange between organic matter and water is limited on CR parent body (see section 4.2), enrichment of the water on the parent body by exchange with the D-rich organic matter seems unlikely. It may rather indicate that water and organic matter in CR were synthesized or exposed to different environments than CI and CM ones prior to accretion.

The CM class constitutes an interesting case of study because it contains meteorites that have undergone different levels of aqueous alteration. Eiler and Kitchen [132] have measured the D/H isotopic ratio of fragments of several CM, and have determined that the D/H ratio decreases with increasing extent of aqueous alteration. They have been able to build a model for the chemical and isotopic evolution on CM parent body during aqueous alteration, and could determine that the water that circulated on this parent body has a $\delta D = -158‰$ ($D/H = 131 \times 10^{-6}$). Moreover, CI chondrites, although being more aqueously altered than CM, have D/H and volatile elements abundance that make

Figure 11. Distribution of D/H ratio in carbonaceous chondrites (whole rock), LL3 ordinary chondrites, IDPs and water in hot cores, from [131]. f is used to normalize the ratios to a reference, which is $D/H = 25 \times 10^{-6}$ for meteorites and IDPs (solar nebula) and 16×10^{-6} for hot cores (interstellar). Vertical lines indicate the values for terrestrial and cometary water. Note the large heterogeneity in the distribution of D/H ratios, reflecting complex processes prior accretion of the parent bodies.

them similar to the least altered CM. Then it leads to the conclusion that CI chondrites are not more altered products of the same process that produced CM. It clearly indicates that CM and CI accreted material with different isotopic properties. Furthermore, the water that circulated on CM parent body had different isotopic composition than on other parent bodies.

The case of LL3 is even more surprising. Ion probe measurements point to isotopically heterogeneous phyllosilicates in the matrix. Indeed, $-230\text{‰} < \delta D < +3600\text{‰}$ ($120 \times 10^{-6} < D/H < 716 \times 10^{-6}$) in Semarkona, with variations observed within a few 100^{th} of microns [129]. Moreover, a systematic study of the isotopic composition of $-\text{OH}$ (i.e. diffused water) in chondrules of LL3 chondrites Semarkona and Bishunpur revealed a wide heterogeneity in those objects that are hundreds of microns large [18]; $-520\text{‰} < \delta D < +2000\text{‰}$ ($75 \times 10^{-6} < D/H < 467 \times 10^{-6}$). These data were interpreted as the alteration of chondrules and matrix minerals precursors by at least two different reservoirs of water, one being depleted in D ($D/H \approx 100 \times 10^{-6}$; $\delta D \approx -360\text{‰}$) and the other one being enriched ($D/H \approx 700 \times 10^{-6}$; $\delta D \approx 3500\text{‰}$), showing that isotopic composition of water was heterogeneous in the early solar nebula. This might be related to the temperature gradient in the protosolar nebula, likely inducing a gradient in the isotopic composition of water [115].

5. IDPS, MICROMETEORITES, STARDUST: WHAT DO WE LEARN ON COMETS?

Meteorites are not the only samples available for study in laboratory. Interplanetary dust particles (IDPs) are small particles collected in the upper atmosphere and are often considered as cometary particles [133]. Some micrometeorites are also likely cometary grains that are collected in the ice from Antarctica [134]. Moreover, the STARDUST mission brought indigenous cometary grains to laboratory.

Due to the small size of these particles (from 1 to a few hundreds of microns), only a limited set of techniques can be used to study the organics in these objects. Ion probes are massively used to determine isotopic composition, while molecular structure is studied by STXM or EELS. Noble gases were tentatively studied in IDPs and micrometeorites [135–137]. Most of the noble gases were found to be solar (solar wind implantation) although Osawa et al. claimed that Xe and Kr in micrometeorites are dominated by a primordial component [137]. Only He was studied in IDPs [135, 136].

