**The amino acid and hydrocarbon contents of the Paris meteorite: Insights into the most primitive CM chondrite**

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The amino acid and hydrocarbon contents of the Paris meteorite: Insights into the most primitive CM chondrite

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Abstract

The Paris meteorite is one of the most primitive carbonaceous chondrites. It is reported to be the least aqueously altered CM chondrite, and to have experienced only weak thermal metamorphism. We have analyzed for the first time the amino acid and hydrocarbon contents of this pristine meteorite by gas chromatography-mass spectrometry (GC-MS). When plotting the relative amino acids abundances of several CM chondrites according to the increasing hydrothermal scale (petrologic subtypes), from the CM2.7/2.8 Paris to the CM2.0 MET 01070, Paris has the lowest relative abundance of β-alanine/glycine (0.15), which fits with the relative abundances of β-alanine/glycine increasing with increasing aqueous alteration for CM chondrites. These results confirm the influence of aqueous alteration on the amino acid abundances and distribution. The amino acid analysis shows that the isovaline detected in this meteorite is racemic (D/L = 0.99 ± 0.08; L-enantiomer excess = 0.35 ± 0.5%; corrected D/L = 1.03; corrected L-enantiomer excess = -1.4 ± 2.6%). The identified hydrocarbons show that Paris has n-alkanes ranging from C_{16} to C_{25} and 3- to 5-ring non-alkylated polycyclic aromatic hydrocarbons (PAHs). The lack of alkylated PAHs in Paris seems to be also related to this low degree of aqueous alteration on its parent body. The extra-terrestrial hydrocarbon content, suggested by the absence of any biomarker, may well have a pre-solar origin. The chemistry of the Paris meteorite may thus be closely related to the early stages of the solar nebula with a contribution from interstellar (molecular cloud) precursors.

1. Introduction

The Paris meteorite is a carbonaceous chondrite which was acquired by the Muséum National d'Histoire Naturelle (MNHN, Paris). It previously belonged to Jacques Corré, who purchased it in 2001 in an auction from senior mining engineer Jean Colonna-Cimera. Although not officially documented, it is suggested that Paris was an observed fall collected immediately after and not exposed to rain based on the fresh black fusion crust and its Na/K ratio (Haack et al. 2012; Hewins et al. 2014). The Paris meteorite shows almost no signs of terrestrial weathering (Bourot-Denise et al. 2010, Zanda et al. 2010, 2011). Analyses of the petrography, oxygen isotopic distribution, bulk, elemental and organic composition of a few fragments of Paris are in agreement with a CM chondrite assignment (Bourot-Denise et al. 2010, Zanda et al. 2011). A CH_{2}/CH_{3} ratio of 2.3 ± 0.2 obtained by Mid-Infrared (Mid-IR) spectroscopy is also in good agreement with the CM meteorite Murchison (Merouane et al. 2011). Paris was initially classified as a type 3.0 chondrite, based on its petrography and mineral composition (Bourot-Denise et al. 2010, Zanda et al. 2010). In particular, a significant contribution of FeNi metal in the matrix confirms that Paris has experienced much less aqueous alteration than other CM chondrites (Caillet Komorowski et al. 2011, Cournede et al. 2011). However, given the presence of phyllosilicates and carbonates (Merouane et al. 2011), Paris cannot be considered as a hydrothermal type 3.0 (Blanchard et al. 2011,). Blanchard et al. (2011) suggest that Paris is one of the least altered CM chondrites on the hydrothermal scale designated by Rubin et al. (2007), being a CM2.7 or CM2.8 given the chemical composition of the poorly characterized phases (PCPs). On the other hand, its aromatic component (obtained by Raman spectroscopy), metal and sulphide compositions, and petrographic relationships indicate weak thermal metamorphism (Kimura et al. 2011),
suggesting that only low temperature metamorphism occurred in the meteorite after
accretion (Bourot-RDenise et al. 2010, Caillet Komorowski et al. 2011, Merouane et al.
2011). Therefore, Blanchard (2011) proposed Paris to be a CM2.7/2.8 A/B chondrite.

The recent comparison between IR spectra of some of Paris’ fragments and the
spectra from solid-state materials in molecular clouds points to a rather primitive
origin for the organic matter in this meteorite (Merouane et al. 2012). Remusat et al.
(2011) analyzed the parent body aqueous alteration influence on the insoluble organic
matter (IOM) present in the Paris meteorite. The NanoSIMS data indicate that most of
the micron-sized organic particles present in the Paris matrix exhibit 0 < δD <2000‰,
which is consistent with other CM matrices (Remusat et al. 2010, 2011). Although
C/H in Paris appears significantly lower than its counterparts in other CMs, data
indicate that aqueous alteration in the CM parent body does not induce significant
modification on the composition of the organic particles from the IOM phase of Paris
(Remusat et al. 2011). On the other hand, the influence of the parent body aqueous
alteration on the content of the soluble organic matter (SOM) has shown to be
significant in the ungrouped C2 chondrite Tagish Lake (Glavin et al. 2010). In
addition, Glavin and Dworkin (2009) have suggested a correlation between the degree
of aqueous alteration and the L-enantiomeric excess (Lee) of isovaline found in
several meteorites, with the lower Lee found in the less aqueously altered meteorites.
In this work we have analyzed for the first time the amino acid and hydrocarbon
contents of the pristine Paris meteorite by gas chromatography-mass spectrometry
(GC-MS) and discussed the effect of the parent body aqueous alteration on the
abundance and distribution of the soluble organic matter.

2. Materials and Methods

2.1 Chemicals and tools

All chemicals (>99% purity) were purchased from Sigma-Aldrich, except the AG®
50W-X8 cation exchange resin (100-200 mesh, from Bio-Rad), ammonium hydroxide
(28–30 wt%, puriss. p.a., from Acros Organics), D- and L-isovaline standards (>99%
purity, from Acros Organics), trifluorocetic anhydride/isopropanol (TFAA-IPA)
derivatization kit (from Alltech), sodium hydroxide (>99% purity, from Boom) and
hydrochloric acid (37%, ≤5 ppm extractable organic substances, from Boom). All
glassware and sample handling tools were wrapped in aluminum foil, and then heated
in an oven at 500 °C for 3 hours.

2.2 Samples

Two interior chips without fusion crust of the Paris meteorite (199.8 mg for sample 1
and 102.9 mg for sample 2) were provided by the Muséum National d'Histoire
Naturelle (MNHN), Paris, France. Sample 2 was selected from the least altered
lithology. A sample of serpentinite (hydrated magnesium silicate) provided by the
Natural History Museum Bern, was heated to 500 °C for 3 hours, subjected to the
same experimental procedure as the meteorite samples and used as a procedural
blank. The two fragments of Paris and the fragment of serpentinite were separately
crushed and homogenized into powder using new ceramic mortars and pestles in a
laminar flow cabinet.
2.3 Amino acid extraction, derivatization and gas chromatography-mass spectrometry (GC-MS) analyses

The two powder samples of the Paris meteorite and two powder samples of serpentinite control blank were analyzed using the optimized procedure for extracting, derivatizing and analyzing amino acids in meteorites (Kvenvolden et al. 1970, Tsugita et al. 1987, Keil and Kirchman 1991, Glavin et al. 1999, Martins et al. 2007, Martins et al. 2013). Each of the powdered samples was placed inside a Pyrex test tube together with 1 ml of HPLC grade water, flame sealed and heated for 24 hours at 100 °C. One of two equal parts of the water supernatants of each sample was subjected to a 6 M HCl acid vapor hydrolysis (150 °C for 3 h). The non-hydrolyzed fraction (that includes the free amino acids) and the acid-hydrolyzed fraction (including the free plus the bound amino acids) hot-water extracts were desalted on a cation exchange resin and the amino acids eluted with 5 ml of 2 M ammonium hydroxide. The eluates were dried under vacuum and derivatised with TFA-IPA.

