Assessing the Effect of Aqueous Alteration on Soluble Organic Matter in Primitive Carbonaceous Chondrites: The Case of Asuka 12236

Serra, Coline; Vinogradoff, Vassilissa; Poinot, Pauline; Blancart Remaury, Quentin; Duvernay, Fabrice; Le Sergeant d'Hendecourt, Louis; Danger, Grégoire; Claeys, Philippe; Goderis, Steven; Schmitt-Kopplin, Philippe

Published in:
ACS Earth and Space Chemistry

DOI:
10.1021/acsearthspacechem.3c00106

Publication date:
2023

Citation for published version (APA):
Serra, C., Vinogradoff, V., Poinot, P., Blancart Remaury, Q., Duvernay, F., Le Sergeant d'Hendecourt, L., Danger, G., Claeys, P., Goderis, S., & Schmitt-Kopplin, P. (2023). Assessing the Effect of Aqueous Alteration on Soluble Organic Matter in Primitive Carbonaceous Chondrites: The Case of Asuka 12236: ACS Earth and Space Chemistry. *ACS Earth and Space Chemistry*, *7*(10), 1980-1991. [00106]. https://doi.org/10.1021/acsearthspacechem.3c00106

Assessing the effect of aqueous alteration on soluble organic matter in primitive carbonaceous chondrites: the case of Asuka 12236.

Coline Serra[1*], Vassilissa Vinogradoff [1*], Pauline Poinot[2], Quentin Blancart Remaury[2], Fabrice Duvernay[1], Louis Le Sergeant d'Hendecourt[1], Grégoire Danger[1,3], Philippe Claeys[4], Steven Goderis[4] and Philippe Schmitt-Kopplin[5.6,7].

[1]Aix-Marseille University, UMR CNRS 7345, PIIM, Institut Origines, Av. Escadrille Normandie Niemen, Centre Saint Jérôme, Marseille 13013, France; [2] Poitiers University, UMR CNRS 7285, IC2MP, Poitiers, France ; [3] Institut Universitaire de France ; [4] Analytical, Environmental & Geo-Chemistry, Vrije Universiteit Brussel, B-1050 Brussels, Belgium ;[5]Helmholtz Munich, Analytical BioGeoChemistry; Ingolstaedter Landstraße 1, 85764 Neuherberg, Germany ; [6]Technische Universität München, Analytische Lebensmittel Chemie; Maximus-von-Forum 2, 85354 Freising, Germany ; [7]Max Planck Institute for Extraterrestrial Physics; Gießebachstraße 1, 85748 Garching bei München, Germany.

* Corresponding authors: vassilissa.vinogradoff@univ-amu.fr, coline.serra@univ-amu.fr

Keywords: meteorites; aqueous alteration; soluble organic matter; amino acids; FTICR; liquid chromatohraphy; extraterrestrial carbon.

Abstract

Carbonaceous chondrites (CC) are considered the closest solid material to the composition of the early Solar System and can provide information on the origin of organic matter (OM) in the system and on Earth. Despite being primitive, their parent bodies have undergone secondary processes shortly after their formation (hydrothermal or metamorphism alterations) that blur their initial organic or mineral composition. The most primitive CC members are hence very precious to study the original composition. Here, we report the characterisation of the soluble organic matter (SOM) of Asuka 12236 classified among the most primitive members of the CM group in comparison with the SOM from other CM chondrites: Paris, Murchison and Aguas Zarcas. Analysis of these SOM were performed using several analytical techniques including elemental analysis, high resolution mass spectrometry and liquid chromatography coupled to different mass spectrometers. Our results show that Asuka 12236 has the lowest H content among the CMs studied here, and presents heterogeneity in its C content, likely indicating variable degrees of aqueous alteration. High resolution mass spectrometry analysis reveals that Asuka 12236 has a molecular diversity similar to the SOM of Murchison and Aguas Zarcas but with higher abundance of sulfur compounds more similar to Paris SOM. The content of organomagnesium-compounds indicates no high pressure or temperature stress but rather mid-temperature aqueous alteration for Asuka 12236, like Murchison SOM, but unlike Paris or Aguas Zarcas SOM. From liquid chromatography coupled with mass spectrometry analysis, we observed the highest concentration of amino acids in Asuka 12236 compared to the other CM chondrites considered here. Amino acids are mainly of alpha forms, witnessing of a Strecker formation or a formose-type reaction under low amounts of water, in agreement with the low H content recorded in this peculiar chondrite. This study of the SOM of chondrites with different alteration degrees highlights that organic compounds may be transformed much more rapidly than the minerals during hydrothermal alteration. This OM evolution depends on the amount of water and/or the temperature and/or pressure, leading towards significant transformation from one chondrite to another while the mineralogy can indicate a low degree of alteration. In addition to better assess the initial OM in chondrites, the impact of aqueous alteration on organic matter calls for additional laboratory experimentation.

1. Introduction

Carbonaceous chondrites (CC), considered the most primitive meteorites, can contain up to 5 % of organic matter (OM)[1]. They can thus provide insight into the initial composition of OM in the protoplanetary disk (see reviews by Remusat et al. [2] and Alexander et al. [3]). Their parent bodies, the asteroids, were formed among the first bodies of the solar system 4.56 billion years ago, and have remained virtually unchanged over time from the planets. However, mineralogical studies have revealed that secondary alteration processes have occurred in the CC parent bodies during the first tens of thousands of years after their formations [4]. These traces of alteration processes range from aqueous alteration (liquid fluid) to metamorphism (high temperature/pressure) which could have blurred the initial organic signatures in the same way as the minerals have been transformed. In this line, the less altered CCs are particularly interesting to study this secondary alteration and obtain clues about the initial composition of the accreted OM. The Mighei-subtype CC group (CM) contains some meteorites having low alteration degrees with a ~2wt% abundance of carbon, making them the most interesting samples for such studies compared to other sub-type groups [5].

To date, classification of the CC regarding the alteration degree (numbers from 1 to 3.0, the latter being the less altered) is only based on petrographic criteria such as volume of iron metal, phyllosilicates composition and quantity, and the chondrule composition [6]. Other criteria such as the hydrogen content (equivalent to water) has been proposed to be related with the alteration degree [7]. The organic matter in CC could also be an indicator of the alteration degree, but the impact of hydrothermal alteration on this OM is poorly constrained. This OM generally comprises a fraction of soluble organic matter (SOM) and a large content of insoluble organic matter (IOM) with a wide diversity of chemical families, which can provide clues on the hydrothermal history of the CC[2,8,9]. Among the organic molecules found in CCs, amino acids and nucleobases are particularly targeted to obtain information on the impact of the hydrothermal process. Indeed, amino acids have different mechanisms of formation leading to different ratios between α, β, γ, *etc* amino acids depending on the amount of water [10,11]. Compared to amino acids, nucleobases have been much less studied in chondrites because of analytical issues[12]. Nucleobases do present many isomers (as amino acids), which raise difficulties to conclude about their strict assignation and do not have chiral properties to discriminate about their extraterrestrial or terrestrial origin. A thorough and holistic characterization of the organic matter in CC is hence of prime importance for correlation with the alteration degree.

This study focuses on a very primitive CM, found in Antarctica in 2012 and recently classified as CM2.9: Asuka 12236[13,14]. Asuka 12236 has been jointly reported to have experienced very low degree of alteration with two other CMs, Asuka 12169 (3.0) and Asuka 12085 (2.8)[13,15]. We chose to study this CM chondrite due to its higher abundance of matrix (linked to the carbon abundance) and its availability for organic matter analysis, which require large mass. Its mineralogy reveals only few secondary alteration minerals such as phyllosilicates, and a high abundance of presolar grains indicating that its parent body would have undergone a low degree of secondary processes[13,14]. We questioned the low aqueous alteration degree of Asuka 12236, established by its mineralogy, by characterizing its soluble organic matter (SOM), and comparing it with SOM extracted from chondrites of the same subtype group but with different aqueous alteration degrees.

We have here studied and compared the SOM composition of Asuka 12236 with Paris (CM2.7-2.8)[16], Murchison (CM2.5)[6] and Aguas Zarcas (CM2)[17] by analyzing their elemental content (C, H, N, S) in bulk grains, and their SOM using Fourier-transform ion cyclotron resonance ultra-high resolution mass spectrometry (FTICR-MS). In addition, a new analysis searching for amino acids and nucleobases in our fragment of Asuka 12236 was performed using a new analytical workflow (liquid chromatography coupled with mass spectrometry). Results were compared to the previous analysis of Asuka 12236 [18] and with other chondrites from literature data [19,20,21]. This SOM comparison between CM chondrites highlights the effect of the low alteration degree of Asuka 12236. In particular, amino acids are key molecules as they can be tracers of the degree of hydrothermal alteration.

2. Materials and methods

2.1. Meteorite samples

Fragments of Asuka 12236 were retrieved during an expedition on the Nansen Ice field in East Antarctica in 2012 by VUB-ULB (Vrije Universiteit Brussel-Université Libre de Bruxelles) and allocated by the Royal institute of the Natural Sciences in Bruxelles. All the glassware material was washed and sonicated with methanol (Sigma Aldrich, UPLC grade), and sterilized at 120°C for 24 hours before use. All procedure of the meteorite extraction took place under a sterilised laminar flow hood (Thermo Fisher Scientific). To remove any surface contamination from the fragment (e.g., terrestrial dust), the whole meteorite fragment of 365 mg was sonicated with 1mL of milliQ water (Merck, conductivity < 18.2 MΩ.cm^{-1}). After centrifugation and removal of the supernatant, the rock was dried in a laminar flow hood (Thermo Fisher Scientific) for 10 hours. The fragment was subsequently crushed into smaller pieces for analysis. Other meteorites (Murchison, Paris and Aguas Zarcas) analyzed and discussed here were provided from personal collections and have followed the same procedure.

