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## Ultrasound assisted extraction of amino acids and nucleobases from clay minerals and astrobiological samples

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### ABSTRACT

The study of organic molecules in meteorite and return samples allows for the understanding of the chemistry that undergoes in our Solar System. The present work aims at studying ultrasound assisted extraction technique as effective extraction method for these molecules in extraterrestrial samples and analogs. Optimal conditions were selected from the investigation of ultrasonic frequency, irradiation duration and solvent effects on amino acids, nucleobases and dipeptides extraction yields from a model clay-rich mineral matrix. Optimal ultrasound-assisted extraction parameters were frequency of 20 kHz within 20 min irradiation time and methanol/water solvent ratio of 1. We then validated this protocol on Mukundpura and Tarda meteorite fragments and compared it to the reference extraction protocol used in astrobiology and based on 24 h extraction time at 100 °C in water. We obtained similar quantitative results without any racemization with both methodologies.

### 1. Introduction

The study of organic molecules in meteorites has been an objective of space exploration missions so far. It unveils fundamental insights into our Solar System history and how precursor materials of life may have been seeded on Earth [1–8]. Over the past five decades, improvements in analytical instrumentation allowed the detection of thousands of molecules in such extraterrestrial samples [9–12]. However, very few studies were dedicated to the extraction step of these compounds from such complex matrices. Hot water extraction (100 °C, 24 h) was and is still the reference extraction method for amino acids [11,13–16]. Recently, alternative techniques have emerged, among which ultrasound-assisted extraction (UAE) [17–19] is promising. Ultrasounds indeed trigger intense mixing and acoustic microstreaming known as local shear stress that contributes to higher transfer rates of compounds from solid to liquid media [20,21]. Ultrasounds can also facilitate this transfer by increasing solvent penetration inside the solid matrix [22,23]. Typically, at low frequency ultrasound (20–80 kHz) irradiation, the generation of cavitation bubble at critical unstable size, sudden

implosion liberates intense energy near the solid matrix surface through a shockwave that could fragment the solid [24]. They increase exchange surface area and allow access to internal surfaces and trapped compounds [17]. Therefore, ultrasonic extraction could circumvent the problem of strong mineral-organic interactions [25]. In Paris meteorite, the organic matter was found to be spatially associated with the fine-grained and partially-hydrated amorphous silicates [26]. Strong interactions are particularly observed with clay minerals, especially with swelling clays i.e. phyllosilicates such as smectites like montmorillonite [27,28].

In this work, we investigated the efficacy of ultrasounds for the extraction of molecules from clay minerals and astrobiological samples. A first set of experiments revealed an optimized ultrasonic extraction of 20 kHz frequency within an irradiation time of 20 min. The optimized ultrasonic extraction was finally compared to the reference one for two meteorites, Mukundpura (with 90 vol% phyllosilicates) [29] and Tarda meteorite (72 vol% phyllosilicates) [30].

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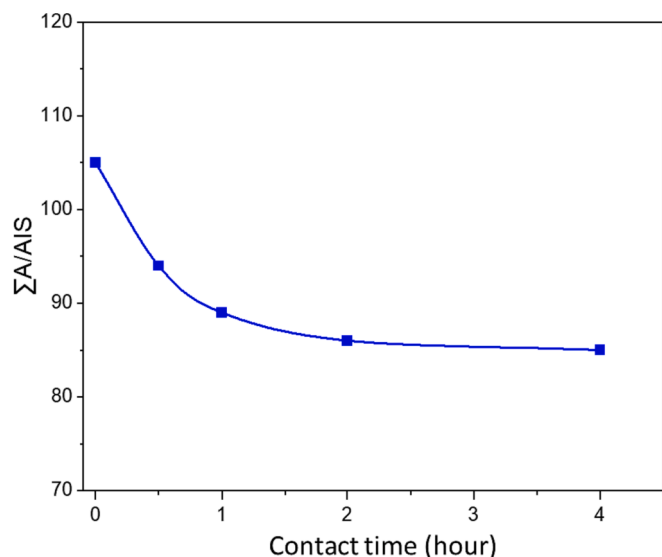


Fig. 1. Evolution of total organics amount in supernatant with contact time.