The hydrolyzed and non-hydrolyzed fractions of sample 1 of the meteorite and one of the serpentinite blank controls were analyzed by GC-MS (Agilent 7673 series injector, Agilent 6890 series GC equipped with an Agilent 5973 inert mass selective detector; MS quad set to 150 °C, MS source to 230 °C, and injection port and the MSD transfer line set to 220 °C). Separation of the D, L-amino acid enantiomers was achieved using a Chirasil-L-Val column (50 m x 0.25 mm ID x 16 µm film thickness) from Alltech, except for the D- and L-isovaline enantiomers, which could not be separated under these chromatographic conditions. Helium was used as carrier gas with a flow of 1 ml/min. The oven program was held for 5 min at 65 °C, increased by 2 °C/min to 80 °C and held for 5 min, increased to 100 °C by 1 °C/min, increased to 200 °C by 2 °C/min and held for 10 min, and finally increased by 10 °C/min to 220 °C and held for 5 min.

Separation of the D, L-isovaline amino acid enantiomers was achieved by using a Chirasil-Dex CB column (25 m x 0.25 mm, 0.25 µm thickness) from Varian, on the hydrolysed fractions of sample 2 of the Paris meteorite and on the second serpentinite blank control sample according to the method of Pizzarello et al. (2008). Separation of these two amino acid enantiomers was obtained by using a Perkin Elmer Clarus SQ8S MS and a Clarus 580 GC, with a helium flow of 0.6 ml/min. The oven program was held for 7 min at 65 °C, increased by 2 °C/min to 85 °C, increased to 200 °C by 4 °C/min, and held for 90 min. The elution times of the derivatized isovaline enantiomers on the Chirasil-Dex CB column were established to be L-isovaline followed by D-isovaline, by running individual isovaline standards.

The amino acids were identified by comparison of the retention times and mass fragmentation pattern with known amino acid standard mixtures. Single ions used to identify and quantify the amino acid content of the meteorite sample are shown in Table 1. Amino acids were quantified by peak area integration of the corresponding ion fragment, which were then converted to abundances using calibration curves and are presented in Table 2. These were created by plotting the ratio of the amino acid standard/internal standard target ion peak area versus the mass of amino acid standard injected into the column.

In order to ensure that there is no analytical artefact causing an apparent lack of any Lee of isovaline in sample 2 of the Paris meteorite, we have determined how much the
Lee value of a racemic isovaline standard mixture would differ from 0%, and have used that to correct the Lee value obtained in the Paris sample. Racemic isovaline standard mixtures were analysed using the same GC-MS method described above for sample 2 of the Paris meteorite. The Lee value for the racemic isovaline standard mixture (Lee = 1.8 ± 1.4%) was calculated using the equation Lee (%) = [(L - D)/(L + D)] x 100, with uncertainties (δx) obtained by propagation of the errors (Table 3). It was calculated by the average of 14 standard samples analyzed separately, and the D- and L-abundances calculated from the corresponding integrated peaks in the single ion GC-MS traces of the racemic isovaline standards. Finally, the corrected isovaline Lee value for the Paris meteorite was obtained by the formula (Lee corrected = Lee not corrected /Lee standard). The enantiomeric excess correction method is based on the method performed by Pizzarello and Cronin (2000).

2.4 Hydrocarbon extraction and GC-MS analyses

The meteorite and serpentinite blank control residues remaining from the amino acid extraction (sample 1) were extracted for hydrocarbons. Each sample was extracted with 3 ml of 93:7 dichloromethane (DCM)/methanol (MeOH) (V/V) by 20 minutes sonication at room temperature, centrifuged for 15 minutes, and the supernatant was pipetted. Extraction was repeated two more times, the extracts were united, reduced to 100 µl and ran on the Agilent GC-MS which was described before (except for the injection port that was set to 250 °C and the MSD transfer line that was set to 310 °C). Separation of the hydrocarbons was achieved using an Agilent J&W DB-5MS (30 m x 0.25 mm ID x 0.25 µm film thickness). The flow of helium was 1.1 ml/min. The oven program was held for 1 min at 50 °C, increased by 4 °C/min to 310 °C and held for 20 min. Hydrocarbons were identified by comparison of the retention time and mass fragmentation pattern with known standards and also the NIST library. Molecular ions used for quantification and identification of the aliphatic and aromatic hydrocarbons present in the Paris meteorite are shown in Table 4 and Table 5, respectively. Hydrocarbon standards were run before and after each sample. Squalane was used as an external standard to identify and quantify the aliphatic non-volatile hydrocarbon fraction, while p-terphenyl was used as an external standard to identify and quantify the aromatic non-volatile hydrocarbon fraction (Table 4 and Table 5, respectively).

3. Results and Discussion

3.1 Amino acid composition and extra-terrestrial content

We have analyzed the amino acid content of the non-hydrolyzed and acid-hydrolyzed fractions of the Paris meteorite. Fig. 1 shows the selected ion GC-MS chromatograms of the acid-hydrolyzed hot-water extracts of Paris (sample 1) and the serpentinite blank. The serpentinite blank does not display any amino acid above the detection limit of the GC-MS (10 pg of amino acid in a sample). Fig. 2 shows the selected ion GC-MS chromatograms of the D- and L-isovaline enantiomers present in the acid-hydrolyzed hot-water extract of Paris (sample 2) and in a D,L-isovaline standard. The abundances of the separated D- and L-isovaline enantiomers present in the acid-hydrolyzed fraction of the Paris meteorite (sample 2) are described in Table 2. These were not included in the total amino acid concentration as they were detected in a
different sample than all other Paris amino acids.

The abundances of the amino acids of the non-hydrolyzed and acid-hydrolyzed fractions of the meteorite (sample 1) are displayed in Table 2. The non-hydrolyzed fraction of the Paris meteorite has an abundance of 7060 parts-per-billion (ppb), while the total amino acid abundance of Paris is 15,760 ppb (Table 2). The percentage of free amino acids in the non-hydrolyzed extract corresponds to 45% of the total amino acid abundance. This is a typical value for CM chondrites in which free amino acids contribute with 40 to 50% of the total amino acid abundance (Shimoyama and Ogasawara 2002, Glavin et al. 2006, 2011, Botta et al. 2007). Glavin et al. (2011) suggested a possible link between higher free/total amino acid ratio and less aqueously altered chondrites based on the ratios measured in Antarctic CR2 chondrites, although that was not observed in the less aqueously altered CR3 chondrite QUE 99177 when compared to the CR2 EET 92042. Considering that Paris is reported to be the least aqueously altered CM chondrite analyzed to date, the data presented in this work does not seem to confirm this hypothesis.

The most abundant amino acids are α-amino acids (12,179 ppb), followed by dicarboxylic amino acids (2,143 ppb), β-amino acids (1,250 ppb) and γ-amino acids (185 ppb) (Table 2). Linear n-α-amino acids are the most abundant fraction of α-amino acids (10,562 ppb), and include glycine (8,252 ± 369 ppb), L-alanine (961 ± 46 ppb), D-alanine (710 ± 32 ppb), α-ABA (α-amino-n-butyric acid) (306 ± 7 ppb), L-norvaline (178 ± 12 ppb) and D-norvaline (155 ± 11 ppb). The amino acids D-norleucine, L-norleucine, D-leucine, L-leucine, D-β-ABA, L-β-ABA, D,L-β-AIB and EACA are not detected above the detection limit of the GC-MS (Table 2).

Insight into the extra-terrestrial nature of the amino acids present in the Paris meteorite is provided by examining the D/L enantiomeric ratios for chiral amino acids. We calculated the amino acid enantiomeric ratios in Paris for aspartic acid, glutamic acid, alanine, valine, norvaline, isovaline and α-ABA (Table 6), all except norvaline and isovaline being typical proteinaceous amino acids. Optically pure α-ABA standards were not available for enantiomeric identification. Therefore, the order of elution of D-α-ABA and L-α-ABA was tentatively assigned, considering that when using a Chirasil-L-Val column the D-enantiomer of all other amino acids elutes first followed by the L-enantiomer. The D/L values were found to range from 0.72 ± 0.03 (aspartic acid) to 0.99 ± 0.08 (isovaline), with the uncertainties based on the absolute errors shown in Table 2 and obtained by error propagation calculation.