2.2. Extraction and Analysis

2.2.1. Elemental analysis

Elementary analyses to determine the proportion of elements C, H, N and S in the bulk were carried out on each chondrite (Asuka 12236, Paris, Aguas Zarcas and Murchison), taking two grains for each of about 2 mg. The analysis was performed using a Thermo Finnigan EA 1112 analyzer at the Spectropole of the *Fédération des Sciences Chimiques* in Marseille, France. Samples were combusted at 970 °C under helium gas with a flow at 140 mL/min. Gas released by combustion were separated by chromatography column and analysed using a thermal conductivity detector. The analytical error of the measure is about 0.1 wt.%.

2.2.2. FTICR analysis 150-1000 m/z

A total of <20 mg of each meteoritic material (for Asuka 12236, Paris, Aguas Zarcas) were used to extract the SOM with solvents allowing the preservation of meteoritic organics as described in Schmitt-Kopplin et al. [9]. The fragments were crushed and extracted with methanol (Sigma Aldrich, UPLC grade) at room temperature. The data of Murchison FTICR analyses are taken from the study published by Schmitt-Kopplin et al. [9].

The analyses were performed using a high-field FT-ICR mass spectrometer from Bruker Daltonics with a 12-T magnet from Magnex in a timedomain transient with 4 megawords, Fourier-transformed into a frequency domain spectrum. The frequency domain was afterward converted to a mass spectrum using the SolariX Control program of Bruker Daltonics. In total, 3,000 scans were accumulated for each mass spectrum in a mass range of 92–1,000 amu. Ions were accumulated for 300 ms before ICR ion detection. The ESI source (Apollo II; Bruker Daltonics) was used in negative ionization mode. The methanolic solutions were injected directly into the ionization source by means of a microliter pump at a flow rate of 120 µL·h^{-1} in ESI with a source heating temperature of 200 °C. After internal calibration, the mass spectra were exported to peak lists at a signal-to-noise ratio ≥3. Elemental formulas were calculated combinatorically within a mass accuracy window of ±0.2 ppm for each peak in batch mode by an in-house software tool and validated via the senior-rule approach/cyclomatic number, assuming valence 2 for S.

FT-ICR-MS analysis enables highly resolved ($R > 10^6$ at m/z 200) and accurate chemical mass analysis of electrospray generated ions within a 200-ppb error window over a wide mass range from m/z 100 to

1000. These exact masses of the ions can routinely be converted into unique compositional formula bearing the light elements C-, H-, N-, O-, S-, Mg (or any other element in the target), also taking account of their possible Cl and Na adducts and of their natural isotopic abundance.

The solvent extracts generated thousands of individual signals that were converted into elementary compositions (formulae); these are all represented in a van Krevelen type of diagrams (H/C vs. O/C) or related (H/C vs m/z) in which each formula is represented by a dot (the size of the dot is proportional to its relative intensity) as a projection of the relative oxygenation degree (O/C) and saturation degree (H/C) for various classes of compound types (CHO, CHNO, CHOS, CHNOS).

2.2.3. Chromatographic analysis

Chromatographic analyses were done only on the Asuka 12236 extracts. Data for other meteorites were found in the literature (Paris: [19]; Muchison: [20]; Aguas Zarcas: [21]). Although amino acid analyses have already been done on Asuka 12236 [18], in view of the heterogeneity of a meteorite we also performed amino acids analyses on our fragment, along with nucleobases analysis and compared it with previous work on Asuka 12236 and other chondrites.

Two different extractions of the SOM of Asuka 12236 were performed for these chromatographic analyses, one at 100 °C and another one at room temperature, both for 24h. For the 100 °C extraction, 226 mg of Asuka 12236 were powdered in an agate mortar and extracted with 1.2 mL of milliQ water (conductivity < 18.2 $M\Omega.cm^{-1}$) in a closed vial for 24h. For the room temperature extraction (25 °C) 108 mg were crushed in 1.0mL of milliQ water in a closed vial for 24h. After centrifugation, aqueous supernatants were aliquoted. For each extraction, one aliquot of 400µL was taken for the chromatography analysis. These two different aliquots were dried under N_2 flow (>99.999%, Air Liquid ALPHAGAZ 1) and remixed in 100µL of milliQ water. Procedural blanks were produced following the same procedure as the meteorite extraction (with 1.2 mL or 1mL of milliQ water at 100 °C or 25 °C respectively). This extraction technique without desalting, acid hydrolysis or derivatization steps allows access to the most pristine material of the meteorite. Indeed, the pre-treatment usually carry out on meteorite extracts often increase the loss and transformation of compounds in addition to introduce analytical biais [21,22].

Two types of chromatographic analyses were carried out on these extracted SOM fractions of Asuka 12236, a non targeted analysis and then a targeted one to search, detect and quantify nucleobases and amino acids.

2.2.3.1. Non targeted analysis of SOM beetween 50-750 m/z with UPLC-HRMS

Non-targeted analysis of Asuka 12236 SOM fraction was performed following the procedure described in Serra et al. [21]. Briefly, the meteorite extract was analysed by liquid chromatography coupled with High-Resolution Mass Spectrometer (Q-Exactive, Hybrid Quadrupole-Orbitrap Mass Spectrometer, Thermo Fisher Scientific) in the range of 50 to 750 m/z. This technique of high resolution allows to obtain the exact molecular ion mass of the compounds. See method detail in supplementary text.

2.2.3.2. *Targeted analysis of SOM with UPLC-MRM-MS analysis*

From the 100µL aliquot of the Asuka 12236 water extracts, 10µL were diluted by a factor 5 in water. For compound quantification, a standard addition procedure was performed. The standard addition procedure is used to facilitate amino acid identification due to the important matrix effects observed in meteoric samples impacting both retention times and intensities, which is different according to the amino acids [21]. Three standard solutions (SA) (SA-1, SA-2 and SA-3) were prepared (see table S2 in supplementrary informations for the different concentrations). Five microliters of each of the standard solutions were added in 10 µL meteoritic extract. Finally, 5 µL of this latest solution were injected.

A Shimadzu Nexera X2 UPLC system coupled to a 8060 triple quadrupole mass spectrometer (TQ MS) (Shimadzu) was used. This technique used multiple reaction monitoring mass spectrometry (MRM-MS) and enabled to obtain the identification of molecules from their transition (see Serra et al. [21] for MRM transitions and MS parameters). 53 amino acids and the 5 natural nucleobases (adenine, cytosine, thymine, guanine, uracil) were targeted with this method. Ionization was carried out by an ESI source working in the positive mode (see details in Serra et al. [21]). Amino acid enantiomers and nucleobases were separated on a chiral column (Crownpak CR (+), Chiral Technologies,). Elution was carried out at 600 µL.min^{-1} with water:methanol (95:5) with 0.5 % trifluoroacetic acid (Sigma-Aldrich).

The error bars on the concentrations were calculated from the directing coefficient and the y-intercept determined by the method of least squares for the corresponding line of 4 points (SA-0; SA-1, SA-2 and SA-3). Co-elution were observed for some amino acids (most of the time enantiomers) so their concentration are given as one single amino acid in Table 2. In the case of isomer co-elution, we also treated the signal as if it was a single amino acid and assumed that the co-eluted amino acids in the meteorite were in the same ratio as those in the standard. The concentration reported in Table 2 for the co-eluted amino acids is then the total.

3. Results

3.1. Elemental analysis

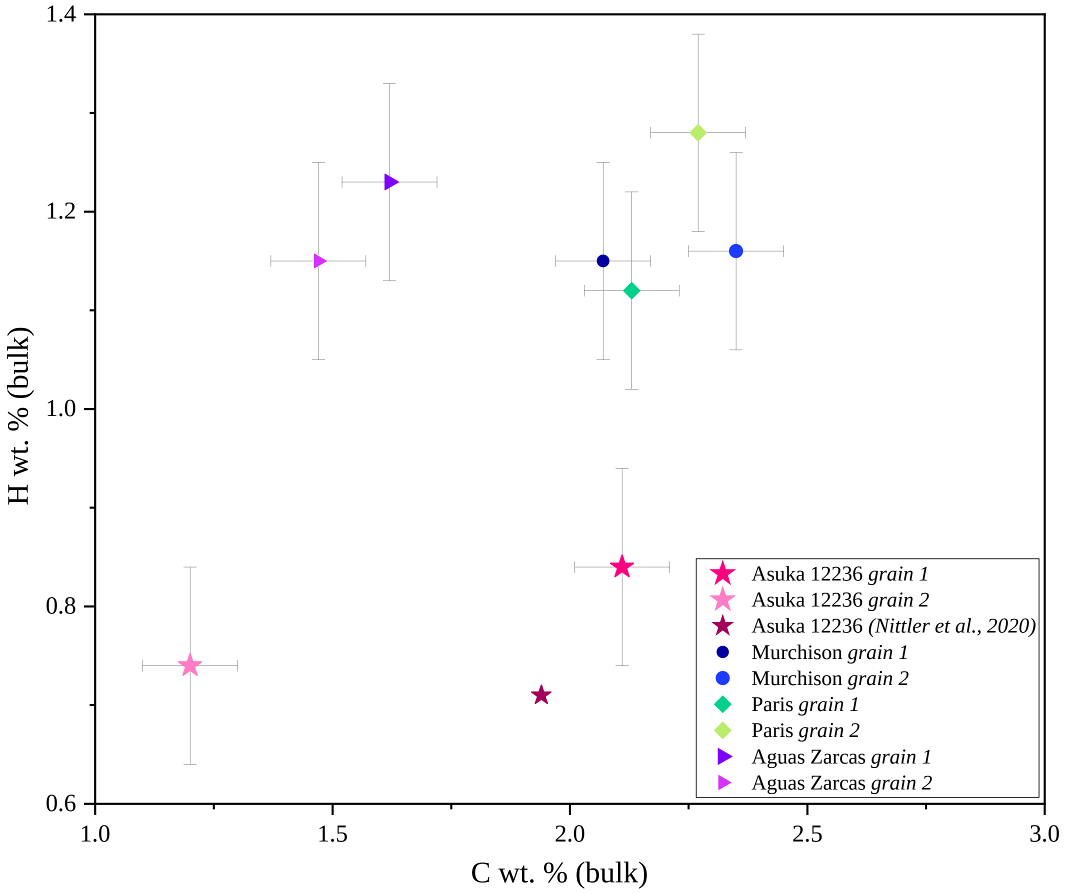


Figure 1. *Elemental analysis of C and H atoms in the different bulk fragments of Asuka 12236, Aguas Zarcas, Paris and Murchison measured in this study (see Table 1 for the data). Elemental analysis of one sample of Asuka 12236 from Nittler et al.* [23] *is reported for comparison. Error bars are 0.1w%.*

Elemental analysis of Asuka 12236 (two grains analyzed in this study and one by Nittler et al. [23]) revealed high heterogeneity in C content and more limited variability in H content (Figure 1, Table 1). Compared to Murchison (CM 2.5), Aguas Zarcas (CM2/CM1), and Paris (CM2.7-2.8), Asuka 12236 presents a low H content (<0.9 wt.%). To note, the grains of Paris analyzed here are likely from the most aqueously altered lithology because of the relatively high H content [16,24].