Table 1  
Taguchi L<sub>16</sub> experiments.

Experiment	Factors		
	Frequency	Methanol	Time
1	20 kHz	0 %	5 min
2	20 kHz	25 %	10 min
3	20 kHz	50 %	20 min
4	20 kHz	75 %	40 min
5	578 kHz	0 %	10 min
6	578 kHz	25 %	5 min
7	578 kHz	50 %	40 min
8	578 kHz	75 %	20 min
9	864 kHz	0 %	20 min
10	864 kHz	25 %	40 min
11	864 kHz	50 %	5 min
12	864 kHz	75 %	10 min
13	1140 kHz	0 %	40 min
14	1140 kHz	25 %	20 min
15	1140 kHz	50 %	10 min
16	1140 kHz	75 %	5 min

## 2. Materials and methods

### 2.1. Reagents and chemicals

Amino acids standard solution of 17 amino acids containing glycine, L-alanine, L-valine, L-leucine, L-isoleucine, L-proline, L-methionine, L-serine, L-threonine, L-phenylalanine, L-aspartic acid, L-glutamic acid, L-lysine, L-tyrosine, L-cystine, L-arginine and L-histidine all at  $2.5 \cdot 10^{-3}$  mol/L in 0.1 N HCl except L-cystine ( $1.25 \cdot 10^{-3}$  mol/L) was purchased from Sigma Aldrich. Lyophilized powders of 3 dipeptides, glycyglycine (Gly-Gly), glycyalalanine (Gly-Ala), alanylalanine (Ala-Ala) and 5 nucleobases adenine, guanine, thymine, cytosine and uracil all above 98 % purity, were purchased from Sigma Aldrich. For experiments, a standard stock solution was prepared at  $10^{-4}$ M in milliQ water ( $18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$ ) and used for the entire study. Methanol and Trifluoroacetic acid (TFA) used for mobile phase were of analytical grade ( $\geq 98$  %, Sigma-Aldrich). L-alanine- $1\text{-}^{13}\text{C}$  ( $\geq 99$  %, Sigma Aldrich) was used as an internal standard for LC-MS/MS analysis.

### 2.2. Instrumentation

Low frequency ultrasonic extraction was performed using a Vibra-Cell (Sonics, Newtown, USA) focused ultrasonic system operating at a