IDPs are micron size grains (from 1 to 50 microns) that are often considered very pristine because they contain numerous isotopic anomalies. Their bulk elemental composition is close to the CI and CM carbonaceous chondrites. Their typical mineralogy is olivine, pyroxene, and in some cases phyllosilicates [138]. Large enrichments in D and ^{15}N can be found in organics in IDPs [139–141] leading to the conclusion that organics are dominated by cold environments chemistry (ISM or outer regions of the protosolar nebula). These enrichments are in the same range as the hot spots found in chondritic IOM (with a maximum at $\text{D}/\text{H} = 4020 \times 10^{-6}$; $\delta\text{D} = 24800\text{‰}$) [139, 141]. The molecular structure of organics in IDPs is broadly similar to the IOM in CI and CM, even if it seems that there are more aliphatic moieties in IDPs and aliphatic chains exhibit a larger branching level [119, 142, 143]; nevertheless, there is a large variability and in some IDPs the carbonaceous fraction appears as graphitic carbon [144]. It must be noted that the D-rich component is likely aliphatic, like in Orgueil [142]. Irradiation experiments and comparison with laboratory produced materials indicate that this organic material has been heated (by coming closer to the Sun or during atmospheric entry) [119]. It is often concluded organic matter in IDPs may represent the precursor of the organic matter found in carbonaceous chondrites.

The study of the organic matter in comets at the laboratory was one goal of the STARDUST mission, which sampled grains of the coma of the meteorite 81P/Wild 2 [11]. Organics in STARDUST grains were found to be in part similar to those found in carbonaceous chondrites [145], with PAHs and also some aliphatic compounds. Nevertheless, there are more O and N containing compounds than in meteorites. D and ^{15}N enrichments were observed [145], along with nanoglobules [101], and are all similar to what is found in carbonaceous chondrites or IDPs. Nevertheless, the organic content in STARDUST grains is doubtful, due to the occurrence of C in the aerogel (material used to collect the grains) and heating induced by impact in this aerogel [146, 147]. Muñoz Caro et al. have moreover shown that the material measured in the aerogel can not be produced by ice photoprocessing but that the difference may arise from the effect of the aerogel [147]. Then, so far, it is hard to conclude anything about the organic matter without assessing contamination levels and the effect of entry in the aerogel. It must be noted that Elsila et al. [148] have detected Glycine in foils returned by the STARDUST mission (not subjected to contamination by the aerogel), confirming the previous remote sensing detection of glycine in comets [149].

Micrometeorites can contain a large amount of organic matter. A class of micrometeorites, the UCAMMs (UltraCarbonaceous Antarctic MicroMeteorites) contain between 50 and 85 vol% of organic matter [134]. Moreover, this organic matter appears to be extremely enriched in D, with D/H isotopic ratios in the highest range of isotopic compositions for IDPs or hot spots in IOM (up to $\text{D}/\text{H} = 4600 \times 10^{-6}$; $\delta\text{D} = 29000\text{‰}$ [150]). Surprisingly, these high enrichments, likely related to cold environments chemistry, are found in the vicinity of high temperature minerals, consistent with important radial mixing in the early solar system.

It then appears that cometary grains have common properties with carbonaceous chondrites. Although they appear to be richer in material with isotopic anomalies, they exhibit the same mixing of high and low temperature components. This shows that radial mixing has to be considered as a common process in the early solar system [151].

6. CONCLUSION

We have presented an overview of the volatile content of extraterrestrial objects available for study in laboratory. Chondrites are the more abundant material and then, the best known. Several hypotheses

have been suggested to explain their formation and to explain the initial components available at the origin of our solar system. Some presolar components have been accreted and preserved in meteorites and comets, like for instance presolar diamonds and SiC. Those grains have trapped isotopic anomalies that allow us to determine their origin. They also have trapped noble gases from various sources (solar and interstellar).

Organic matter is a complex component with a heterogeneous isotopic composition. This heterogeneity can not be fully explained by parent body effects. Organics seem to be a mixing of components with several origins. Water also seems to have a heterogeneous isotopic composition. Organic particles and water have likely been exposed to various environments in the protosolar nebula (or the molecular cloud that gave birth to the solar system) and have acquired fingerprints in their molecular and isotopic properties.