Asuka 12236 also contained sulfur (2.2-2.7 wt.%; Table 1), in a similar abundance to the other CM chondrites studied here, ranging between 2.5 and 4.3 wt.% (Murchison has the highest S content). Remarkably, the nitrogen content in the grains appears correlated with the carbon content of Asuka 12236, indicating its likely involvement in organic molecules. In addition, the N/C ratio of Asuka 12236 is the highest (~0.06) among the measured CM chondrites (0.04-0.05; Table 1).

Table 1. *The bulk Hydrogen, Carbon, Nitrogen and Sulfur elemental composition of chondrites analyzed in this study. For each meteorite, two grains were analyzed.*

	C %wt.	N %wt.	H %wt.	S% wt.	N/C	H/C
Asuka 12223 (grain 1)	2.11	0.13	0.84	2.67	0.06	0.40
Asuka 12236 (grain 2)	1.20	0.07	0.74	2.15	0.06	0.62
Asuka 12236 [23]	1.94	0.12	0.71	/	0.06	0.37
Murchison (grain 1)	2.07	0.09	1.15	4.29	0.04	0.56
Murchison (grain 2)	2.35	0.10	1.16	3.02	0.04	0.49
Paris (grain 1)	2.13	0.10	1.12	3.11	0.05	0.53
Paris (grain 2)	2.27	0.11	1.28	2.19	0.05	0.56
Aguas Zarcas (grain 1)	1.62	0.06	1.23	2.98	0.04	0.76
Aguas Zarcas (grain 2)	1.47	0.06	1.13	2.54	0.04	0.77

3.2. High resolution and non-targeted analysis of SOM: FTICR

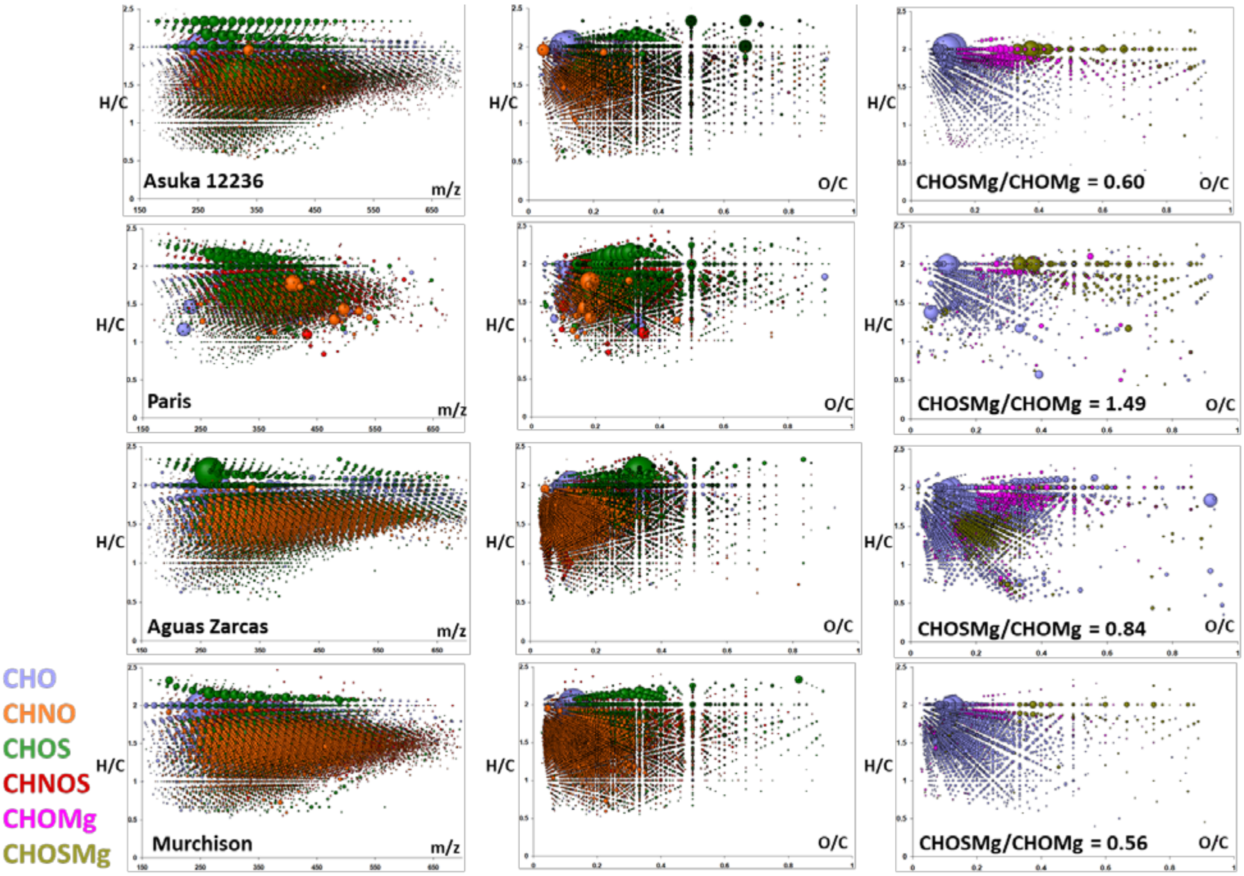


Figure 2. *Mass spectrometry data represented in van Krevelen diagrams of Asuka 12236 compared to Paris, Aguas Zarcas and Murchison meteorite. The colour code is expressed in the figure and the bubble sizes are related to the original signal intensity in the mass spectra.*

The FTICR-MS ESI(-) profiles of the methanol extracts of Asuka 12236 showed a complex and dense mass spectrometric signature with molecular signal distribution roughly in between Murchison/Aguas Zarcas and Paris. Asuka 12236 shows a diversity in low H/C molecules versus m/z (0.5<H/C<1) similar to Murchison and Aguas Zarcas, but resembles more of the Paris signature because of the poor distribution seen in high molecular masses (550-650 m/z). We note a unique linear molecular distribution of the CHOS formulae with high H/C ratio for Asuka 12236.

The Van Krevelen H/C versus O/C highlighted the differences in term of carbon oxidation state/oxygen content in the formulae (Figure 2, Figure S1), and Asuka 12236 had a high abundance of highly oxygenated compounds very similar to Aguas Zarcas also for its number of N and S per formulae (Figure S1).

The chemical families of organomagnesium compounds (CHOMg) were demonstrated to reflect high pressure stress [25] while the sulfurized organomagnesium compounds (CHOSMg) reflect high temperature stress [26]. Asuka 12236 shows similarity to Murchison in the temperature pressure history with a CHOSMg/CHOMg ratio of 0.60 and 0.56, respectively. However, Paris shows the highest value of the ratio reflecting possible thermal processing of the sample. Aguas Zarcas shows a high abundance in CHOSMg (rather aromatic) leading to the increase in the ratio and reflecting its previously described thermal history [27].

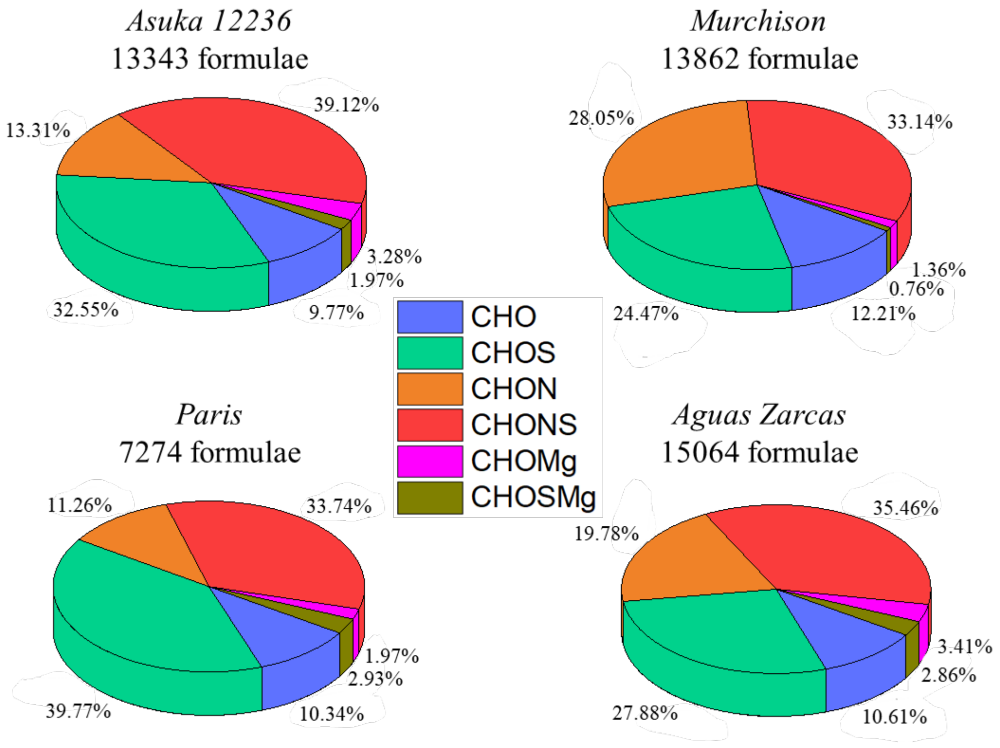


***Figure 3**. Relative distribution of the chemical families containing C, H, N, O, S and Mg atoms observed by FTICR in the SOM of Asuka 12236, Aguas Zarcas and Paris compared to the Murchison meteorite.*

Asuka 12236 contains around 13343 different formulae composed of C, H, N, O, S and Mg, essentially CHONS followed by the CHOS families. Compared with Murchison and Aguas Zarcas, measured under the same conditions (extraction, method and instrument), Asuka 12236 has a similar SOM diversity with a slightly higher sulfurization such as already observed with Aguas Zarcas. The Paris meteorite, considered to be very primitive, presented the same relative abundance for the molecular family as Asuka 12236 but twice less diverse in composition (Figure 3).