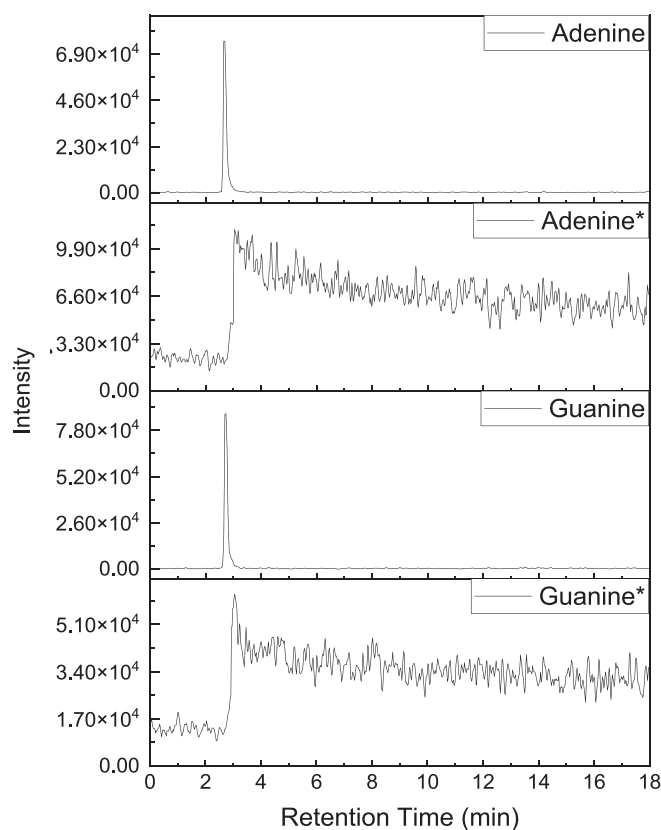


Fig. 2. UPLC-MS/MS TIC of adenine and guanine before and after contact (labelled\*) with montmorillonite.

fixed 20 kHz frequency and equipped with a 2-mm microprobe. Higher frequencies were applied by a piezo-electric system which included a variable generator linked to transducers operating at 578 kHz, 864 kHz and 1140 kHz (MEINHARDT Ultrasonics, Germany). Temperature was kept at an average 25 °C with a Minichiller cooler (Huber).

### 2.3. Mineral matrix

SWy-3 montmorillonite was purchased from the Clay Mineral Society (Chantilly, USA). The  $< 1 \mu\text{m}$  fraction was collected by centrifugation and Na-saturated using three saturation cycles in a 1 M NaCl solution. The excess of salt was removed by dialysis until chlorine ions were no more detected by  $\text{AgNO}_3$  test. Samples containing 60 % silica (purchased from Fisher Scientific (Leics, UK)) and 40 %  $\text{Na}^+$  montmorillonite were set as the experimental mineral matrices for this study. 200 mg were spiked with 2 mL of targets solution at 0.1 mM and stirred for 2 h in each glass reactor. Preliminary tests showed that organic molecules amount in the supernatant was constant after 2 h (Fig. 1). The solution was left to settle for 15 min, then recovered and centrifuged for 12 min at 15000 rpm. Mineral matrix was dried overnight at 40 °C. Supernatant was analyzed by UPLC-MS/MS. For all 16 experiments, supernatants were at similar concentration matching an average of 75 % of the initial spiking concentration. The average 25 % retained on the mineral was then defined as the targeted amounts of organics.

### 2.4. Experiments

According to literature, ultrasound frequency and irradiation time are two of the most key parameters on ultrasound-assisted extraction as they affect cavitation phenomenon [23,31,32]. Solvent type is also an important factor since it directly influences the solubility of organic compounds. Therefore, these were the key variables to be considered. A

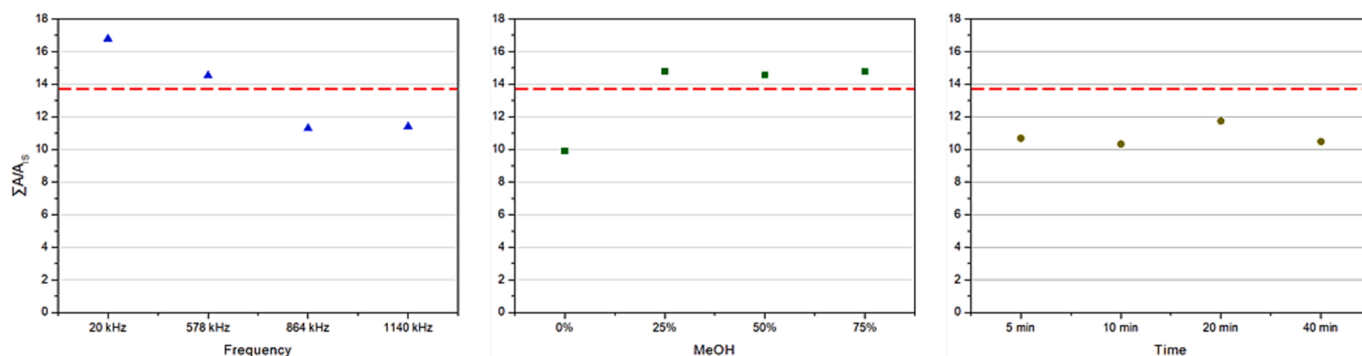


Fig. 3. Frequency, %MeOH and duration effects on molecules recoveries.