An initial D/L amino acid enantiomeric ratio smaller than 1 before Paris fell to Earth could explain the detected D/L ratios for aspartic acid, glutamic acid and alanine (Table 6). In fact, Glavin et al. (2012) found small D/L ratios (i.e. smaller than 0.4) for aspartic and glutamic acids in the Tagish Lake chondrite, with carbon isotope measurements of D- and L-aspartic acid falling well outside of the terrestrial range and indicating that the measured aspartic acid enanti-enrichment was indigenous to the meteorite. These results were explained by differences in the solid–solution phase behaviour of aspartic acid and glutamic acid, which can form conglomerate enantiopure solids during crystallization (Glavin et al. 2012, Viedma 2001; Viedma et al. 2008). However, Glavin et al. (2012) points out that alanine can only form racemic crystals as its solid–solution phase behavior is different. Therefore, crystallization does not entirely explain the results observed in the Paris meteorite.
Alternatively, we may consider an initial D/L enantiomeric ratio equal to 1 before the Paris meteorite fell to Earth. The results presented in Table 6 may indicate a certain degree of terrestrial contamination (i.e. D/L ranging from 0.72 to 0.84 for aspartic acid, glutamic acid and alanine), but with most of the amino acids being indigenous to Paris (D/L ratios for valine, norvaline and α-ABA are nearly racemic ≈ 0.9, and D/L for isovaline is 0.99). Typical D/L amino acid ratios of soil range from <0.04 to 0.35 (e.g. Peeters et al. 2009, Martins et al. 2011). While some terrestrial contamination from the meteorite landing site cannot be rejected, these values are much smaller than the ones observed in the Paris meteorite. Paris shows almost no signs of terrestrial weathering (Bourot-Denise et al. 2010, Zanda et al. 2010, 2011), while recent analysis of the Na/K ratio suggests that it was collected immediately after its fall and was not exposed to rain (Haack et al. 2012; Hewins et al. 2014), which significantly reduces the percolation of the landing site soil through the meteorite. Also, the serpentinite control blank did not contain any amino acids (Fig. 1), showing that any contamination present in Paris has not originated during the extraction procedure, but more likely during the handling history of this meteorite.

It is also important to report the presence of the 2-methyl α-amino acids α-aminoisobutyric acid (α-AIB) (312 ± 10 ppb) and isovaline (117 ± 4 ppb for sample 1, and 221 ± 7 ppb for L-isovaline and 220 ± 16 ppb for D-isovaline in sample 2) (Table 2), which are rare in the terrestrial biosphere but common in other CM2 meteorites (Kotra et al. 1979, Shimoyama et al. 1979a, 1979b, 1985, Pizzarello and Cronin 2000, Ehrenfreund et al. 2001a, Shimoyama and Ogasawara 2002, Glavin et al. 2006, 2011, Botta et al. 2002).

The best way to evaluate the source of amino acids would be to measure the compound-specific stable isotope ratios of carbon, hydrogen, and/or nitrogen. However, we were unable to produce isotope measurements of the amino acids in Paris (i.e. several replicate isotope measurements to obtain a significant standard deviation) due to the limited meteorite sample available for analysis and the fact that the abundance of amino acids extracted is below the detection limit of current state of the art gas chromatography combustion isotope ratio mass spectrometers (GC-C-IRMS).

3.2 L-enantiomer excess of isovaline

The detection of non-racemic isovaline (corresponding to a Lee for isovaline) in carbonaceous chondrites has been reported and extensively discussed by several authors (Cronin and Pizzarello 1997, 1999; Pizzarello and Cronin 2000; Pizzarello et al. 2003, 2008, 2012; Glavin and Dworkin 2009; Glavin et al. 2011). Significant differences were also observed within the same meteorite sample, with different fragment of the Murchison meteorite having Lee for isovaline ranging from 0 to 18.5 ± 2.6 % (Pizzarello et al. 2003, Glavin and Dworkin 2009). Although isovaline may be found in the D-configuration in fungal peptides (Keller et al. 1990; Bruckner et al. 2009), it is a non-proteinogenic α-dialkyl amino acid which is rare on Earth, and therefore the observed Lee is unlikely due to terrestrial contaminations of meteoritic samples. On the other hand, an abiotic synthesis, in the absence of any asymmetric field or chiral and slightly asymmetric molecular precursor, should produce only racemic mixtures of L- and D-isovaline.
One promising mechanisms which may explain the origin of the observed Lee in meteoritic amino acids is the asymmetric photo-processing of amino acids or their precursors by ultra violet circularly polarized light (UV-CPL) in space (Bonner and Rubenstein 1987; Bailey et al. 1998; Lucas et al. 2005). In support of this hypothesis, non-racemic proteinogenic and non-proteinogenic amino acids have been obtained in laboratory from UV-CPL photo-processing of initially achiral interstellar/circumstellar ice analogues, with the two CPL helicities (R and L) inducing Lee of opposite signs whereas UV-Linearly Polarized Light (UV-LPL) did not induce any Lee (Marcellus et al. 2011; Modica et al. 2014). The presence of non-racemic meteoritic isovaline may be consistent with UV-CPL photo-processing, provided that a secondary mechanism for amplification of Lee is invoked to explain the large Lee observed in some cases.

A possible correlation between the Lee of isovaline found in individual fragments of Murchison and the relative abundance of hydrous silicate minerals has been noted (Pizzarello et al. 2003). This suggests that although aqueous alteration does not create by itself an isovaline asymmetry in this meteorite, it may amplify a small enantiomeric excess. Therefore, a large enantiomeric excess may be obtained from a small initial Lee (such as the one produced by UV-CPL), which then may be amplified under aqueous conditions as experimentally demonstrated by Soai et al. (1995) and Blackmond (2004). Thus, amplification of a small initial Lee by aqueous alteration on the meteorite parent body has been suggested as a secondary mechanism (Glavin and Dworkin 2009). Isovaline, as well as other α-dialkyl amino acids is resistant to racemization under aqueous conditions (Pollock et al. 1975). Therefore, its enantiomeric imbalance should not have been canceled. Our results on Paris, the least aqueously altered CM chondrite analyzed to date, presents an opportunity to verify if aqueous alteration can play a role in the isovaline Lee amplification.

The selected ion GC-MS chromatograms of the D- and L-isovaline enantiomers present in Paris (sample 2) and in a pure racemic isovaline standard (carried through the same analytical procedure as the Paris sample) are shown in Fig. 2. The mass spectra for the peaks assigned to the L-isovaline in Paris and the L-isovaline in the standard are also shown, with the same fragmentation pattern being observed in both the mass spectra. A D/L isovaline ratio (not-corrected) of 0.99 ± 0.08 was measured for Paris (Table 6). The isovaline Lee value was also calculated using the equation Lee (%) = [(L - D)/(L + D)] x 100, with uncertainties (δx) obtained by propagation of the errors (Table 3). In the case of the Paris meteorite, the isovaline Lee (0.3%) and the uncertainties (δx = ± 4.0%) are based, respectively on the absolute values and absolute errors presented in Table 2. A pure isovaline racemic standard mixture (Lee = 1.8 ± 1.4%, Table 3) was used for correction of the D/L isovaline ratio and Lee value obtained for Paris to take into account the intrinsic effects of the chiral column. The corrected isovaline Lee value corresponds to -1.4 ± 2.6% (Lee corrected = Lee not corrected - Lee standard), and the corrected D/L isovaline ratio corresponds to 1.03.