3.3. Targeted analysis of Asuka 12226 SOM using liquid chromatography coupled with mass spectrometry

Analyses searching for amino acids and nucleobases were done on our fragment of Asuka 12236 without acid hydrolysis of the extract, to reveal only the free amino acid content and investigate the effect of the low aqueous alteration degree on such polar molecules.

Two complementary analyses were done using Ultra Performance Liquid Chromatography coupled with High Resolution Mass Spectrometry (UPLC-HRMS) for the profiling of compounds with identification using their exact molecular ions masses and Ultra Performance Liquid Chromatography coupled with Multiple Reaction Monitoring Mass Spectrometry (UPLC-MRM-MS) to confirm amino acid and nucleobase identifications based on their MS characteristic transitions, and to provide their quantification. The analytical protocol is based on the work of Serra et al. [21] allowing analysis without any derivatisation nor desalting steps. Because of important matrix effect in meteorite samples (both in the intensity peak and shift of the retention time) as already observed in previous study [21] the quantification of amino acids is obtained by standard addition procedure.

Here, we were also especially attentive to extraction procedure and bias during analysis of the targeted molecules. To test the effect of temperature extraction, we have extracted the SOM from Asuka 12236 at 100°C and at room temperature (25°C).

After a first analysis in UPLC-HRMS (see UPLC-HRMS analysis in supplementary text), the final identification and quantification for amino acids and natural nucleobases were carried out coupling chiral column and mass tandem spectrometry apparatus to obtain fragmentation pattern (UPLC-MRM-MS) (see methods). The method allowed for a precise separation in a very short time analysis of a wide range of amino acid enantiomers (example in Figure 4).

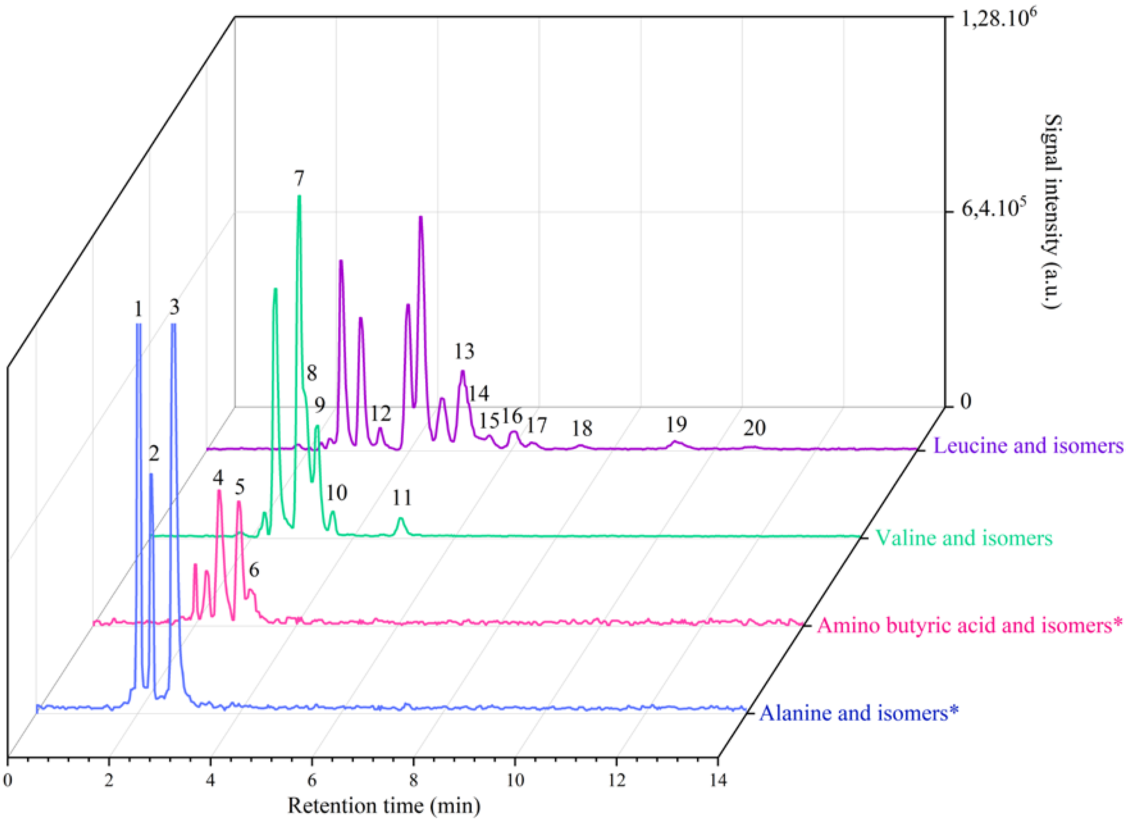


Figure 4. *Chiral separation using UPLC-MRM-MS on the aqueous extract at 100 °C of Asuka 12236.* ***1-20*** *: 1. sarcosine ; 2. D-alanine ; 3. β-alanine + L-alanine ; 4. N-ethylglycine ; 5. 2AIBA + D-2-ABA + L-3-ABA ; 5. L-2-ABA ; 6. D-3AIBA + L-3-AIBA + γ-ABA ; 7. D/L-isovaline + D-valine ; 8. L-valine ; 9. D-norvaline ; 10. 5-aminovaleric acid ; 11. L-norvaline ;12. D/L-β-leucine ;13. D-alloisoleucine ; 14. D-isoleucine ; 15. L-alloisoleucine ; 16. L-isoleucine ; 17. D-leucine ; 18. D-norleucine ; 19. L-leucine ; 20. L-norleucine. * Signals were increased by ten to be shown on the same intensity scale.*

Over the 53 amino acids present in the standard solution (*D* and *L* forms), 43 were detected by UPLC-MRM-MS in the 100°C extract and 41 in the room temperature extract (*D*/*L* -serine were not detected at room temperature) (Table 2). Arginine and tyrosine detected by UPLC-HRMS were not confirmed by UPLC-MRM-MS analysis and were therefore isomers in the first analysis (Table S3). Proline was a contaminant of the MRM-MS apparatus and therefore cannot be included in the list of quantified compounds. While histidine was not detect in UPLC-HRMS (Table S3) it has been detected by UPLC-MRM-MS analysis, which has better selectivity in a sample of this complexity (Figure S4).

Of note, no known amino acid or natural nucleobase contamination was found in the procedural blanks, only an unknown isomer of alanine was observed in the blank extracted at 100 °C indicating no terrestrial amino acid contamination during extraction or analytical procedures.

Cytosine, adenine and guanine previously detected by UPLC-HRMS were not validated in both extracts by UPLC-MRM-MS. For example, in figure S3 the different signals obtained on the two apparatuses for guanine in the 100°C extract were in reality indicative of a guanine isomer, confirmed with the procedure of standard addition.

Quantification by UPLC-MRM-MS was performed using standard addition method (Table 2). The standard addition procedure is illustrated for alanine, leucine, valine and aminobutyric acids families in figure S5. A significant matrix effect in retention time is observed for various amino acids such as L -isoleucine, D -leucine, D -norleucine, L -leucine, L -norleucine and histidine, and the standard addition procedure allow to confirm their identification. The concentrations of 39 and 37 amino acid enantiomers were respectively quantified in the 100°C and room temperature water extracts of Asuka 12236. For glycine, we were not able to firmly quantified it because of its bad ionization in ESI mode and matrix effect [21,28]. Regarding histidine, which has never been detected in a meteorite, a possible quantification is reported in table 2, however, due to co-elution of the enantiomers and the non identification by UPLC-HRMS we can not firmly confirm its indigeneous nature.

Table 2. *Concentrations of identified free amino acids (ppb) in Asuka 12236 water extracts at 100°C and room temperature determined by standard addition with UPLC-MRM-MS (see Materials and Method). Data are compared to previous identification and quantification of free amino acids by LC-FD-TOF/MS of Asuka 12236* [18]*, extracted by water for 24h at 100°C but analysed after desalting and derivatization with OPA/NAC (no hydrolysis).*

*Signs are: -: Not investigated; #: detected but not quantified due to interfering peaks or other analytical issue; *:possible quantification for histidine;* $^{\Delta}$: *co-elution observed for D-2-aminobutyric acid and L-2-aminobutyric acid in the work from Glavin et al.* [18].