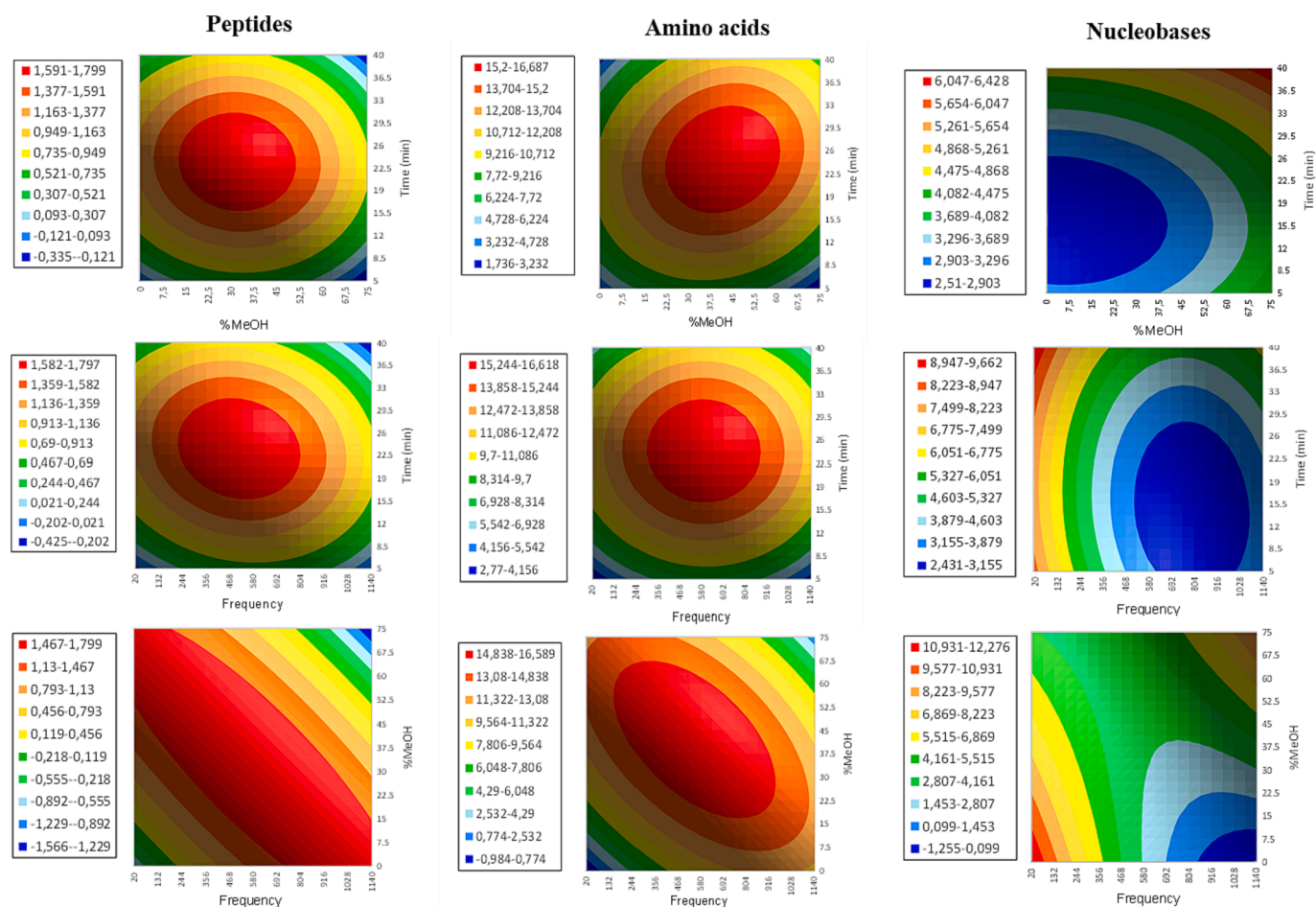


Fig. 4. Surface plots of amino acids, peptides and nucleobases recoveries in function of frequency, %MeOH and duration.

fractional factorial experimental design was set with these three parameters. The Taguchi  $L_{16}$  orthogonal array is detailed in Table 1.