In order to test the hypothesis that aqueous alteration on the meteorite parent body is responsible for the high Lee of isovaline observed in the most aqueously altered carbonaceous meteorites, we have compared the isovaline Lee values across CM chondrites with different degrees of aqueous alteration as Glavin and Dworkin (2009) have done. This was achieved for the CM chondrites for which the D- and L-isovaline composition is available and according to the hydrothermal scale (petrologic subtypes) designated by Rubin et al. (2007): the CM2.7/2.8 Paris (this study;
hydrothermal classification proposed by Blanchard 2011), the CM2.5 Murchison (Glavin and Dworkin 2009, Pizzarello et al. 2003), the CM2.4/2.5 Murray (Pizzarello et al. 2003), and the CM2.0 SCO 06043 (Glavin et al. 2011) (Table 3). The Lee for isovaline values increase from -1.4 ± 2.64% for the CM2.7/2.8 Paris, to 6.0% for the CM2.4/2.5 Murray (no associated error was provided), and finally to 16.5 ± 7.5% for the CM2.0 SCO 06043 (Table 3). To note the large range of Lee values for different samples of the Murchison meteorite, from 0 to 18.5 ± 2.6% (Pizzarello et al. 2003, Glavin and Dworkin 2009, Table 3), which may be explained by the different degrees of aqueous alteration characterizing different lithologies of the same meteorite. The data in Table 3 clearly show that the most primitive CM analysed to date, the CM2.7/2.8 Paris has an isovaline Lee close to zero (-1.4 ± 2.6%). Our data thus support the correlation found by Glavin and Dworkin (2009), suggesting that aqueous alteration played an important role in the isovaline enantiomeric enrichment.

3.3 Possible formation pathways for α-amino acids

The most abundant amino acids in Paris are α-amino acids (12,179 ppb). In particular, linear n-α-amino acids contribute with the most abundant fraction of α-amino acids (10,563 ppb). Possible formation pathways for α-amino acids include a two-step process in which the precursors (including carbonyl compounds, ammonia, and hydrogen cyanide) were formed in the interstellar and/or presolar cloud and then incorporated into the meteorite parent body (Peltzer and Bada 1978, Lerner and Cooper 2005). In addition, the laboratory simulated photochemistry of interstellar/presolar/interstellar analogs also allows the formation of soluble organic matter, including many different amino acids (Berstein et al. 2002, Munoz Caro et al. 2002, Meinert et al. 2012). However, as amino acids will not survive in environments subject to high UV flux, at least in the gas phase, this requires that amino acids or their precursors are incorporated into a totally or at least partially UV shielded environment, such as the inside of interstellar grains. Grains may then slowly grow later to planetesimals and finally to the meteorite parent body (Ehrenfreund et al. 2001b). In the course of the evolution from the molecular cloud to the formation of planetesimals in the solar nebula, the Strecker-cyanohydrin amino acid synthesis may have then further taken place during aqueous alteration within the meteorite parent body (Peltzer and Bada 1978, Lerner and Cooper 2005). However, the significant abundance and diversity of amino acids and di-amino acids found in non-hydrolyzed and hydrolyzed fractions of laboratory ice analogues experiments do not invoke any aqueous alteration phase of the samples (Nuevo et al. 2008, Meinert et al. 2012). Instead it suggests the possibility of radical-radical reactions to form peptide bonds as recently described by Kaiser et al. (2013).

The α-amino acid carbonyl precursors (i.e. aldehydes and ketones) were thought to be synthesized by the addition of a single-carbon atom donor to the growing alkane chain. Considering that the abundance of the α-amino acid is dependent on the precursor carbonyl compound, the relatively high concentration of glycine in Paris (when compared to the other CM2s) may be due to a high abundance of formaldehyde on the parent body of the Paris meteorite. Alternatively, some fraction of glycine may have a terrestrial origin. Considering an initial D/L enantiomeric ratio equal to 1 for chiral protein amino acids in Paris and that any Lee is due to terrestrial contamination, it is possible to have an estimate of the possible level of contamination for glycine. The lowest D/L amino acid ratio observed for Paris (D/L = 0.72 ± 0.03 for aspartic acid; Table 6) may indicate the highest level of contamination experienced by this
meteorite, which corresponds to a Lee value of 19.2%. The original glycine value (8252 ppb; Table 2) may be corrected to give a lower limit of glycine of 6670 ppb.

3.4 Effect of aqueous alteration on the amino acid abundances and distribution

Aqueous alteration on the meteorite parent body of CM chondrites was an important alteration process of their mineral, isotopic and volatile content (Clayton and Mayeda 1984, Tomeoka and Buseck 1985, Zolensky and McSween 1988, 1997, Brownin et al. 1996, Palmer and Lauretta 2011). In relation to the soluble organic composition, not only the enantiomer enrichment (see section 3.2), but also the relative distribution of amino acids in carbonaceous chondrites seems to be influenced by the degree of aqueous alteration on the parent body (Glavin et al. 2006, 2011, Martins et al. 2007).

In order to further investigate the influence of aqueous alteration on the amino acid abundance and distribution on CM chondrites, we have plotted the relative abundances of a complete set of amino acid isomers/enantiomers (i.e. for all 4-carbon amino acids) for CM chondrites with different degrees of aqueous alteration according to the hydrothermal scale (petrologic subtypes) designated by Rubin et al. (2007), and for which the amino acid composition is fully available. These include the CM2.7/2.8 Paris (hydrothermal classification proposed by Bourot-Denise et al. 2010), the CM2.5 Murchison, the CM2.4/2.5 Murray, the CM2.4 Y-791198, the CM2.2 Nogoya, the CM2.0 MET 01070, and the CM2.0 SCO 06043 (this study, Ehrenfreund et al. 2001a, Botta et al. 2002, Shimoyama and Ogasawara 2002, Glavin et al. 2011). Fig. 3 shows the relative abundances (i.e. the ratio of amino acid abundance/total abundance for all the 4-carbon amino acids) for the 4-carbon α-amino acids (α-ABA and α-AIB), β-amino acids (β-ABA and β-AIB) and γ-amino acids (γ-ABA), and Fig. 4 gives the relative abundances for α-AIB/α-ABA (i.e. ratio of branched versus linear 4-carbon amino acids). The relative abundances for β-alanine/glycine, α-AIB/glycine and β-alanine/α-AIB were plotted in Fig. 5. The least altered CM chondrites are on the left of the plots, while the most altered are on the right (Fig. 3, Fig. 4, Fig. 5).

There is no linear trend between the relative amino acid abundances and the increasing aqueous alteration for each of the individual 4-carbon α-, β- and γ-amino acids sets (Fig. 3). However, it is possible to see that the least and medium aqueously altered CM chondrites (i.e. Paris, Murchison, Murray and Y-791198) have much higher relative abundances of 4-carbon α-amino acids than β- and γ-amino acids, when compared to the most aqueously altered CM chondrites. This may be an indication that the Strecker-cyanohydrin amino acid synthesis has been more active in this type of CM chondrite. Also, extensive aqueous alteration on the meteorite parent body may result in the decomposition of α-amino acids (Botta et al. 2007, Martins et al. 2007) as the degradation of α-amino acids may be the result, for example of low-temperature chemical oxidation from aqueous alteration during the early history of the meteorite parent body. Indeed it has been shown that increasing oxidation removes the aliphatic portions of the soluble and macromolecular organic material (Sephton et al. 2004, Cody and Alexander 2005, Martins et al. 2006). Moreover, extensive aqueous alteration on the meteorite parent body may also result in hydrolysis of lactams, leading to the synthesis of β- and γ-amino acids (Cooper and Cronin 1995); and/or may favour the Michael addition of ammonia to α,β-unsaturated nitriles (forming β-amino alkynitriles) followed by hydrolysis to form β-amino acids (Cronin and Chang 1993). In addition, the least and medium aqueously altered CM chondrites have relative 4-carbon α-amino acids abundances higher than 0.6, while the most
aqueously altered CM chondrites, such as MET 01070 and SCO 06043, have 4-carbon α-amino acids abundances smaller than 0.4 (Fig. 3). Our data also show that Paris has one of the highest relative abundance of 4-carbon α-amino acids in CM chondrites (0.77), only comparable to Y-791198 (0.81) (Fig. 3).