Form of amino acids	Amino acids	Asuka 12236 (free content)		
		Tamb	100°C	Glavin et al, 2020
α	glycine	#	#	11635 ± 225
α	sarcosine	55573 ± 9847	33996 ± 3895	-
α	D-alanine	93106 ± 39053	19158 ± 2172	2227 ± 89
β	β-alanine	43485 ± 9360	19263 ± 3012	1167 ± 54
α	L-alanine			2316 ± 89
α	2-aminoisobutyric acid	960 ± 52	4009 ± 298	1753 ± 20
α	D-2-aminobutyric acid			1547 ± 103 $^{\Delta}$
β	L-3-aminobutyric acid			329 ± 11
α	L-2-aminobutyric acid	1024 ± 52	2160 ± 553	1547 ± 103 $^{\Delta}$
β	D-3-aminoisobutyric acid	288 ± 115	1050 ± 239	#
β	L-3-aminoisobutyric acid			#
γ	ɣ-aminobutyric acid			206 ± 10

α	D-serine	0	225 ± 98	129 ± 6
α	L-serine			292 ± 8
α	D-isovaline	1570 ± 195	4228 ± 858	457 ± 36
α	L-isovaline			480 ± 24
α	D-valine			597 ± 12
α	L-valine	577 ± 70	1412 ± 140	668 ± 24
α	D-norvaline	686 ± 101	1279 ± 157	284 ± 6
δ	5-Aminovaleric acid	132 ± 75	330 ± 112	-
α	L-norvaline	#	#	291 ± 6
β	D-β-leucine	123 ± 89	179 ± 71	-
β	L-β-leucine			
α	D-alloisoleucine	526 ± 37	707 ± 197	-
α	D-isoleucine	145 ± 54	281 ± 25	#
α	L-alloisoleucine	135 ± 71	247 ± 33	-
α	L-isoleucine	349 ± 103	400 ± 75	#
α	D-leucine	179 ± 33	268 ± 52	#
α	D-norleucine	156 ± 67	194 ± 44	-
α	L-leucine	470 ± 81	339 ± 34	#
α	L-norleucine	206 ± 60	194 ± 60	-
α	D-aspartic acid	613 ± 35	1148 ± 149	226 ± 27
α	L-aspartic acid	394 ± 88	984 ± 102	240 ± 13
α	D-glutamic acid	#	#	93 ± 10
α	L-glutamic acid	#	#	132 ± 15
α	D-phenylalanine	264 ± 74	468 ± 109	-
α	L-phenylalanine	304 ± 102	430 ± 84	-
α	D-histidine*	74 ± 33*	369 ± 39*	-
α	L-histidine*			
α	D-threonine	175 ± 47	1101 ± 118	#
α	D-homoserine			
α	L-threonine	242 ± 61	407 ± 180	#
α	L-homoserine	115 ± 33	4962 ± 1931	-

Based on the chiral analysis, we quantified two enantiomers of phenylalanine, aspartic acid, norleucine, leucine, isoleucine and alloisoleucine. We observed racemic proportions in the case of the L/D-phenylalanine, L/D-aspartic acid, and L/D-norleucine, which indicate that they are probably not terrestrial contamination. Isotopic analyses of these detected amino acids should be performed to definitely validate their origin. Excesses in L form were observable for leucine and isoleucine, which are classical Earth contaminations (Table 2). However, alloisoleucine has an enantiomeric excess in D-form. This can be explained by the epimerization at the C2-level to its diastereoisomers L-isoleucine [29,30] as it is observed in other chondrites like CM Murchison and the CM Murray [31].

For the extraction of small amino acids, like alanine isomers, the concentration obtained is higher in the room temperature extract (Figure S6-A). In contrast, the larger amino acids are present at a higher concentration with the extraction at 100°C (Figure S6-B). We thus observed an anti correlation between C2-C3 amino acids and C4 and more amino acids, which might suggest an effect of the extraction temperature.

Moreover, standard addition procedures highlighted the presence of many more isomers than those reported in Asuka 12236 extract (Figure S4; Figure S5; Table 2). We estimated that there are probably significantly more amino acids in the Asuka 12236 SOM than those firmly identified.

4. Discussion

4.1. A global look to the diversity of the SOM

Elemental analysis has revealed differences in the C and H content in the bulk of the chondrite suggesting some degree of heterogeneity in Asuka 12236 and in its OM distribution. As many CMs, Asuka 12236 can also present several lithologies since it has not been characterized as a breccia [13], enlightening this heterogeneity. According to Alexander et al. [7], it is possible to correlate the proportion of H to the amount of water seen by the parent body of the meteorite and thus to its alteration degree [7,32]. Asuka 12236 with 0.71< H %wt. <0.84 measured in this study, is therefore classified among the least altered chondrites (Figure 1), in agreement with its mineralogy [13,14].

The diversity of polar organic molecules in Asuka 12236 has been revealed by FTICR-MS analysis, showing the occurrence of around 13211 molecular formulae containing C, H, O, N and S, almost as much as in Murchison [9]. Most of the families present are sulphur-rich organic molecules (CHONS and CHOS) with a total of 72% for the Asuka 12236 SOM. A similar proportion is observed in the Paris SOM (74%), while Murchison and Aguas Zarcas contain around 58 and 63% respectively (Figure 3). Such distributions in the chondrites thus appear not to be correlated with the bulk abundance of sulfur seen by elemental analysis (Table 1), which also displayed inorganic sulfur. Interestingly, Paris and Asuka 12236, both classified as very primitive [13,14,16], have the same proportion of sulfur organic compounds. However, this organic sulfur does not present the same molecular distribution (Figure 2). The formation and evolution of sulfur-bearing phases in meteorites are uncertain, and to which extend secondary processes such as aqueous and mid-temperature heating could have allowed for the incorporation of sulfur with the organic molecules, remains unknown and needs further investigation. For example, Aguas Zarcas was shown to have a large heterogeneity in its matrix, and the extensive sulfurization of the OM (mainly under the form of polysulfurized compounds) was proposed to result from intensive aqueous alteration and heating [27]. Complementary investigations on the speciation of sulfur (aromatic vs aliphatic) in the SOM of Asuka 12236 and Paris in addition to the one in their IOM, could aid in deciphering the effect of aqueous alteration on the sulfur matter [33,34].

In addition, chemical families of CHOMg and CHOSMg have been proposed to provide information on high pressure and high temperature stress respectively undergone by the parent body [25,26]. The distribution of these compounds in Asuka 12236 is similar to Murchison composition, suggesting that the parent body of Asuka 12236 did not experience high pressure and high temperature conditions. On the contrary, Paris SOM seems to have undergone temperature stress seen by the high CHOSMg/CHOMg ratio (Figure 2), while petrologically classified as primitive as Asuka 12236. These results show that Asuka 122236 is hence only reflecting a low degree of aqueous alteration and temperature, in agreement with its mineralogy [13,14].

4.2. A closer look to amino acids and nucleobases

Asuka 12236 SOM not only has a very high diversity of amino acids but also the highest concentration of free amino acids to date, as previously shown by Glavin et al. [18] and observed here in our fragment. Comparing the sum of the concentration of 22 free amino acids present in the SOM of Asuka 12236 with those in the SOM of Paris, Murchison and Aguas Zarcas, we notice a concentration between 15 to 20 times higher in Asuka 12236 than for the other CM chondrites (Figure 5).

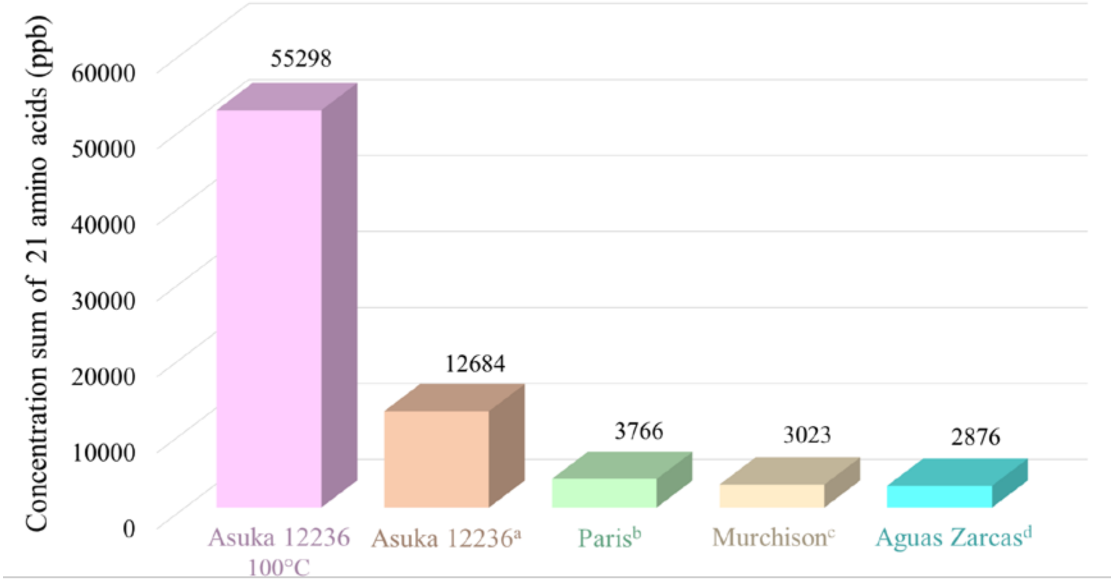


Figure 5. *Sum of the concentration of 21 free amino acids for different meteorite extracts at 100 °C. (L/D alanine, β-alanine, L/D-2-aminobutyric acid, 2-aminoisobutyric acid, L/D-3-aminobutyric acid, L/D-3-aminoisobutyric acid, γ-aminobutyric acid, L/D-aspartic acid, L/D-glutamic acid, L/D-leucine, L/D-valine and L/D-isovaline). From left to right: Asuka 12236 extracted at 100°C (this work), Asuka 12236*

studied by Glavin et al.,[18] *(a);Paris studied by Martins et al.,* [19] *(b); Murchison studied by Glavin et al.* [20] *(c); Aguas Zarcas studied by Serra et al.,* [21] *(d). Data presented here for comparison were from chondrites extracted at 100°C then analyzed without acid hydrolysis (free content in amino acids) but with different analytical techniques than here, involving desalting and derivatization steps (for Paris and Murchison analyses).*

The numerous and abundant amino acids found in Asuka 12236 are in agreement with previous analysis done by Glavin et al. [18] and their relative abundance is comparable in both studies (the smallest being the most important like alanine and isomers) (Table 2). The difference in the abundance in amino acids in our study compared to Glavin et al. [18] (5 times higher here) could be due to heterogeneity between the meteorite samples analysed (in agreement with elemental analysis, Figure 1). Indeed, this heterogeneity of organic matter within a single chondrite has already been observed on Murchison, for example, with numerous amino acid analyses on different fragments using the same protocol yielding significantly different amounts [22]. Furthermore, the difference observed can also be the result of the applied analytical protocol [21,35,36]. The analytical strategy used here was done without desalting nor derivatization steps on the extract, avoiding as much as possible the loss of small polar molecules. New extraction techniques for the detection of amino acids in extremely small samples for return mission also avoid desalting and HCl hydrolysis steps [35,36].