The discovery of high temperature condensates in comets has proven that grains migrated over long distance in the protosolar nebula before they accreted to form the parent bodies. This resulted, at the radial distance of carbonaceous chondrites accretion, in an association of primitive high temperature grains (CAIs) with ice and organic particles. Secondary processes on parent bodies may have induced modifications on the different components, making the picture more complicated. Hence, the volatile components we recover are likely the result of processes occurring in molecular clouds, protosolar nebula and parent bodies.

B. Zanda, M. Gounelle and F. Robert are thanked for helpful discussion in the preparation of this manuscript. I am grateful to E. Dartois and E. Quirico for their useful reviews.

References

- [1] Zinner, E., D.H. Heinrich, and K.T. Karl, in *Treatise on Geochemistry* (Pergamon Oxford, 2007), 17–33
- [2] Scott, E.R.D., A.N. Krot, D.H. Heinrich, and K.T. Karl, in *Treatise on Geochemistry* (Pergamon Oxford, 2007), 143–190
- [3] Brearley, A.J., D.H. Heinrich, and K.T. Karl, in *Treatise on Geochemistry* (Pergamon Oxford, 2007), 247–268
- [4] Bunch, T.E. and S. Chang, *Geochim. Cosmochim. Acta*, **44**, 1543–1577 (1980)
- [5] Weisberg, M.K., T.J. McCoy, and A.N. Krot, in *Meteorites and the Early Solar System II*, 2006), 19–52
- [6] Truran Jr, J.W., A. Heger, D.H. Heinrich, and K.T. Karl, in *Treatise on Geochemistry* (Pergamon Oxford, 2003), 1–15
- [7] Amelin, Y., A.N. Krot, I.D. Hutcheon, and A.A. Ulyanov, *Science*, **297**, 1678–1683 (2002)
- [8] Anders, E. and N. Grevesse, *Geochim. Cosmochim. Acta*, **53**, 197–214 (1989)
- [9] Lodders, K., *Astrophys. J.*, **591**, 1220–1247 (2003)
- [10] Kallemeyn, G.W. and J.T. Wasson, *Geochim. Cosmochim. Acta*, **45**, 1217–1230 (1981)
- [11] Brownlee, D., et al., *Science*, **314**, 1711–1716 (2006)
- [12] Brearley, A.J., in *Meteorites and the Early Solar System II*, 2006), 584–624
- [13] DuFresne, E.R. and E. Anders, *Geochim. Cosmochim. Acta*, **26**, 1085–1114 (1962)
- [14] Bischoff, A., *Meteorit. Planet. Sci.*, **33**, 1113–1122 (1998)
- [15] Kerridge, J.F., *Earth Planet. Sci. Lett.*, **29**, 194–200 (1976)
- [16] Hutchison, R., C.M.O. Alexander, and D.J. Barber, *Geochim. Cosmochim. Acta*, **51**, 1875–1882 (1987)
- [17] Alexander, C.M.O.D., D.J. Barber, and R. Hutchison, *Geochim. Cosmochim. Acta*, **53**, 3045–3057 (1989)