We have also plotted the relative abundances for α-AIB/α-ABA (i.e. ratio of branched versus linear 4-carbon amino acids) versus increasing aqueous alteration (Fig. 4). The data clearly show that aqueous alteration has no influence on the distribution of the branched-to-straight chain 4-carbon amino acids.

There is an observable increasing relative abundance of the amino acid β-alanine (glycine = 1) with increasing aqueous alteration (Fig. 5). The Paris meteorite, the least aqueously altered CM chondrite analyzed to date has a ratio of β-alanine/glycine of 0.15 ± 0.02. This is the smallest β-alanine/glycine ratio observed in CM chondrites. Even if we account for a possible fraction of terrestrial contamination for glycine (section 3.3) the β-alanine/glycine lower limit ratio would be 0.19, which is still the smallest for all CM chondrites and would still fit the linear trend of increasing β-alanine/glycine with increasing aqueous alteration. The only data point that does not fit this trend is Y-791198. Shimoyama and Ogasawara (Shimoyama and Ogasawara 2002) did not provide any associated error for the detected amino acid abundances, and therefore it is not possible to infer without doubt whether this meteorite fits the increasing β-alanine trend. In addition, it may be that the classification of CM2.4 for Y-791198 as determined by Rubin et al. (2007) is not accurate. In fact, this carbonaceous chondrite has been previously indicated as weakly aqueously altered. Metzler et al. (1992) stated that Y-791198 appears to have escaped from the influence of aqueous solutions on its parent body, which is supported by Chizmadia and Brearley (2008) who stated that Y-791198 is probably one of the least altered CM2 chondrite studied to date. In any case, if we disregard the β-alanine point for Y-791198 in Fig. 5, we may say that the increase of the relative abundance of the amino acid β-alanine with increasing aqueous alteration as observed in Fig. 5 is in agreement with the observations by Glavin et al. (2006, 2011). Extensive aqueous alteration seems to favor the synthesis of β-amino acids (in particular β-alanine) in the parent body of CM chondrites, with possible synthetic pathways already mentioned with the discussion from Fig. 3.

CM chondrites seem to fit nicely the trend of increasing β-alanine/α-AIB with increasing aqueous alteration (Fig. 5). Paris is the exception to the rule with a β-alanine/α-AIB ratio of 4.0 ± 0.5 (Fig. 5). A possible explanation to this value is a low abundance of α-AIB in the Paris meteorite when compared to other CM chondrites, which may result from a low abundance of carbonyl compound (i.e. acetone) on the meteorite parent body. This could indicate that Paris originated from a distinct parent body from other CM chondrites. However, there is no bulk compositional or petrologic evidence to fully support this (Bourot-Denise et al. 2010, Zanda et al. 2011, Merouane et al. 2011). Alternatively Paris may have originated from a different source region with distinct chemical conditions within the same parent body. The low degree of aqueous alteration on its parent body may have also been responsible for the low abundance of α-AIB in the Paris meteorite, as it could have partly inhibited the step from the aminonitrile intermediate to α-AIB during the Strecker-cyanohydrin synthesis.

In relation to the relative abundance of α-AIB/glycine, Glavin et al. (2011) did not
observe any strong trends in relative $\alpha$-AIB abundances with aqueous alteration, but noted that the relative abundances of $\alpha$-AIB tended to be higher in carbonaceous chondrites that experienced less aqueous alteration. Our results do not support this last observation by Glavin et al. (2011), as Paris is the least aqueously altered CM chondrite analyzed to date and has a relative abundance of $\alpha$-AIB/glycine equal to 0.038 ± 0.002 (95% confidence interval). In fact, data from Botta et al. (2007) also did not show a trend for the relative abundance of $\alpha$-AIB versus aqueous alteration in the CM1 and CM2s analyzed in that study. Glavin et al. (2011) also noted that the total $\alpha$-AIB abundance was approximately 100 to 1000 times more abundant in CM2s and CM3s compared to CM1s. Paris has a low $\alpha$-AIB abundance (312 ± 10 ppb; Table 2), which is closer to CM1 than CM2 values. Therefore, our data suggests that aqueous alteration does not correlate with the total $\alpha$-AIB abundance, in contrast with previous analysis of CM chondrites. We do acknowledge that these differences could be explained by sample heterogeneity and the fact that different meteorites have been analyzed for amino acids by different groups. However, such problems were not observed for the relative abundances of $\beta$-alanine/glycine in the CM chondrites (Fig. 5).

### 3.5 Hydrocarbon composition and extra-terrestrial content

The hydrocarbon content of the Paris meteorite was analysed. Fig. 6 shows the single ion GC-MS traces ($m/z$ 57) corresponding to $n$-alkanes present in the Paris meteorite (sample 1) and serpentinite blank, with the corresponding abundances presented in Table 4. The Paris meteorite has 7,670 ppb of aliphatic hydrocarbons ($n$-alkanes) ranging from $C_{16}$ to $C_{25}$. The most abundant $n$-alkane is heptadecane ($C_{17}H_{36}$) with 2,499 ± 230 ppb, followed by octadecane ($C_{18}H_{38}$) with 1,799 ± 91 ppb (Table 4).

This class of organic molecules has been detected in other CM chondrites including YR791198 ($C_{12}$ to $C_{20}$, with total abundance of 10 ppb), and Murchison (more than 35,000 ppb) (Naraoka et al. 1988, Kvenvolden et al. 1970). In addition, Cronin and Pizzarello (1990) have found $C_{15}$ to $C_{30}$ branched alkyl-substituted mono-, di-, and tricyclic alkanes in the Murchison meteorite.

The aromatic hydrocarbons detected in Paris and serpentinite blank are shown in Fig. 7. Table 5 shows the detected abundances for each detected aromatic hydrocarbon.

The aromatic hydrocarbon content of Paris ranged from 3- to 5-ring non-alkylated polycyclic aromatic hydrocarbons (PAHs), with total abundance of 8,722 ppb (Table 5). No alkylated PAH was detected. The most abundant aromatic hydrocarbons are fluoranthene (3,455 ± 195 ppb), pyrene (3,089 ± 181 ppb), and phenanthrene (1,662 ± 58 ppb). The CM2 Y-791198 has much simpler aromatic hydrocarbon content, with 2- to 4-ring hydrocarbons and total abundance of only 3,670 ppb (Naraoka et al. 1988). Although the CM2 Murchison has a similar distribution of aromatic hydrocarbons when compared to Y-791198, their abundances are much higher, ranging from 12,920 to 30,300 ppb (Perring and Ponnamperuma 1971) (Table 5).

Previous analyses of carbonaceous chondrites suggest that these are highly susceptible to hydrocarbon contamination (Sephton et al. 2001, Cronin and Pizzarello 1990). For example, the $\delta^{13}$C values of the $n$-alkanes from Murchison, Cold Bokkeveld, and Orgueil do not have the $^{13}$C-enrichment characteristic of other meteoritic organic molecules, agreeing instead with values of terrestrial fossil hydrocarbons (Sephton et al. 2001). While it was not possible to perform compound-specific stable isotope ratios of carbon, hydrogen, and/or nitrogen (due to the very limited amount of sample...
available), the study of specific biomarkers sheds light into the presence of terrestrial organisms and the environments the Paris meteorite may have been in contact. Our data show no even or odd number predominance of \( n \)-alkanes in Paris (Table 4 and Fig. 6), contrasting with an odd number predominance of \( n \)-alkanes resulting from a marine environment or an even number predominance from carbonate rocks (Moldowan et al. 1985). Typical terrestrial hydrocarbon signatures such as the isoprenoids pristane (\( m/z \) 268) and phytane (\( m/z \) 282), hopanes (\( m/z \) 191), squalene (\( m/z \) 410), or steranes (\( m/z \) 217) were not detected in the Paris meteorite. In addition, Paris did not contain any typical signature of biological aromatic hydrocarbon at \( m/z \) 133 (Summons and Powell 1986). Finally, the serpentinite blank did not contain any \( n \)-alkane or aromatic hydrocarbon (Fig. 6 and Fig. 7, respectively), suggesting that the hydrocarbons detected in Paris are not experimental artefacts generated during extraction. Therefore, our data strongly suggest that the hydrocarbons detected are indigenous to the Paris meteorite.