### 3. Extraction of spiked mineral matrix

In each glass reactor, 4 mL of solvent were added to the dried sample. For 20 kHz experiments, the ultrasonic probe was introduced inside the reactor which was then sealed to limit solvent evaporation during extraction. For higher frequencies, the reactor was directly sealed and submerged in the jacketed glass ultrasonic reactor. At the end of the extraction, the mineral matrix suspension was removed by centrifugation for 15 min at 15000 rpm and the solution was recovered for analysis. To 10  $\mu\text{L}$  of each extract, 10  $\mu\text{L}$  of a  $5.10^{-5}$  M L-alanine- $^{13}\text{C}$  and 80

$\mu\text{L}$  of mobile phase were added.

### 4. Extraction of meteorites

Preceding subsampling of the meteorite specimens, the fragments of Tarda and Mukundpura were rinsed at room temperature with a 1 mL  $\text{H}_2\text{O}/\text{MeOH}$  (1:1, v:v) for 5 min then dried at  $40^\circ\text{C}$ . Tarda meteorite collapsed in the rinsing solution as it is mainly constituted of friable materials [33,34]. Consequently, there is no direct way of separating native organic molecules from environmental earth contaminant for Tarda samples. Specimen were subsampled and powdered in an agate mortar then divided into 2 samples. Mukundpura meteorite was split in 2 samples of 200 mg each while Tarda was split in 2 samples of 350 mg.