- [18] Deloule, E., F. Robert, and J.C. Doukhan, *Geochim. Cosmochim. Acta*, **62**, 3367–3378 (1998)
- [19] Alexander, C.M.O.D., S.D. Newsome, M.L. Fogel, L.R. Nittler, H. Busemann, and G.D. Cody, *Geochim. Cosmochim. Acta*, **74**, 4417–4437 (2010)
- [20] Pizzarello, S., G.W. Cooper, and G.J. Flynn, in *Meteorites and the Early Solar System II* (University of Arizona Press Tucson, USA, 2006), 625–651
- [21] Yuen, G.U. and K.A. Kvenvolden, *Nature*, **246**, 301–303 (1973)
- [22] Yuen, G.U., N. Blair, D.J. Des Marais, and S. Chang, *Nature*, **307**, 252–254 (1984)
- [23] Krishnamurthy, R.V., S. Epstein, J.R. Cronin, S. Pizzarello, and G.U. Yuen, *Geochim. Cosmochim. Acta*, **56**, 4045–4058 (1992)
- [24] Sephton, M.A., C.T. Pillinger, and I. Gilmour, *Precambrian Res.*, **106**, 47–58 (2001)
- [25] Cooper, G., N. Kimmich, W. Belisle, J. Sarinana, K. Brabham, and L. Garrel, *Nature*, **414**, 879–883 (2001)
- [26] Cooper, G.W. and J.R. Cronin, *Geochim. Cosmochim. Acta*, **59**, 1003–1015 (1995)
- [27] Hayatsu, R., M.H. Studier, L.P. Moore, and E. Anders, *Geochim. Cosmochim. Acta*, **39**, 471–488 (1975)
- [28] Sephton, M.A., C.T. Pillinger, and I. Gilmour, *Geochim. Cosmochim. Acta*, **62**, 1821–1828 (1998)
- [29] Gilmour, I., D.H. Heinrich, and K.T. Karl, in *Treatise on Geochemistry* (Pergamon Oxford, 2003), 269–290
- [30] Kvenvolden, K.A., J. Lawless, K. Pering, E. Peterson, J. Flores, C. Ponnampuruma, I.R. Kaplan, and C. Moore, *Nature*, **228**, 923–926 (1970)
- [31] Lawless, J., K.A. Kvenvolden, E. Peterson, C. Ponnampuruma, and E. Jarosewich, *Nature*, **236**, 66–67 (1972)
- [32] Martins, Z. and M. Sephton, in *Amino Acids, Peptides and Proteins in Organic Chemistry. Vol. I – Origins and Synthesis of Amino Acids* (Wiley VCH Weinheim, 2009), 3–42
- [33] Engel, M.H. and B. Nagy, *Nature*, **296**, 837–840 (1982)