3.6 Possible formation pathways for hydrocarbons

The effect of parent body processing on organic matter may also be observed on the hydrocarbon composition and distribution. The Paris meteorite does not contain any alkylated PAHs, while alkylated PAHs species were detected in Murchison and Y-791198 (Table 4). Our results suggest that aqueous alteration may be responsible for the alkylation of PAHs. This is in agreement with the results by Elsila et al. (2005), who suggested that higher relative abundances of alkylated PAHs to correlate with a higher degree of aqueous alteration on the meteorite parent body of CM2 chondrites. This seems to be particularly true for naphthalene and its alkylation species and to a lesser extent to the alkylation of phenanthrene in the CM2 meteorites (Table 4, this article; Elsila et al. 2005). We note that dimethynaphthalene and methylphenanthrene were not detected in Y-791198, and other alkylated PAHs species were present in much lower abundance than in Murchison. This reinforces the idea that the classification of CM2.4 for Y-791198 as determined by Rubin et al. (2007) may not be accurate, and that Y-791198 is indeed a weakly aqueously altered CM chondrite (Metzler et al. 1992, Chizmadia and Brearley 2008).

4. Conclusion

The Paris meteorite is reported to be the least aqueously altered CM chondrite analyzed to date. The analysis of the amino acid content of Paris shows that the degree of aqueous alteration may be responsible for the amino acid abundances and distribution. Isovaline detected on the Paris meteorite was racemic (D/L = 0.99 ± 0.08; L-enantiomer excess = 0.35 ± 0.5%; corrected D/L = 1.03; corrected L-enantiomer excess = -1.4 ± 2.6%). This may support the hypothesis that aqueous alteration is responsible for the high L-enantiomer excess of isovaline observed in the most aqueously altered carbonaceous meteorites.

Extensive aqueous alteration in the parent body of carbonaceous meteorites results in the decomposition of \( \alpha \)-amino acids and the synthesis of \( \beta \)- and \( \gamma \)-amino acids. Our data reinforce the hypothesis that the relative abundance of \( \beta \)-alanine increases with increasing aqueous alteration in the parent body of CM chondrites. The Paris meteorite has a ratio of \( \beta \)-alanine/glycine of 0.15 (\( \beta \)-alanine/glycine lower limit ratio
of 0.19), which is the lowest ever measured for a CM chondrite. In addition, our results show no link between the degree of aqueous alteration and the free/total amino acid ratios, $\alpha$-AIB/glycine ratios, or $\beta$-alanine/$\alpha$-AIB ratios in CM chondrites. The data also seem to indicate that aqueous alteration has no influence on the distribution of the branched-to-straight chain 4-carbon amino acids in CMs.

The analysis of the hydrocarbon content of the Paris meteorite shows no alkylated aromatic hydrocarbons, suggesting that the higher relative abundances of alkylated PAHs correlate with a higher degree of aqueous alteration on the meteorite parent body of CM2 chondrites. The extra-terrestrial aliphatic and aromatic hydrocarbon content of Paris may have an interstellar origin or contribution from interstellar precursors. It may also be the case for the amino acids (or their precursors) as these may be formed in photo/thermochemical processes in interstellar/pre-cometary ices analogs. Therefore the organic content of the primitive CM chondrite Paris possibly relates to late phases of condensed phase chemistry in molecular clouds.

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Figure Legends

**Fig. 1** - The 10 to 70 min region of the single ion GC-MS traces (m/z 126, 140, 154, 168, 180, 182, 184 and 210) of the derivatized (N-TFA, O-isopropyl) HCl-hydrolysed hot-water extracts of the Paris meteorite (sample 1) and serpentinite blank. The identification of the amino acid peaks is given in Table 1. D- and L-isovaline enantiomers could not be separated under the chromatographic conditions. Enantiomeric identification of D- and L-α-ABA was only tentatively as optically pure standards were not available. It was based on the fact that the enantiomer of D-amino acids elutes first followed by the L-enantiomer when using the Chirasil-L-Val column.

**Fig. 2** - The single ion GC-MS traces (m/z 168) of the derivatized (N-TFA, O-isopropyl) racemic D- and L-isovaline mixture (bottom) and D- and L-isovaline in the HCl-hydrolyzed extract of the Paris meteorite (sample 2; top). Peak number 2 corresponds to L-isovaline and peak number 3 corresponds to D-isovaline. The insets show the GC-MS mass spectrum for the peak assigned to the derivatized (N-TFA, O-isopropyl) amino acid standard L-isovaline (bottom) and for the peak assigned to derivatized (N-TFA, O-isopropyl) amino acid L-isovaline in the Paris meteorite (top; sample 2).

**Fig. 3** - Relative abundances (total = α- plus β- plus γ-amino acids) for the 4-carbon amino acid content of α- (dots), β- (grey) and γ-amino acids (white) for CM chondrites with different degrees of aqueous alteration according to the hydrothermal scale (petrologic subtypes) designated by Rubin et al. (2007). These include the CM2.7/2.8 Paris (this study; Table 2), the CM2.5 Murchison (Shimoyama and Ogasawara 2002), the CM2.4/2.5 Murray (Ehrenfreund et al. 2001a, Botta et al. 2002), the CM2.4 Y-791198 (Shimoyama and Ogasawara 2002), the CM2.2 Nogoya (Botta et al. 2002), the CM2.0 MET 01070, and the CM2.0 SCO 06043 (Glavin et al. 2011).

**Fig. 4** - Relative abundances of α-AIB/α-ABA for CM chondrites with different degrees of aqueous alteration according to the hydrothermal scale (petrologic subtypes) designated by Rubin et al. (2007). These include the CM2.7/2.8 Paris (this study; Table 2), the CM2.5 Murchison (data of Murchison a) from Shimoyama and Ogasawara 2002; data of Murchison b) from Glavin et al. 2011), the CM2.4/2.5 Murray (Ehrenfreund et al. 2001a, Botta et al. 2002), the CM2.4 Y-791198 (Shimoyama and Ogasawara 2002), the CM2.2 Nogoya (Botta et al. 2002), the CM2.0 MET 01070, and the CM2.0 SCO 06043 (Glavin et al. 2011). The uncertainties are obtained by standard propagation calculation.

**Fig. 5** - Relative abundances of α-AIB/glycine (dots), β-alanine/glycine (grey) and β-alanine/α-AIB (white) for CM chondrites with different degrees of aqueous alteration according to the hydrothermal scale (petrologic subtypes) designated by Rubin et al. (2007). These include the CM2.7/2.8 Paris (this study; Table 2), the CM2.5 Murchison (data of Murchison a) from Shimoyama and Ogasawara 2002; data of Murchison b) from Glavin et al. 2011), the CM2.4/2.5 Murray (Ehrenfreund et al. 2001a, Botta et al. 2002), the CM2.4 Y-791198 (Shimoyama and Ogasawara 2002), the CM2.2 Nogoya (Botta et al. 2002), the CM2.0 MET 01070, and the CM2.0 SCO 06043 (Glavin et al. 2011). The uncertainties are obtained by standard propagation
calculation.