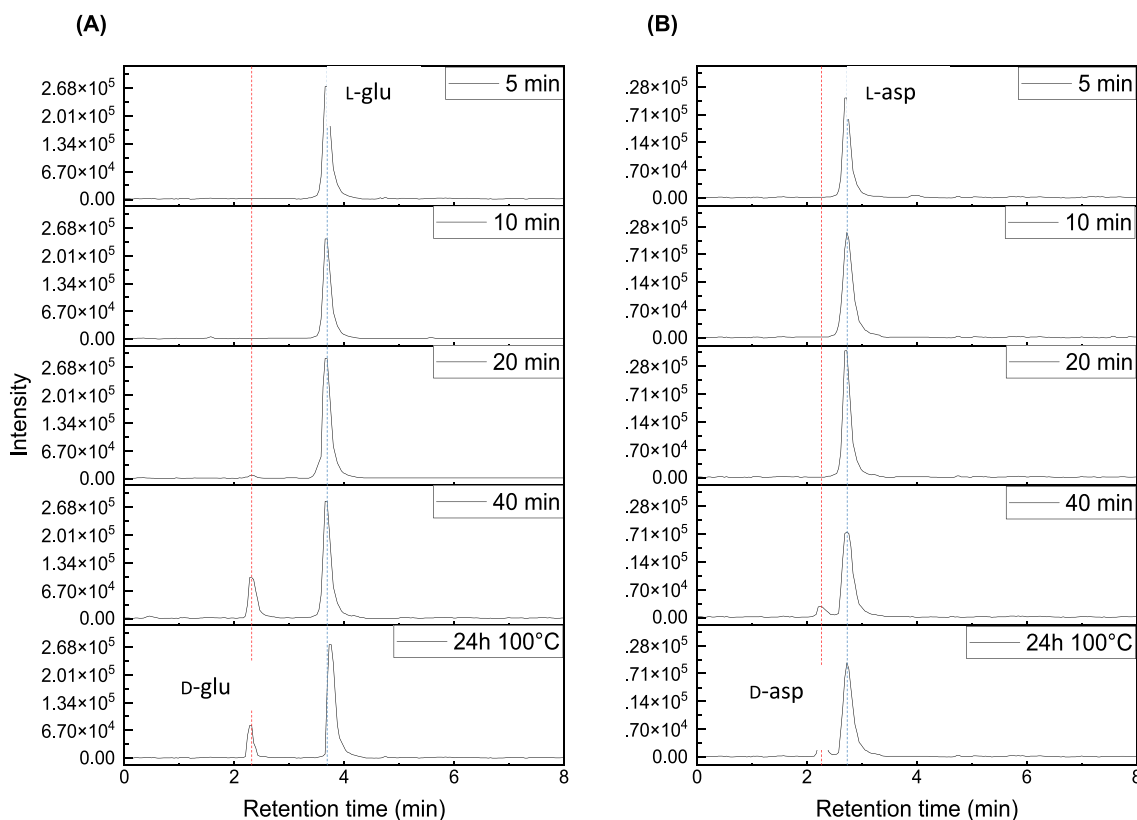


Fig. 5. TIC chromatograms representing time effect on glutamic acid (A) and aspartic acid (B) in a standard solution of L-amino acids exposed to 20 kHz ultrasounds compared to results of exposure to the reference method conditions (24 h 100 °C).

For one sample, the powder was transferred in a clean glass vial and a 2 mL H<sub>2</sub>O/MeOH (1:1, v:v) solution was added. 20 kHz ultrasonic extraction was performed for 20 min following the optimized protocol then supernatant was recovered for analysis after centrifugation at 15000 rpm for 15 min. For the second, 2 mL of milliQ water was added then the reactor was filled with N<sub>2</sub> atmosphere, sealed and placed in the oven at 100 °C for 24 h. Finally, the liquid phase was recovered and centrifuged at 15000 rpm for 10 min. 200 µL of each extract was evaporated to dryness under N<sub>2</sub> and solubilized in 15 µL of H<sub>2</sub>O/MeOH or H<sub>2</sub>O respectively. 5 µL of a 5.10<sup>-6</sup> M aqueous solution of L-alanine-1-<sup>13</sup>C was added to each sample before analysis and quantification

#### 4.1. UPLC-MS/MS analysis

UPLC-MS/MS analysis was performed on a Shimadzu Nexera X2 UPLC-8050 coupled to a triple quadrupole mass spectrometer (Shimadzu, Kyoto, Japan) equipped with a Crownpak CR guard column (10 mm x 4.0 mm, 5 µm film thickness, Chiral Technologies Europe, Illkirch-Graffenstaden, France) in line with a Crownpak CR(+) chiral analytical column (150 mm x 4.0 mm, 5 µm film thickness, Chiral Technologies). A water/methanol (95:5, v/v) with 0.5 % TFA mobile phase was used at a constant flow of 650 µL.min<sup>-1</sup>. 5 µL of the resulting solution were injected.

## 5. Results and discussion

### 5.1. UAE parameter effects

Results were expressed as the sum of chromatographic responses (ratio of compound area over internal standard area). All molecules were detected and quantified, except adenine and guanine (Fig. 2). Indeed, fine clay particles could have strongly associated with these nucleobases thus leading to peak tailing. Adenine and guanine were thus

not further considered for the quantitative analysis.

We first tested three extraction factors (frequency, concentration of MeOH, and time) which could influence extraction yields of 23 targeted molecules. For that, a Tagushi plan was constructed and resulted in 16 experiments that allow investigation of 4 levels of the 3 factors. The chromatographic response of the experiments in function of factors is shown in Fig. 3. Mean recovery corresponds to 65 % yields (Red dashed line in Fig. 3).