- [34] Bada, J.L., J.R. Cronin, M.-S. Ho, K.A. Kvenvolden, J.G. Lawless, S.L. Miller, J. Orò, and S. Steinberg, *Nature*, **310**, 494–497 (1983)
- [35] Engel, M.H. and S.A. Macko, *Nature*, **389**, 265–267 (1997)
- [36] Engel, M.H., S.A. Macko, and J.A. Silfer, *Nature*, **348**, 47–49 (1990)
- [37] Pizzarello, S. and J.R. Cronin, *Geochim. Cosmochim. Acta*, **64**, 329–338 (2000)
- [38] Cronin, J.R. and S. Pizzarello, *Science*, **275**, 951–954 (1997)
- [39] Glavin, D.P. and J.P. Dworkin, *Proc. Natl. Acad. Sci. U. S. A.*, **106**, 5487–5492 (2009)
- [40] Pizzarello, S., M. Zolensky, and K.A. Turk, *Geochim. Cosmochim. Acta*, **67**, 1589–1595 (2003)
- [41] Rubenstein, E., W.A. Bonner, H.P. Noyes, and G.S. Brown, *Nature*, **306**, 118 (1983)
- [42] Takahashi, J., et al., *Int. J. Mol. Sci.*, **10**, 3044–3064 (2009)
- [43] Meierhenrich, U.J., J.J. Filippi, C. Meinert, S.V. Hoffmann, J.H. Bredehoft, and L. Nahon, *Chem. Biodivers.*, **7**, 1651–1659 (2010)
- [44] Takano, Y., J. Takahashi, T. Kaneko, K. Marumo, and K. Kobayashi, *Earth Planet. Sci. Lett.*, **254**, 106–114 (2007)
- [45] Noorduyn, W.L., et al., *Nat. Chem.*, **1**, 729–732 (2009)
- [46] Meierhenrich, U.J., L. Nahon, C. Alcaraz, J.H. Bredehoft, S.V. Hoffmann, B. Barbier, and A. Brack, *Angew. Chem.-Int. Edit.*, **44**, 5630–5634 (2005)
- [47] Nuevo, M., et al., *Astronomy & Astrophysics*, **457**, 741–751 (2006)
- [48] Pizzarello, S., X. Feng, S. Epstein, and J.R. Cronin, *Geochim. Cosmochim. Acta*, **58**, 5579–5587 (1994)
- [49] Pizzarello, S. and W. Holmes, *Geochim. Cosmochim. Acta*, **73**, 2150–2162 (2009)
- [50] Pizzarello, S., Y. Huang, and M. Fuller, *Geochim. Cosmochim. Acta*, **68**, 4963–4969 (2004)
- [51] Pizzarello, S. and Y. Huang, *Geochim. Cosmochim. Acta*, **69**, 599–605 (2005)
- [52] Cronin, J.R., G.W. Cooper, and S. Pizzarello, *Adv. Space Res.*, **15**, 91–97 (1995)