Among the CM chondrites, only one other meteorite has revealed such a high concentration of amino acids: Yamato 791198 [37,38], a CM2 with a similar degree of alteration as Murchison [7,39]. When taking the same 22 amino acids into account in figure 5, Yamato 791198 has about 33175 ppb of free amino acids, which is closer to the 55298 ppb reported for Asuka 12236 compared to others. Nonetheless, Yamato 791198 is more altered than Asuka 12236 and information on its bulk SOM composition (for example by FTICR) are missing.

The distribution of amino acids detected in Asuka 12236 SOM is consistent with an abiotic formation process, the smallest being the most abundant (sarcosine, L/D-alanine) (Table 2). One of the favored ways in aqueous conditions of forming amino acids is by Strecker reaction leading to the formation of α-amino acids (such as glycine, sarcosine, L/D-alanine; Table 1). Michael's addition allows the formation of β-amino acids and requires a larger amount of water than Strecker's synthesis [10]. Asuka 12236 with a large amount of α-amino acids is consistent with a preferential formation by Strecker reaction and a low amount of water. These results are in agreement with the previous studies correlating the relative abundance of amino acid forms to the aqueous alteration degree [11,22]. In addition, another mechanism of amino acid formation can occur during aqueous alteration: the formose ammoniated reaction, which can compete with the Strecker synthesis depending on the availability and abundance of precursors (HCN versus H_2CO and NH_3). In this case, not only α-amino acid but also β and γ can be produced [40–42]. In addition, amino acids as well as their precursos may have been formed during the evolution of ices from the dense molecular cloud to the protoplanetary disk, and therefore be initially incorporated into primitive bodies [43,44]. The high abundance of amino acids found in Asuka 12236 relative to the Paris chondrite is nonetheless surprising since both are primitive meteorites with a rather low degree of aqueous alteration. Altogether, it seems possible that the Paris and Asuka 12236 parent bodies, while being both CMs, did not receive the same initial pool of organic matter, the parent body of Asuka 12236 being initially richer in amino acids or in their precursors than that of Paris. Furthermore, as Paris SOM undergone temperature stress unlike Asuka 12236 (Figure 2), its amino acid or precursor contents could have been degraded during the alteration.

Even if Asuka 12236 is classified with a low degree of alteration, it has nevertheless undergone some water hydration with the likely transformation of the OM. For example, studies on organic molecules such as hexamethylenetetramine and other polar molecules (i.e. aldehydes) show a rapid degradation under low heating aqueous condition (150°C) [40–42,45,46,47]. Here, our extraction at 100°C of the SOM can mimic the conditions of a higher aqueous alteration and may thus have transformed some of the organic compounds hindering the real organics distribution. For example, we have observed that the extraction temperature (100°C versus room temperature) has an impact on the amino acids distribution (Figure S6). We may suggest that chemical reactions can occur during the extraction, especially for amino acids.

In addition, natural nucleobases were expected in Asuka 12236, because it belongs to the CM group [48]. However, none of the five natural nucleobases were identified in the SOM of Asuka 12236 thanks to the two complementary mass spectrometric analyses (UHPLC- HRMS and MRM-MS). Instead, many isomers are likely present (Figure S3) but the lack of standards did not allow their identifications and request further investigations. Interestingly, Murchison and Aguas Zarcas do contain guanine in their SOM [21,48,49] which could suggest that nucleobases are related to the aqueous alteration degree.

4.3. A wider look to the primitivity of the chondrite

According to its mineralogy, Asuka 12236 was classified as part of the CM group with a low water alteration degree: CM2.9 [13]. This classification is based on petrographic information such as iron volume, volume of phyllosilicates and mafic silicates in the chondrules or measurement of the chemical composition of the phyllosilicates [13,14].

We questioned here the low aqueous alteration degree of Asuka 12236, seen by its mineralogy, by characterizing its soluble organic matter (SOM), and comparing it with SOM extracted from chondrites having higher degree of aqueous alteration. At first glance, such task can be seen as particularly difficult due to the large uncertainties regarding the initial organic abundance and composition in the parent body, and the conditions of aqueous alteration (including minerals). Several hints from its organic content indicate that Asuka 12236 has nonetheless undergone a low degree of mid-temperature aqueous alteration: 1) the low content in H equivalent to the water content in hydrated minerals (Figure 1); 2) the high N/C ratio, while nitrogen bearing molecules are sensitive to aqueous alteration (Figure 1; Table 1) [45,50]; 3) the low ratio CHOMg/CHOSMg indicating no high pressure or temperature stress (Figure 2) [25,26] ; 4) the large abundance of amino acids whereas these molecules are sensitive to alteration (Table 2; Figure 5) [18,51] ; 5) the proportion of α-amino acids over the β, δ and γ amino acids testifying of a formation mechanism with a low water content (Table 2) [11,18,22].

Compared to the Paris chondrite, considered as a very primitive chondrite, Asuka 12236 has both greater diversity and abundance of SOM and amino acids [19], while being mineralogically classified as less altered than Paris [13]. Similar to Paris, Asuka 12236 has nonetheless clearly some signs of aqueous alteration but highly scattered and scarce [16,24,13,14].

Several scenarios can account for the evolution of organic matter in primitive chondrites, including Asuka 12236: 1) the composition of the accreted organic material, which can differ somehow from one source to the other (gas phase, ice-solid,…); 2) the conditions of aqueous alteration (quantity of fluid, temperature, pH); 3) the nature of the minerals around that will also be affected by aqueous alteration, changing the fluid conditions and type of interactions [52]. Even if the degree of alteration is low, the transformation of the organic matter may not be negligible leading to difficult correlations between the organic composition and alteration degree. We hypothesized that even if Asuka 12236 has undergone a low degree of aqueous alteration, its organic matter has rapidly reacted to this alteration with water, likely increasing the diversity of molecules to as high as more altered chondrites (like Murchison). This increase in organic diversity has been observed on asteroid analogs under aqueous alteration conditions [40,42,45,46].

However, probably due to a limited quantity of water in Asuka 12236, the chemical alteration stopped and signs of low alteration degree on the OM remain (such as the high abundance of α-amino acids). More studies are requested to assess if the composition of organic matter in meteorites may enable a more precise sensing of water alteration effects, which are the least predictable compared to pressure or temperature effects.

5. Conclusions

Here, from its content in soluble organic matter and in comparison with others chondrites, we try to understand the effect of aqueous alteration in Asuka 12236 OM, in agreement with its alteration degree as defined by the petrology (classified as CM2.9[13]). Elemental bulk analysis presents heterogeneity in the sample likely reflecting different lithologies in the chondrite. The overview of the molecular compounds presented in Asuka 12236 shows a high diversity of molecules, close to the Murchison one but with a richer composition in sulfur molecules (CHOS and CHONS families) more similar to Paris. However, the molecular distribution of the SOM shows that Asuka 12236 is less alterated than Paris, which suffered from temperature stress.

Targeted analysis searching for amino acids and nucleobases was performed on Asuka 12236 SOM. None of the five natural nucleobases are detected in the SOM of Asuka 12236 but isomers are present. Yet, a high diversity of amino acids is quantified (~ 40 amino acids with standard addition procedure), dominated by α-amino acids showing a preferential formation by Strecker or a formose type reactions. The abundance in amino acids found in Asuka 12236 is the highest to date among the CM chondrites. The SOM composition in Asuka 12236 can reflect a low degree of mid-temperature aqueous alteration since hints of primitivity remain (α-amino acids, low H content).

This study reinforces the difficulty of linking a low degree of alteration with the composition of OM since the organic compounds might be transformed much more rapidly than minerals during an episode of hydrothermal alteration. Additional studies on organic matter from the most primitive chondrites (such as Asuka 12269, the next in line after Asuka 12236) could bring new pieces for the alteration puzzle in carbonaceous asteroids [15]. Overall, we need also to better assess the transformation of the initial OM that was present in the protoplanetary disk during the first stage of aqueous alteration in the parent body to better understand the current organic composition of chondrites.

6. Acknowledgments

This research was carried out within research programs supported by the French National Space Agency (APR Prem’s, 5472, P.P.). V.V., G.D., F.D., and L.d’H. gratefully acknowledge support from the CNES, INSU and the national programms (PNP and PCMI) of CNRS/INSU France for supporting this research. We acknowledge Gregory Excoffier (Spectropole of the Fédération des Sciences Chimiques Marseille, Aix Marseille University) for his help with elemental analysis. P.C. and S.G. thank the VUB Strategic Research for support and BELSOP together with the International Polar foundation for making the collection of meteorites in Antarctica possible. Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)—Project-ID 364653263—TRR235 (CRC 235). We thank Zelimir Gabelica (Université de Haute Alsace, École Nationale Supérieure de Chimie de Mulhouse, F-68094 Mulhouse Cedex, France) for the Paris meteorite.

7. Supporting information

Supplementary information is provided to detail the chromatographic methods and present more graphic results for the high-resolution analysis and the targeted analysis of amino acids.

8. References

(1) Pearson, V. K.; Sephton, M. A.; Franchi, I. A.; Gibson, J. M.; Gilmour, I. Carbon and Nitrogen in Carbonaceous Chondrites: Elemental Abundances and Stable Isotopic Compositions. *Meteorit. Planet. Sci.* **2006**, *41* (12), 1899–1918. https://doi.org/10.1111/j.1945-5100.2006.tb00459.x.

(2) Remusat, L. Organics in Primitive Meteorites. In *Planetary Mineralogy*; Lee, M. R., Leroux, H., Eds.; European Mineralogical Union, 2015; Vol. 15, p 0. https://doi.org/10.1180/EMU-notes.15.2.

(3) Alexander, C. M. O.; Cody, G. D.; De Gregorio, B. T.; Nittler, L. R.; Stroud, R. M. The Nature, Origin and Modification of Insoluble Organic Matter in Chondrites, the Major Source of Earth's C and N. *Geochemistry* **2017**, *77* (2), 227–256. https://doi.org/10.1016/j.chemer.2017.01.007.

(4) Brearley, A. J. The Action of Water. *Meteor. Early Sol. Syst. II* **2006**, *943*, 587–624.

(5) Scott, E. R. D.; Krot, A. N. Chondrites and Their Components. *Treatise Geochem.* **2003**, *1*, 711. https://doi.org/10.1016/B0-08-043751-6/01145-2.