**Fig. 6** - The single ion GC-MS traces \((m/z \ 57)\) of the DCM/MeOH extracts of the Paris meteorite and serpentinite blank (zoom x10). The quantification of each peaks corresponding to \(n\)-alkanes is given in Table 4. The external standard (squalane) was run several times before and after each sample.

**Fig. 7** - The single ion GC-MS traces \((m/z \ 178, 202, 228, 252)\) of the DCM/MeOH extracts of the Paris meteorite (zoom x25 for \(m/z \ 228\), and zoom x50 for \(m/z \ 252\)) and serpentinite blank (zoom x50). Identification is as follows 1-Phenanthrene; 2-Anthracene; 3-Fluoranthe; 4-Pyrene; 5-Benz[a]anthracene; 6-benzo[a]phenanthrene; 7-Triphenylene; 8-Benzo[c]phenanthrene; 9-Benzo[a]pyrene; 10-Benzo[e]pyrene. The quantification of each peak corresponding to aromatic hydrocarbons is given in Table 5. The external standard (p-terphenyl) was run several times before and after each sample.
Table Legends

**Table 1** – Amino acid peak identification in the GC-MS chromatograms (Fig. 1) of the hydrolyzed serpentinite blank, and the hydrolyzed Paris meteorite. Molecular ions used for quantification (first ion) and identification and are also displayed.

**Table 2** – Summary of the average total amino acid abundances (in ppb) in the hydrolyzed and non-hydrolyzed fractions of the Paris meteorite measured by GC-MS. Separation of the D- and L-isovaline enantiomers was achieved on sample 2 of the Paris meteorite.

**Table 3** - L-enantiomer excess values (Lee (%)) for isovaline in the Paris meteorite, the CM chondrites Murchison, Murray, SCO 06043, and one racemic standard.

**Table 4** – Summary of the average hydrocarbon abundances (in ppb) in the aliphatic fractions of the Paris meteorite measured by GC-MS. Molecular ions used for quantification and identification of the aliphatic hydrocarbons are also displayed. Squalane was used as an external standard to identify and quantify the aliphatic non-volatile hydrocarbon fraction.

**Table 5** – Summary of the average hydrocarbon abundances (in ppb) in the aromatic fractions of the Paris meteorite measured by GC-MS. Molecular ions used for quantification and identification of the aromatic hydrocarbons are also displayed. P-terphenyl was used as an external standard to identify and quantify the aromatic non-volatile hydrocarbon fraction.

**Table 6** - Amino acid enantiomeric ratios (D/L) in the Paris meteorite.
Table 1. Amino acid peak identification in the GC-MS chromatograms of the serpentine blank (hydrolyzed), and the Paris meteorite (hydrolyzed). Molecular ions used for quantification (first ion) and identification and are also displayed.

| Peak # | Amino acid          | Single ion (m/z) |
|--------|---------------------|------------------|
| 1      | α-AIB               | 154              |
| 2      | L-Isoleucine\(^a\)  | 168              |
| 3      | D-Isoleucine\(^a\)  | 168              |
| 4      | D-Alanine           | 140/168          |
| 5      | L-Alanine           | 140/168          |
| 6      | D-α-ABA\(^b\)      | 154              |
| 7      | L-α-ABA\(^b\)      | 154              |
| 8      | D-Valine            | 168              |
| 9      | L-Valine            | 168              |
| 10     | Glycine             | 126/154          |
| 11     | D,L-β-AIB\(^b,c\)  | 182/153          |
| 12     | D-Norvaline         | 168              |
| 13     | L-Norvaline         | 168              |
| 14     | β-Alanine           | 168/185          |
| 15     | D-β-ABA\(^b\)      | 140/182/153      |
| 16     | L-β-ABA\(^b\)      | 140/182/153      |
| 17     | D-Leucine           | 140/182          |
| 18     | L-Leucine           | 140/182          |
| 19     | D-Norleucine        | 182/114          |
| 20     | L-Norleucine        | 182/114          |
| 21     | γ-ABA               | 182/154          |
| 22     | D-Aspartic acid     | 184/212          |
| 23     | L-Aspartic acid     | 184/212          |
| 24     | EACA                | 210              |
| 25     | D-Glutamic acid     | 180/198          |
| 26     | L-Glutamic acid     | 180/198          |

\(^a\) Isoleucine enantiomers could not be separated using the Chirasil-L-Val column. Instead, D- and L-isoleucine enantiomers were separated using the Chirasil-Dex CB column.

\(^b\) Optically pure standard not available for enantiomeric identification. However, the order of elution of D-α-ABA and L-α-ABA was tentatively identified, as the enantiomer of D-amino acids elutes first followed by the L-enantiomer when using the Chirasil-L-Val column.

\(^c\) Enantiomers could not be separated under the chromatographic conditions.
Table 2. Summary of the average total amino acid abundances (in ppb) in the hydrolyzed and non-hydrolyzed fractions of the Paris meteorite (sample 1) measured by GC-MS. Separation of the D- and L-isovaline enantiomers was achieved on sample 2 of the Paris meteorite.

| Amino acid                  | Paris non-hydrolysed | Paris hydrolysed |
|-----------------------------|----------------------|------------------|
| **Linear α-amino acids**    |                      |                  |
| Glycine                     | 3380 ± 146           | 8252 ± 369       |
| D-Alanine                   | 296 ± 8              | 710 ± 32         |
| L-Alanine                   | 433 ± 43             | 961 ± 46         |
| D,L-α-ABA<sup>b</sup>      | 121 ± 4              | 306 ± 7          |
| D-α-ABA<sup>c</sup>        | 58 ± 3               | 145 ± 14         |
| L-α-ABA<sup>c</sup>        | 63 ± 4               | 161 ± 4          |
| D-Norvaline                 | <30<sup>b</sup>      | 155 ± 3          |
| L-Norvaline                 | <50<sup>b</sup>      | 178 ± 6          |
| D-Norleucine                | <1<sup>b</sup>       | <1<sup>b</sup>   |
| L-Norleucine                | <1<sup>b</sup>       | <5<sup>b</sup>   |
| **2-methyl α-amino acids**  |                      |                  |
| α-AIB                       | 87 ± 6               | 312 ± 10         |
| D,L-Isovaline<sup>d</sup>  | 26 ± 2               | 117 ± 4          |
| L-Isovaline (sample 2)<sup>e</sup> | n.d.     | 221 ± 7          |
| D-Isovaline (sample 2)<sup>e</sup> | n.d.     | 220 ± 16         |
| **Other branched α-amino acids** |                  |                  |
| D-Valine                    | 218 ± 8              | 574 ± 14         |
| L-Valine                    | 226 ± 28             | 614 ± 23         |
| D-Leucine                   | <1<sup>b</sup>       | <1<sup>b</sup>   |
| L-Leucine                   | <1<sup>b</sup>       | <1<sup>b</sup>   |
| **Non-α-amino acids**       |                      |                  |
| β-Alanine                   | 620 ± 28             | 1250 ± 152       |
| D,L-β-AIB<sup>b,d</sup>    | <1<sup>b</sup>       | <1<sup>b</sup>   |
| D,L-β-ABA<sup>b</sup>      | <1<sup>b</sup>       | <1<sup>b</sup>   |
| γ-ABA                       | 126 ± 10             | 185 ± 23         |
| EACA                        | <1<sup>b</sup>       | <1<sup>b</sup>   |
| **Dicarboxylic α-amino acids** |                  |                  |
| D-Aspartic acid             | 89 ± 4               | 135 ± 5          |
| L-Aspartic acid             | 120 ± 7              | 199 ± 5          |
| D-Glutamic acid             | 600 ± 48             | 828 ± 54         |
| L-Glutamic acid             | 720 ± 45             | 981 ± 80         |
| **Total**                   | 7,060 (45%)<sup>f</sup> | **15,760** |

<sup>a</sup>Quantification of the amino acids included background level correction using a serpentine blank. The associated errors are based on the standard deviation of the average value of eight to nine separate measurements (N) with a standard error, δx = σx . N<sup>1/2</sup>

<sup>b</sup>Optically pure standard not available for enantiomeric identification.