- [53] Cronin, J.R. and S. Chang, in *The chemistry of life's origins* (Kluwer Academic Publishers Dordrecht, 1993), 209–258
- [54] Remusat, L., S. Derenne, F. Robert, and H. Knicker, *Geochim. Cosmochim. Acta*, **69**, 3919–3932 (2005)
- [55] Wieler, R., H. Busemann, and I.A. Franchi, in *Meteorites and the Early Solar System II*, (2006), 499–521
- [56] Podosek, F.A., D.H. Heinrich, and K.T. Karl, in *Treatise on Geochemistry* (Pergamon Oxford, 2003), 381–405
- [57] Lewis, R.S., B. Srinivasan, and E. Anders, *Science*, **190**, 1251–1262 (1975)
- [58] Busemann, H., H. Baur, and R. Wieler, *Meteorit. Planet. Sci.*, **35**, 949–973 (2000)
- [59] Huss, G.R., R.S. Lewis, and S. Hemkin, *Geochim. Cosmochim. Acta*, **60**, 3311–3340 (1996)
- [60] Marrocchi, Y., S. Derenne, B. Marty, and F. Robert, *Earth Planet. Sci. Lett.*, **236**, 569–578 (2005)
- [61] Cody, G.D. and C.M.O.D. Alexander, *Geochim. Cosmochim. Acta*, **69**, 1085–1097 (2005)
- [62] Cody, G.D. C.M.O.D. Alexander, and F. Tera, *Geochim. Cosmochim. Acta*, **66**, 1851–1865 (2002)
- [63] Gardinier, A., S. Derenne, F. Robert, F. Behar, C. Largeau, and J. Maquet, *Earth Planet. Sci. Lett.*, **184**, 9–21 (2000)
- [64] Cronin, J.R., S. Pizzarello, and J.S. Fries, *Geochim. Cosmochim. Acta*, **51**, 299–303 (1987)
- [65] Sephton, M.A., G.D. Love, J.S. Watson, A.B. Verchovsky, I.P. Wright, C.E. Snape, and I. Gilmour, *Geochim. Cosmochim. Acta*, **68**, 1385–1393 (2004)
- [66] Sephton, M.A., C.T. Pillinger, and I. Gilmour, *Planet. Sp. Sc.*, **47**, 181–187 (1999)
- [67] Remusat, L., S. Derenne, and F. Robert, *Geochim. Cosmochim. Acta*, **69**, 4377–4386 (2005)
- [68] Huang, Y., M.R. Alexandre, and Y. Wang, *Earth Planet. Sci. Lett.*, **259**, 517–525 (2007)
- [69] Orthous-Daunay, F.-R., E. Quirico, P. Beck, O. Brissaud, and B. Schmitt, in *Lunar and Planetary Science Conference*, abstract #1803 (2010)
- [70] Hayatsu, R., R.E. Winans, R.G. Scott, R.L. McBeth, L.P. Moore, and M.H. Studier, *Science*, **207**, 1202–1204 (1980)
- [71] Shimoyama, A. and H. Katsumata, *Chemistry Letters*, **3**, 202–203 (2001)
- [72] Komiya, M. and A. Shimoyama, *Bull. Chem. Soc. Jpn.*, **69**, 53–58 (1996)
- [73] Orthous-Daunay, F.R., E. Quirico, L. Lemelle, P. Beck, V. de Andrade, A. Simionovici, and S. Derenne, in *Lunar and Planetary Science Conference*, abstract #1777 (2009)
- [74] Binet, L., D. Gourier, S. Derenne, and F. Robert, *Geochim. Cosmochim. Acta*, **66**, 4177–4186 (2002)
- [75] Binet, L., D. Gourier, S. Derenne, S. Pizzarello, and L. Becker, *Meteorit. Planet. Sci.*, **39**, 1649–1654 (2004)
- [76] Binet, L., D. Gourier, S. Derenne, F. Robert, and I. Ciofini, *Geochim. Cosmochim. Acta*, **68**, 881–891 (2004)
- [77] Remusat, L., C. Le Guillou, J.-N. Rouzaud, L. Binet, F. Robert, and S. Derenne, *Meteorit. Planet. Sci.*, **43**, 1099–1111 (2008)
- [78] Derenne, S., F. Robert, L. Binet, D. Gourier, J.-N. Rouzaud, and C. Largeau, in *33rd Lunar and planetary science conference*, abstract #1182. pdf (2002)
- [79] Derenne, S., J.-N. Rouzaud, C. Clinard, and F. Robert, *Geochim. Cosmochim. Acta*, **69**, 3911–3917 (2005)
- [80] Shimoyama, A., *Adv. Space Res.*, **19**, 1045–1052 (1997)
- [81] Pearson, V.K., M.A. Sephton, A.T. Kearsley, P.A. Bland, I.A. Franchi, and I. Gilmour, *Meteorit. Planet. Sci.*, **37**, 1829–1833 (2002)
- [82] Alpern, B. and Y. Benkheiri, *Earth Planet. Sci. Lett.*, **19**, 422–428 (1973)
- [83] Brearley, A.J., *Science*, **285**, 1380–1382 (1999)
- [84] Pearson, V.K., A.T. Kearsley, M.A. Sephton, and I. Gilmour, *Planet. Sp. Sc.*, **55**, 1310–1318 (2007)