(6) Rubin, A. E.; Trigo-Rodríguez, J. M.; Huber, H.; Wasson, J. T. Progressive Aqueous Alteration of CM Carbonaceous Chondrites. *Geochim. Cosmochim. Acta* **2007**, *71* (9), 2361–2382. https://doi.org/10.1016/j.gca.2007.02.008.

(7) Alexander, C. M. O.; Howard, K. T.; Bowden, R.; Fogel, M. L. The Classification of CM and CR Chondrites Using Bulk H, C and N Abundances and Isotopic Compositions. *Geochim. Cosmochim. Acta* **2013**, *123*, 244–260. https://doi.org/10.1016/j.gca.2013.05.019.

(8) Danger, G.; Ruf, A.; Maillard, J.; Hertzog, J.; Vinogradoff, V.; Schmitt-Kopplin, P.; Afonso, C.; Carrasco, N.; Schmitz-Afonso, I.; d'Hendecourt, L. L. S.; Remusat, L. Unprecedented Molecular Diversity Revealed in Meteoritic Insoluble Organic Matter: The Paris Meteorite's Case. *Planet. Sci. J.* **2020**, *1* (3), 55. https://doi.org/10.3847/PSJ/abb60f.

(9) Schmitt-Kopplin, P.; Gabelica, Z.; Gougeon, R. D.; Fekete, A.; Kanawati, B.; Harir, M.; Gebefuegi, I.; Eckel, G.; Hertkorn, N. High Molecular Diversity of Extraterrestrial Organic Matter in Murchison Meteorite Revealed 40 Years after Its Fall. *Proc. Natl. Acad. Sci.* **2010**, *107* (7), 2763–2768. https://doi.org/10.1073/pnas.0912157107.

(10) Elsila, J. E.; Aponte, J. C.; Blackmond, D. G.; Burton, A. S.; Dworkin, J. P.; Glavin, D. P. Meteoritic Amino Acids: Diversity in Compositions Reflects Parent Body Histories. *ACS Cent. Sci.* **2016**, *2* (6), 370–379. https://doi.org/10.1021/acscentsci.6b00074.

(11) S. Burton, A.; C. Stern, J.; E. Elsila, J.; P. Glavin, D.; P. Dworkin, J. Understanding Prebiotic Chemistry through the Analysis of Extraterrestrial Amino Acids and Nucleobases in Meteorites. *Chem. Soc. Rev.* **2012**, *41* (16), 5459–5472. https://doi.org/10.1039/C2CS35109A.

(12) Martins, Z. The Nitrogen Heterocycle Content of Meteorites and Their Significance for the Origin of Life. *Life* **2018**, *8* (3), 28. https://doi.org/10.3390/life8030028.

(13) Kimura, M.; Imae, N.; Komatsu, M.; Barrat, J. A.; Greenwood, R. C.; Yamaguchi, A.; Noguchi, T. The Most Primitive CM Chondrites, Asuka 12085, 12169, and 12236, of Subtypes 3.0–2.8: Their Characteristic Features and Classification. *Polar Sci.* **2020**, *26*, 100565. https://doi.org/10.1016/j.polar.2020.100565.

(14) Nittler, L. R.; Alexander, C. M. O.; Patzer, A.; Verdier-Paoletti, M. J. Presolar Stardust in Highly Pristine CM Chondrites Asuka 12169 and Asuka 12236. *Meteorit. Planet. Sci.* **2021**, *56* (2), 260–276. https://doi.org/10.1111/maps.13618.

(15) Noguchi, T.; Yabuta, H.; Itoh, S.; Sakamoto, N.; Mitsunari, T.; Okubo, A.; Okazaki, R.; Nakamura, T.; Tachibana, S.; Terada, K.; Ebihara, M.; Imae, N.; Kimura, M.; Nagahara, H. Variation of Mineralogy and Organic Material during the Early Stages of Aqueous Activity Recorded in Antarctic Micrometeorites. *Geochim. Cosmochim. Acta* **2017**, *208*, 119–144. https://doi.org/10.1016/j.gca.2017.03.034.

(16) Hewins, R. H.; Bourot-Denise, M.; Zanda, B.; Leroux, H.; Barrat, J.-A.; Humayun, M.; Göpel, C.; Greenwood, R. C.; Franchi, I. A.; Pont, S.; Lorand, J.-P.; Cournède, C.; Gattacceca, J.; Rochette, P.; Kuga, M.; Marrocchi, Y.; Marty, B. The Paris Meteorite, the Least Altered CM Chondrite so Far. *Geochim. Cosmochim. Acta* **2014**, *124*, 190–222. https://doi.org/10.1016/j.gca.2013.09.014.

(17) Garvie, L. A. J. Mineralogy of the 2019 Aguas Zarcas (CM2) Carbonaceous Chondrite Meteorite Fall. *Am. Mineral.* **2021**, *106* (12), 1900–1916. https://doi.org/10.2138/am-2021-7815.

(18) Glavin, D. P.; McLain, H. L.; Dworkin, J. P.; Parker, E. T.; Elsila, J. E.; Aponte, J. C.; Simkus, D. N.; Pozarycki, C. I.; Graham, H. V.; Nittler, L. R.; Alexander, C. M. O. Abundant Extraterrestrial Amino Acids in the Primitive CM Carbonaceous Chondrite Asuka 12236. *Meteorit. Planet. Sci.* **2020**, *55* (9), 1979–2006. https://doi.org/10.1111/maps.13560.

(19) Martins, Z.; Modica, P.; Zanda, B.; d'Hendecourt, L. L. S. The Amino Acid and Hydrocarbon Contents of the Paris Meteorite: Insights into the Most Primitive CM Chondrite. *Meteorit. Planet. Sci.* **2015**, *50* (5), 926–943. https://doi.org/10.1111/maps.12442.

(20) Glavin, D. P.; Elsila, J. E.; McLain, H. L.; Aponte, J. C.; Parker, E. T.; Dworkin, J. P.; Hill, D. H.; Connolly Jr., H. C.; Lauretta, D. S. Extraterrestrial Amino Acids and L-Enantiomeric Excesses in the CM2 Carbonaceous Chondrites Aguas Zarcas and Murchison. *Meteorit. Planet. Sci.* **2021**, *56* (1), 148–173. https://doi.org/10.1111/maps.13451.

(21) Serra, C.; Lange, J.; Remaury, Q. B.; Timoumi, R.; Danger, G.; Laurent, B.; Remusat, L.; Rodier, C. G.; Poinot, P. Integrative Analytical Workflow to Enhance Comprehensive Analysis of Organic Molecules in Extraterrestrial Objects. *Talanta* **2022**, *243*, 123324. https://doi.org/10.1016/j.talanta.2022.123324.

(22) Glavin, D. P.; Callahan, M. P.; Dworkin, J. P.; Elsila, J. E. The Effects of Parent Body Processes on Amino Acids in Carbonaceous Chondrites. *Meteorit. Planet. Sci.* **2010**, *45* (12), 1948–1972. https://doi.org/10.1111/j.1945-5100.2010.01132.x.

(23) Nittler, L. R.; Alexander, C. M. O.; Foustoukos, D.; Patzer, A.; Verdier-Paoletti, M. J. Asuka 12236, the Most Pristine CM Chondrite to Date. **2020**, 2276.

(24) Marrocchi, Y.; Gounelle, M.; Blanchard, I.; Caste, F.; Kearsley, A. T. The Paris CM Chondrite: Secondary Minerals and Asteroidal Processing. *Meteorit. Planet. Sci.* **2014**, *49* (7), 1232–1249. https://doi.org/10.1111/maps.12329.

(25) Ruf, A.; Kanawati, B.; Hertkorn, N.; Yin, Q.-Z.; Moritz, F.; Harir, M.; Lucio, M.; Michalke, B.; Wimpenny, J.; Shilobreeva, S.; Bronsky, B.; Saraykin, V.; Gabelica, Z.; Gougeon, R. D.; Quirico, E.; Ralew, S.; Jakubowski, T.; Haack, H.; Gonsior, M.; Jenniskens, P.; Hinman, N. W.; Schmitt-Kopplin, P. Previously Unknown Class of Metalorganic Compounds Revealed in Meteorites. *Proc. Natl. Acad. Sci.* **2017**, *114* (11), 2819–2824. https://doi.org/10.1073/pnas.1616019114.

(26) Matzka, M.; Lucio, M.; Kanawati, B.; Quirico, E.; Bonal, L.; Loehle, S.; Schmitt-Kopplin, P. Thermal History of Asteroid Parent Bodies Is Reflected in Their Metalorganic Chemistry. *Astrophys. J. Lett.* **2021**, *915* (1), L7. https://doi.org/10.3847/2041-8213/ac0727.

(27) Kerraouch, I.; Kebukawa, Y.; Bischoff, A.; Zolensky, M. E.; Wölfer, E.; Hellmann, J. L.; Ito, M.; King, A.; Trieloff, M.; Barrat, J.-A.; Schmitt-Kopplin, P.; Pack, A.; Patzek, M.; Hanna, R. D.; Fockenberg, T.; Marrocchi, Y.; Fries, M.; Mathurin, J.; Dartois, E.; Duprat, J.; Engrand, C.; Deniset, A.; Dazzi, A.; Kiryu, K.; Igisu, M.; Shibuya, T.; Wakabayashi, D.; Yamashita, S.; Takeichi, Y.; Takahashi, Y.; Ohigashi, T.; Kodama, Y.; Kondo, M. Heterogeneous Nature of the Carbonaceous Chondrite Breccia Aguas Zarcas – Cosmochemical Characterization and Origin of New Carbonaceous Chondrite Lithologies. *Geochim. Cosmochim. Acta* **2022**, *334*, 155–186. https://doi.org/10.1016/j.gca.2022.07.010.

(28) Antignac, J.-P.; De Wasch, K.; Monteau, F.; De Brabander, H.; Andre, F.; Le Bizec, B. The Ion Suppression Phenomenon in Liquid Chromatography–Mass Spectrometry and Its Consequences in the Field of Residue Analysis. *Anal. Chim. Acta* **2005**, *529* (1–2), 129–136. https://doi.org/10.1016/j.aca.2004.08.055.