Ultrasound frequency and amount of methanol had a significant effect of the extraction process whereas ultrasound irradiation duration has no major effect on recoveries. A 33 % decrease in recovery was noticed with increasing frequency (from low to high frequency). Low frequencies could ease shear forces produced by cavitation and mass transfer rate. Indeed, as shown earlier, physical effects produced by ultrasounds are effective at low frequencies, from 20 kHz to 80 kHz, due to longer rarefaction phase allowing for the growth of cavitation bubbles [35]. Similar results were observed for 864 and 1140 kHz that could be a due to lower rates of hydroxyl radical formation (OH-radicals not quantified because it is out of scope of this work) at 20 kHz and 1.1 MHz compared to 300 – 800 kHz frequencies [36]. This could indeed prevent molecules from degradation.

Moreover, a 50 % decrease in recovery was observed when methanol was omitted but recoveries were similar for other MeOH percentages. The results could be related to the improved compounds solubility in methanol rather than methanol extraction efficacy.

We next studied UAE effect on our molecular targets' structure and properties. To this end, we studied response surface plots of each family (amino acids, nucleobases and peptides) (Fig. 4).

Nucleobases recoveries differed significantly with the factors. The 3 detected nucleobases are better recovered with low frequencies, high methanol percentage and long duration.

On the other hand, no significant difference was observed for amino acids and peptides recoveries. The same tendency was observed when

**Table 2**

Amino acids and nucleobases identified and quantified for Mukundpura and Tarda following UAE and Hot water extraction protocols.

Compounds	Quantification (nmol/g)			
	Mukundpura 20 kHz UAE	Mukundpura H <sub>2</sub> O 24 h 100 °C	Tarda 20 kHz UAE	Tarda H <sub>2</sub> O 24 h 100 °C
Glycine	56.1	46.69	40.61	32.52
Sarcosine	9.66	7.76	1.02	0.97
D-Alanine	24.80	34.45	<LOQ	0.98
β-Alanine	20.90	32.82	2.94	1.67
L-Alanine				
N-Ethylglycine	3.71	8.58	6.25	5.36
2-Aminoisobutyric acid (α-AIB)	73.61	73.53	11.57	13.93
D-2-Aminobutyric acid				
DL-3-Aminobutyric acid (β-ABA)				
L-2-Aminobutyric acid	3.14	5.82	<LOQ	0.44
D-3-Aminoisobutyric acid	21	15.14	4.3	4.28
L-3-Aminoisobutyric acid				
γ-Aminobutyric acid				
DL-Serine	4.62	6.39	1.77	3.49
DL-Proline*	5.20	6.66	4.02	5.95
D-Isovaline	10.50	11.68	<LOQ	nd
L-Isovaline				
D-Valine				
L-Valine	1.91	4.66	0.32	0.52
D-Norvaline	nd	nd	nd	nd
5-Aminovaleric acid	4.64	5.49	0.17	0.20
L-Norvaline	2.18	3.25	0.22	0.5
DL-β-Leucine	7.2	12.63	nd	nd
D-Alloisoleucine	nd	nd	nd	nd
D-Isoleucine	5.37	6.97	<LOQ	<LOQ
L-Alloisoleucine	7.36	7.3	nd	nd
L-Isoleucine	20.90	28.3	<LOQ	<LOQ
D-Leucine	6.77	7.83	0.85	0.45
D-Norleucine	7.20	5.6	nd	nd
L-Leucine	16.8	11.86	2.24	4.33
L-Norleucine	3.21	5.46	nd	nd
D-Aspartic acid	8.02	nd	1.08	nd
L-Aspartic acid	5.99	nd	2.58	2.40
D-Glutamic acid	nd	nd	1.13	1.02
L-Glutamic acid	11	4.87	0.86	0.95
Uracil	3.28	1.09	nd	nd
Guanine	4.06	3.75	nd	nd

\*: confirmed contamination; nd: not detected; < LOQ: inferior to the limit of quantification

amino acids are studied in function of their properties (hydrophobic, neutral, acidic, basic).