- [85] Murae, T., *Adv. Space Res.*, **24**, 469–476 (1999)
- [86] Remusat, L., Y. Guan, Y. Wang, and J.M. Eiler, *Astrophys. J.*, **713**, 1048–1058 (2010)
- [87] Orthous-Daunay, F.R., E. Quirico, L. Lemelle, P. Beck, V. de Andrade, A. Simionovici, and S. Derenne, Speciation of sulfur in the insoluble organic matter from carbonaceous chondrites by XANES spectroscopy. *Earth Planet. Sci. Lett.*, **300**, 321–328 (2010)
- [88] Yabuta, H., H. Naraoka, K. Sakanishi, and H. Kawashima, *Meteorit. Planet. Sci.*, **40**, 779–787 (2005)
- [89] Sephton, M.A., C.T. Pillinger, and I. Gilmour, *Geochim. Cosmochim. Acta*, **64**, 321–328 (2000)
- [90] Yabuta, H., L.B. Williams, G.D. Cody, C.M.O.D. Alexander, and S. Pizzarello, *Meteorit. Planet. Sci.*, **42**, 37–48 (2007)
- [91] Quirico, E., G. Montagnac, J.N. Rouzaud, L. Bonal, M. Bourot-Denise, S. Duber, and B. Reynard, *Earth Planet. Sci. Lett.*, **287**, 185–193 (2009)
- [92] Bonal, L., E. Quirico, M. Bourot-Denise, and G. Montagnac, *Geochim. Cosmochim. Acta*, **70**, 1849–1863 (2006)
- [93] Bonal, L., M. Bourot-Denise, E. Quirico, G. Montagnac, and E. Lewin, *Geochim. Cosmochim. Acta*, **71**, 1605–1623 (2007)
- [94] Oba, Y. and H. Naraoka, *Meteorit. Planet. Sci.*, **44**, 943–953 (2009)
- [95] Mostefaoui, S., E. Zinner, P. Hoppe, F.J. Stadermann, and A. El Goresy, *Meteorit. Planet. Sci.*, **40**, 721–743 (2005)
- [96] Amari, S., R.S. Lewis, and E. Anders, *Geochim. Cosmochim. Acta*, **58**, 459–470 (1994)
- [97] Le Guillou, C., J.N. Rouzaud, L. Remusat, A. Jambon, and M. Bourot-Denise, *Geochim. Cosmochim. Acta*, **74**, 4167–4185 (2010)
- [98] Garvie, L.A.J. and P.R. Buseck, *Earth Planet. Sci. Lett.*, **224**, 431–439 (2004)
- [99] Garvie, L.A.J., G. Baumgardner, and P.R. Buseck, *Meteorit. Planet. Sci.*, **43**, 899–903 (2008)
- [100] Nakamura, K., M.E. Zolensky, S. Tomita, S. Nakashima, and K. Tomeoka, *Int. J. Astrobio.*, **1**, 179–189 (2002)
- [101] De Gregorio, B.T., R.M. Stroud, L.R. Nittler, C.M.O.D. Alexander, A.L.D. Kilcoyne, and T.J. Zega, *Geochim. Cosmochim. Acta*, **74**, 4454–4470 (2010)
- [102] Nakamura-Messenger, K., S. Messenger, L.P. Keller, S.J. Clemett, and M.E. Zolensky, *Science*, **314**, 1439–1442 (2006)
- [103] Alexander, C.M.O.D., M. Fogel, H. Yabuta, and G.D. Cody, *Geochim. Cosmochim. Acta*, **71**, 4380–4403 (2007)
- [104] Robert, F. and S. Epstein, *Geochim. Cosmochim. Acta*, **46**, 81–95 (1982)
- [105] Geiss, J. and G. Gloecker, *Sp. Sc. Rev.*, **84**, 239–250 (1998)
- [106] Yang, J. and S. Epstein, *Geochim. Cosmochim. Acta*, **47**, 2199–2216 (1983)
- [107] Busemann, H., A.F. Young, C.M.O.D. Alexander, P. Hoppe, S. Mukhopadhyay, and L.R. Nittler, *Science*, **312**, 727–730 (2006)
- [108] Remusat, L., F. Robert, A. Meibom, S. Mostefaoui, O. Delpoux, L. Binet, D. Gourier, and S. Derenne, *Astrophys. J.*, **698**, 2087–2092 (2009)
- [109] Remusat, L., Y. Guan, and J.M. Eiler, in *Goldschmidt Conference*, abstract #A1089-A1089 (2009)
- [110] Wang, Y., Y. Huang, C.M.O.D. Alexander, M. Fogel, and G. Cody, *Geochim. Cosmochim. Acta*, **69**, 3711–3721 (2005)
- [111] Remusat, L., F. Palhol, F. Robert, S. Derenne, and C. France-Lanord, *Earth Planet. Sci. Lett.*, **243**, 15–25 (2006)
- [112] Gourier, D., F. Robert, O. Delpoux, L. Binet, H. Vezin, A. Moissette, and S. Derenne, *Geochim. Cosmochim. Acta*, **72**, 1914–1923 (2008)
- [113] Millar, T.J., in *Solar system history from isotopic signatures of volatile elements*. (ISSI, 2003), 73–86
- [114] Sandford, S., M.P. Bernstein, and J.P. Dworkin, *Meteorit. Planet. Sci.*, **36**, 1117–1133 (2001)