(29) Pizzarello, S.; Huang, Y.; Alexandre, M. R. Molecular Asymmetry in Extraterrestrial Chemistry: Insights from a Pristine Meteorite. *Proc. Natl. Acad. Sci.* **2008**, *105* (10), 3700–3704. https://doi.org/10.1073/pnas.0709909105.

(30) Pizzarello, S.; Groy, T. L. Molecular Asymmetry in Extraterrestrial Organic Chemistry: An Analytical Perspective. *Geochim. Cosmochim. Acta* **2011**, *75* (2), 645–656. https://doi.org/10.1016/j.gca.2010.10.025.

(31) Pizzarello, S.; Zolensky, M.; Turk, K. A. Nonracemic Isovaline in the Murchison Meteorite: Chiral Distribution and Mineral Association. *Geochim. Cosmochim. Acta* **2003**, *67* (8), 1589–1595. https://doi.org/10.1016/S0016-7037(02)01283-8.

(32) Alexander, C. M. O.; Bowden, R.; Fogel, M. L.; Howard, K. T.; Herd, C. D. K.; Nittler, L. R. The Provenances of Asteroids, and Their Contributions to the Volatile Inventories of the Terrestrial Planets. *Science* **2012**, *337* (6095), 721–723. https://doi.org/10.1126/science.1223474.

(33) Naraoka, H.; Hashiguchi, M.; Okazaki, R. Soluble Sulfur-Bearing Organic Compounds in Carbonaceous Meteorites: Implications for Chemical Evolution in Primitive Asteroids. *ACS Earth Space Chem.* **2023**, *7* (1), 41–48. https://doi.org/10.1021/acsearthspacechem.2c00157.

(34) Orthous-Daunay, F.-R.; Quirico, E.; Lemelle, L.; Beck, P.; deAndrade, V.; Simionovici, A.; Derenne, S. Speciation of Sulfur in the Insoluble Organic Matter from Carbonaceous Chondrites by XANES Spectroscopy. *Earth Planet. Sci. Lett.* **2010**, *300* (3), 321–328. https://doi.org/10.1016/j.epsl.2010.10.012.

(35) Potiszil, C.; Yamanaka, M.; Ota, T.; Tanaka, R.; Kobayashi, K.; Nakamura, E. Detection of Meteoritic Amino Acids in Extremely Small Sample Sizes: Implications for Sample Return Missions. Preprints February 22, 2023. https://doi.org/10.20944/preprints202302.0374.v1.

(36) Potiszil, C.; Ota, T.; Yamanaka, M.; Sakaguchi, C.; Kobayashi, K.; Tanaka, R.; Kunihiro, T.; Kitagawa, H.; Abe, M.; Miyazaki, A.; Nakato, A.; Nakazawa, S.; Nishimura, M.; Okada, T.; Saiki, T.; Tanaka, S.; Terui, F.; Tsuda, Y.; Usui, T.; Watanabe, S.; Yada, T.; Yogata, K.; Yoshikawa, M.; Nakamura, E. Insights into the Formation and Evolution of Extraterrestrial Amino Acids from the Asteroid Ryugu. *Nat. Commun.* **2023**, *14* (1), 1482. https://doi.org/10.1038/s41467-023-37107-6.

(37) Shimoyama, A.; Harada, K.; Yanai, K. Amino Acids from the Yamato-791198 Carbonaceous Chondrite from Antarctica. *Chem. Lett.* **1985**, *14* (8), 1183–1186. https://doi.org/10.1246/cl.1985.1183.

(38) Shimoyama, A.; Ogasawara, R. Dipeptides and Diketopiperazines in the Yamato-791198 and Murchison Carbonaceous Chondrites. *Orig. Life Evol. Biosph.* **2002**, *32* (2), 165–179. https://doi.org/10.1023/A:1016015319112.

(39) Akai J.; Kanno J. Mineralogical study of matrix- and groundmass-phyllosilicates, and isolated olivines in Yamato-791198 and -793321: With special reference to new finding of 14 Å chlorite in groundmass. **1986**, *41*, 259–275.

(40) Kebukawa, Y.; Chan, Q. H. S.; Tachibana, S.; Kobayashi, K.; Zolensky, M. E. One-Pot Synthesis of Amino Acid Precursors with Insoluble Organic Matter in Planetesimals with Aqueous Activity. *Sci. Adv.* **2017**, *3* (3), e1602093. https://doi.org/10.1126/sciadv.1602093.

(41) Koga, T.; Naraoka, H. Synthesis of Amino Acids from Aldehydes and Ammonia: Implications for Organic Reactions in Carbonaceous Chondrite Parent Bodies. *ACS Earth Space Chem.* **2022**, *6* (5), 1311–1320. https://doi.org/10.1021/acsearthspacechem.2c00008.

(42) Vinogradoff, V.; Remusat, L.; McLain, H. L.; Aponte, J. C.; Bernard, S.; Danger, G.; Dworkin, J. P.; Elsila, J. E.; Jaber, M. Impact of Phyllosilicates on Amino Acid Formation under Asteroidal Conditions. *ACS Earth Space Chem.* **2020**, *4* (8), 1398–1407. https://doi.org/10.1021/acsearthspacechem.0c00137.

(43) Elsila, J. E.; Dworkin, J. P.; Bernstein, M. P.; Martin, M. P.; Sandford, S. A. Mechanisms of Amino Acid Formation in Interstellar Ice Analogs. *Astrophys. J.* **2007**, *660* (1), 911–918. https://doi.org/10.1086/513141.

(44) Meinert, C.; Filippi, J.-J.; de Marcellus, P.; Le Sergeant d’Hendecourt, L.; Meierhenrich, U. J. N-(2-Aminoethyl)Glycine and Amino Acids from Interstellar Ice Analogues. *ChemPlusChem* **2012**, *77* (3), 186–191. https://doi.org/10.1002/cplu.201100048.

(45) Vinogradoff, V.; Bernard, S.; Le Guillou, C.; Remusat, L. Evolution of Interstellar Organic Compounds under Asteroidal Hydrothermal Conditions. *Icarus* **2018**, *305*, 358–370. https://doi.org/10.1016/j.icarus.2017.12.019.

(46) Isono, Y.; Tachibana, S.; Naraoka, H.; Orthous-Daunay, F.-R.; Piani, L.; Kebukawa, Y. Bulk Chemical Characteristics of Soluble Polar Organic Molecules Formed through Condensation of Formaldehyde: Comparison with Soluble Organic Molecules in Murchison Meteorite. *Geochem. J.* **2019**, *53* (1), 41–51. https://doi.org/10.2343/geochemj.2.0551.

(47) Kebukawa, Y.; Kilcoyne, A. L. D.; Cody, G. D. EXPLORING THE POTENTIAL FORMATION OF ORGANIC SOLIDS IN CHONDRITES AND COMETS THROUGH POLYMERIZATION OF INTERSTELLAR FORMALDEHYDE. *Astrophys. J.* **2013**, *771* (1), 19. https://doi.org/10.1088/0004-637X/771/1/19.

(48) Callahan, M. P.; Smith, K. E.; Cleaves, H. J.; Ruzicka, J.; Stern, J. C.; Glavin, D. P.; House, C. H.; Dworkin, J. P. Carbonaceous Meteorites Contain a Wide Range of Extraterrestrial Nucleobases. *Proc. Natl. Acad. Sci.* **2011**, *108* (34), 13995–13998. https://doi.org/10.1073/pnas.1106493108.

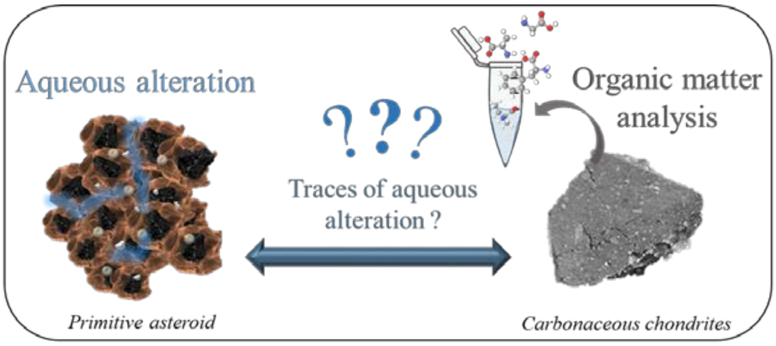
(49) Oba, Y.; Takano, Y.; Furukawa, Y.; Koga, T.; Glavin, D. P.; Dworkin, J. P.; Naraoka, H. Identifying the Wide Diversity of Extraterrestrial Purine and Pyrimidine Nucleobases in Carbonaceous Meteorites. *Nat. Commun.* **2022**, *13* (1), 2008.

(50) Danger, G.; Vinogradoff, V.; Matzka, M.; Viennet, J.-C.; Remusat, L.; Bernard, S.; Ruf, A.; Le Sergeant d’Hendecourt, L.; Schmitt-Kopplin, P. Exploring the Link between Molecular Cloud Ices and Chondritic Organic Matter in Laboratory. *Nat. Commun.* **2021**, *12* (1), 3538. https://doi.org/10.1038/s41467-021-23895-2.

(51) Burton, A. S.; Grunsfeld, S.; Elsila, J. E.; Glavin, D. P.; Dworkin, J. P. The Effects of Parent-Body Hydrothermal Heating on Amino Acid Abundances in CI-like Chondrites. *Polar Sci.* **2014**, *8* (3), 255–263. https://doi.org/10.1016/j.polar.2014.05.002.

(52) Vinogradoff, V.; Le Guillou, C.; Bernard, S.; Viennet, J. C.; Jaber, M.; Remusat, L. Influence of Phyllosilicates on the Hydrothermal Alteration of Organic Matter in Asteroids: Experimental Perspectives. *Geochim. Cosmochim. Acta* **2020**, *269*, 150–166. https://doi.org/10.1016/j.gca.2019.10.029.

FOR TOC ONLY


Aqueous alteration
???
Traces of aqueous alteration ?
Organic matter analysis
Primitive asteroid
Carbonaceous chondrites