<sup>c</sup>Tentative identification of D- and L-isovaline, considering that the enantiomer of the D-amino acids elutes before the L-amino acid on a Chirasil-L-Val column.

<sup>d</sup>Enantiomers could not be separated with the chromatographic conditions when using a Chirasil-L-Val column.
Separation of the D- and L-isovaline enantiomers was achieved on sample 2 of the Paris meteorite by using a Chirasil-Dex CB column. Abundances were not included in the total amino acid concentration.

Total amino acid concentrations rounded to two significant digits.

Percentage of free amino acids in the non-hydrolysed extracts were calculated by dividing the free amino acid concentration by the total (free + bound) amino acid concentration measured in the hydrolyzed extracts.

These concentrations are upper limits and were not included in the total amino acid concentration.

n.d.- Not determined.
Table 3. L-enantiomer excess values (Lee (%)) of isovaline in the Paris meteorite, the CM chondrites Murchison, Murray, SCO 06043, and one racemic standard.\textsuperscript{a}

| Meteorite                  | Lee (%) ± \(\delta x\) (N) |
|----------------------------|-----------------------------|
| Paris (CM2.7/2.8)         | 0.3 ± 4.0 (9)               |
| Paris corrected (CM2.7/2.8)| -1.4 ± 2.6 (9)              |
| Murchison (CM2.5)\textsuperscript{b} | 18.5 ± 2.6 (20)           |
| Murchison (CM2.5)\textsuperscript{c} | 0 to 15.2 ± 0.2 to 1.3 (5 to 33) |
| Murray (CM2.4/2.5)\textsuperscript{d} | 6.0 (20)                   |
| SCO 06043 (CM2.0)\textsuperscript{e} | 16.5 ± 7.5 (8)             |
| Racemic isovaline standard\textsuperscript{f} | 1.8 ± 1.4 (14)             |

\textsuperscript{a}The values for the L-enantiomer excess (Lee (%)) are calculated using the equation Lee (%) = \([\frac{(L - D)}{(L + D)}] \times 100\), with uncertainties (\(\delta x\)) for N separate measurements obtained by standard propagation calculation. In the case of the Paris meteorite, the Lee (%) and the uncertainties (\(\delta x\)) are based, respectively on the absolute values and absolute errors showed in Table 2.

\textsuperscript{b}Data from Glavin and Dworkin (2009).

\textsuperscript{c}Data from Pizzarello et al. (2003) for several samples of the Murchison meteorite.

\textsuperscript{d}Data from Pizzarello et al. (2003).

\textsuperscript{e}Data from Glavin et al. (2011).

\textsuperscript{f}Used for Lee (%) correction of the Paris meteorite sample.
Table 4. Summary of the average total aliphatic (n-alkanes) hydrocarbon abundances (in ppb) in the Paris meteorite measured by GC-MS.

| Aliphatic Hydrocarbons | Paris     |
|------------------------|-----------|
| C_{16}H_{34}           | 697 ± 30  |
| C_{17}H_{36}           | 2499 ± 230|
| C_{18}H_{38}           | 1799 ± 91 |
| C_{19}H_{40}           | 722 ± 38  |
| C_{20}H_{42}           | 449 ± 22  |
| C_{21}H_{44}           | 406 ± 24  |
| C_{22}H_{46}           | 379 ± 25  |
| C_{23}H_{48}           | 311 ± 19  |
| C_{24}H_{50}           | 239 ± 16  |
| C_{25}H_{52}           | 170 ± 14  |
| Total                  | 7,670     |

Quantification of the hydrocarbons included background level correction using a serpentine blank. The associated errors are based on the standard deviation of the average value between six separate measurements (N) with a standard error, δx = σx . N^{-1/2}.
Table 5. Summary of the average total aromatic hydrocarbon abundances (in ppb) in the Paris meteorite measured by GC-MS. Molecular ions used for quantification and identification and are also displayed. Abundances for the CM chondrites Murchison and Yamato (Y)-791198 are also displayed.\textsuperscript{a,b,c}

| Aromatic Hydrocarbons         | Molecular ion (m/z) | Paris         | Murchison sample 1\textsuperscript{b} | Murchison sample 2\textsuperscript{b} | Y-791198\textsuperscript{c} |
|-------------------------------|---------------------|---------------|----------------------------------------|---------------------------------------|-----------------------------|
| Naphthalene                   | 128                 | n.d.          | 1120                                   | 6400                                  | 860                         |
| 1-Methylnaphthalene           | 142                 | n.d.          | 320                                    | 1000                                  | 160                         |
| 2-Methylnaphthalene           | 142                 | n.d.          | 320                                    | 1600                                  | 240                         |
| Dimethylnaphthalene           | 154                 | n.d.          | 240                                    | 200                                   | n.d.                        |
| Diphenyl                      | 154                 | n.d.          | n.d.                                   | n.d.                                  | 170                         |
| Acenaphthene                  | 156                 | n.d.          | 1120                                   | 5800                                  | 630                         |
| Fluorene                      | 166                 | n.d.          | 80                                     | 400                                   | n.d.                        |
| Phenanthrene                  | 178                 | 1662 ± 58     | 2560                                   | 4800                                  | 510                         |
| Anthracene                    | 178                 | 164 ± 11      | 50                                     | 100                                   | 390                         |
| Methylphenanthrene            | 192                 | n.d.          | 110                                    | 200                                   | n.d.                        |
| Fluoranthene                  | 202                 | 3455 ± 195    | 3700                                   | 4900                                  | 370                         |
| Pyrene                        | 202                 | 3089 ± 181    | 3300                                   | 4900                                  | 340                         |
| Benzo[b]anthracene            | 228                 | 22 ± 2        | n.d.                                   | n.d.                                  | n.d.                        |
| Benzo[a]phenanthrene          | 228                 | 24 ± 3        | n.d.                                   | n.d.                                  | n.d.                        |
| Triphenylene                  | 228                 | 83 ± 10       | n.d.                                   | n.d.                                  | n.d.                        |
| Benzo[c]phenanthrene          | 228                 | 82 ± 7        | n.d.                                   | n.d.                                  | n.d.                        |
| Benzo[a]pyrene                | 252                 | 90 ± 8        | n.d.                                   | n.d.                                  | n.d.                        |
| Benzo[e]pyrene                | 252                 | 52 ± 5        | n.d.                                   | n.d.                                  | n.d.                        |

\textsuperscript{a}Quantification of the hydrocarbons included background level correction using a serpentine blank. The associated errors are based on the standard deviation of the average value between six separate measurements (N) with a standard error, \( \delta x = \sigma x \cdot N^{1/2} \).

\textsuperscript{b}Data from Pering and Ponnampерuma (1971).

\textsuperscript{c}Data from Naraoka et al. (1988).

n.d. – Not detected.
Table 6. Amino acid enantiomeric ratios (D/L) in the Paris meteorite\textsuperscript{a}

| Amino Acid | Paris   |
|------------|---------|
| Aspartic acid | 0.72 ± 0.03 |
| Glutamic acid  | 0.84 ± 0.09 |
| Alanine    | 0.74 ± 0.05 |
| Valine      | 0.93 ± 0.04 |
| Norvaline  | 0.87 ± 0.03 |
| Isovaline  | 0.99 ± 0.08 |
| \(\alpha\)-ABA\textsuperscript{b} | 0.90 ± 0.09 |

\textsuperscript{a}The uncertainties are based on the absolute errors shown in Table 2, and are obtained by standard propagation calculation.

\textsuperscript{b}Optically pure standard not available for enantiomeric identification. The order of elution of D-\(\alpha\)-ABA and L-\(\alpha\)-ABA was tentatively identified, as the enantiomer of D-amino acids elutes first followed by the L-enantiomer when using a Chirasil-L-Val column.