- [115] Robert, F., Planet. Sp. Sc., **50**, 1227–1234 (2002)
- [116] Kerridge, J.F., S. Chang, and R. Shipp, Geochim. Cosmochim. Acta, **51**, 2527–2540 (1987)
- [117] Gensheimer, P.D., R. Mauersberger, and T.L. Wilson, Astron. Astrophys., **314**, 281–294 (1996)
- [118] Schilke, P., C.M. Walmsley, G. Pineau des Forêts, E. Roueff, D.R. Flower, and S. Guilloteau, Astron. Astrophys., **256**, 595–612 (1992)
- [119] Muñoz Caro, G.M., et al., Astron. Astrophys., **459**, 147–159 (2006)
- [120] Ceccarelli, C. and C. Dominik, Astron. Astrophys., **440**, 583–593 (2005)
- [121] Parise, B., S. Leurini, P. Schilke, E. Roueff, S. Thorwirth, and D.C. Lis, Astronomy & Astrophysics, **508**, 737–749 (2009)
- [122] Aleon, J., The astrophysical journal, **722**, 1342 (2010)
- [123] Schimmelmann, A., A.L. Sessions, and M. Mastalerz, Annu. Rev. Earth Planet. Sci., **34**, 501–533 (2006)
- [124] Alexander, R., R.I. Kagi, and A.V. Larcher, Geochim. Cosmochim. Acta, **46**, 219–222 (1982)
- [125] Alexander, R., R.I. Kagi, and A.V. Larcher, Org. Geochem., **6**, 755–760 (1984)
- [126] Sessions, A.L., S.P. Sylva, R.E. Summons, and J.M. Hayes, Geochim. Cosmochim. Acta, **68**, 1545–1559 (2004)
- [127] de Leuw, S., A.E. Rubin, A.K. Schmitt, and J.T. Wasson, Geochim. Cosmochim. Acta, **73**, 7433–7442 (2009)
- [128] Hoppe, P., D. MacDougall, G. Lugmair, and W. nter, Meteorit. Planet. Sci., **42**, 1309–1320 (2007)
- [129] Deloule, E. and F. Robert, Geochim. Cosmochim. Acta, **59**, 4695–4706 (1995)
- [130] Méheut, M., M. Lazzeri, E. Balan, and F. Mauri, Geochim. Cosmochim. Acta, **74**, 3874–3882 (2010)
- [131] Robert, F., in *Meteorites and the Early Solar System II*, 2006), 341–351
- [132] Eiler, J.M. and N. Kitchen, Geochim. Cosmochim. Acta, **68**, 1395–1411 (2004)
- [133] Busemann, H., A.N. Nguyen, G.D. Cody, P. Hoppe, A.L.D. Kilcoyne, R.M. Stroud, T.J. Zega, and L.R. Nittler, Earth Planet. Sci. Lett., **288**, 44–57 (2009)
- [134] Dobrica, E., C. Engrand, J. Duprat, M. Gounelle, H. Leroux, E. Quirico, and J.-N. Rouzaud, Meteorit. Planet. Sci., **44**, 1643–1661 (2009)
- [135] Nier, A.O. and D.J. Schlutter, Meteoritics, **27**, 166–173 (1992)
- [136] Pepin, R.O., R.L. Palma, and D.J. Schlutter, Meteorit. Planet. Sci., **35**, 495–504 (2000)
- [137] Osawa, T., T. Nakamura, and K. Nagao, Meteorit. Planet. Sci., **38**, 1627–1640 (2003)
- [138] Bradley, J.P., D.H. Heinrich, and K.T. Karl, in *Treatise on Geochemistry* (Pergamon Oxford, 2007), 1–24
- [139] Aléon, J., C. Engrand, F. Robert, and M. Chaussidon, Geochim. Cosmochim. Acta, **65**, 4399–4412 (2001)
- [140] Aléon, J., F. Robert, M. Chaussidon, and B. Marty, Geochim. Cosmochim. Acta, **67**, 3773–3783 (2003)
- [141] Messenger, S., Nature, **404**, 968–971 (2000)
- [142] Keller, L.P., S. Messenger, G.J. Flynn, S. Clemett, S. Wirick, and C. Jacobsen, Geochim. Cosmochim. Acta, **68**, 2577–2589 (2004)
- [143] Flynn, G.J., L.P. Keller, M. Fesser, S. Wirick, and C. Jacobsen, Geochim. Cosmochim. Acta, **67**, 4791–4806 (2003)
- [144] Bajt, S., H.N. Chapman, G.J. Flynn, and L.P. Keller, in *Lunar and Planetary Institute Science Conference Abstracts*, abstract #57 (1996)
- [145] Sandford, S.A., et al., Science, **314**, 1720–1724 (2006)
- [146] Spencer, M.K. and R.N. Zare, Science, **317**, 1680c- (2007)
- [147] Muñoz Caro, G.M., E. Dartois, and K. Nakamura-Messenger, Astron. Astrophys., **485**, 743–751 (2008)

- [148] Elsila, J.E., D.P. Glavin, and J.P. Dworkin, *Meteorit. Planet. Sci.*, **44**, 1323–1330 (2009)
- [149] Crovisier, J., D. Bockelée-Morvan, P. Colom, N. Biver, D. Despois, D.C. Lis, and the Team for target-of-opportunity radio observations of comets, *Astron. Astrophys.*, **418**, 1141–1157 (2004)
- [150] Duprat, J., et al., *Science*, **328**, 742–745 (2010)
- [151] Ciesla, F.J., *Icarus*, **200**, 655–671 (2009)