As chirality measurement is mandatory in amino acids analyses, we decided to investigate the impact of UAE parameters on amino acids racemization. Whatever the frequency used, long duration ultrasound extraction induced partial racemization of some L-amino acids as did the reference protocol (24 h at 100 °C in water). Indeed, the D-form was detected for durations longer than 20 min for aspartic acid and glutamic acid (Fig. 5).

Considering these results, 40 min duration should be avoided, even though nucleobases were better extracted with longer time. Thus, 20 min duration was selected since potential degrading effects are minimal compared to the reference method. Optimal conditions were set as 20 min extraction using a H<sub>2</sub>O/MeOH (1:1, v:v) at 20 kHz frequency.

## 5.2. Application on meteorite samples

To validate the efficacy of these optimal extraction conditions, ultrasound assisted extraction was performed on meteorite fragments and results were compared to the current hot water extraction. Mukundpura and Tarda meteorite fragments were used for these experiments.

Table 2 details all identified compounds. Mukundpura meteorite is far richer in amino acids and nucleobases diversity than Tarda meteorite, which confirms previous studies [33]. 35 amino acids and 2 nucleobases were detected in the Mukundpura extracts whereas only 22 amino acids were identified in Tarda with concentrations ranging from ~ 0.22 to 73,61 nmol/g. As shown earlier, the two meteorites had similar relative amino acid distributions dominated by glycine, alanine, β-alanine, and amino-butyric acid isomers. Several non-protein amino acids, including α-aminoisobutyric acid (α-AIB), β-amino-n-butyric acid (β-ABA), and isovaline were identified in both samples (Table 2).

Overall, ultrasonic extracts and hot water extracts provided similar results. For Mukundpura, a total of 349 nmol/g of organics was extracted by 20 kHz UAE and 358 nmol/g was extracted by reference method. We could however notice a slight loss in D- and L-alanine (along with β-Alanine) in the case of Mukundpura ultrasound extract compared to reference method (24.8 and 20.9 nmol/g compared to 34.45 and 32.82 nmol/g, respectively). On the contrary, 50 % gain for L-glutamic acid was found for UAE protocol and DL-aspartic acid was only recovered with this protocol. For Tarda meteorite, 83 nmol/g of organics were recovered with 20 kHz UAE extraction compared to 80 nmol/g for hot water extracts.

If the amino acids detected have been formed by abiotic processes, they would originally have been racemic (D/L ~1). In this case study, amino acids in both meteorites were not racemic. Contamination of the meteorite by terrestrial L-amino acids after they fell to Earth could thus not be excluded. However, the presence of 4-carbon amino acids such as α-ABA or β-ABA and addition the D/L > 1 for glutamic acid in Tarda and for aspartic acid for Mukundpura, suggests an extraterrestrial origin of D-amino acids.

## 6. Conclusion

An ultrasound-assisted extraction protocol was optimized to extract a set of organic molecules from meteorites. Ultrasound frequency, water/methanol ratio and irradiation duration effects were studied on model montmorillonite-rich minerals to select most suitable conditions for amino acids, nucleobases and dipeptides extraction. The selected conditions matched previously developed protocol for *in-situ* applications in terms of frequency and solvent type [19]. However, we demonstrated that duration must not exceed 20 min if amino acids are targeted to avoid any racemization. Since we obtained similar extraction yields as the reference hot water extraction, we could envisage ultrasounds extraction as a faster and low energetic alternative for the extraction of organic matter from extraterrestrial samples.

## Author contributions

C.G-R. directed and supervised the whole study; C.G-R. and P.A conceptualized the analyses strategy; R.T. performed the experiments, collected and treated the data; M.D and A.P supervised procedure; B.G., G.R., P.P. supervised the project and reviewed the paper; R.T. wrote the paper with contribution of all authors. All authors have given approval to the final version of the paper.

## CRedit authorship contribution statement

**Ramzi Timoumi:** Writing – original draft, Investigation. **Prince Amaniampong:** Writing – review & editing, Methodology. **Aurelie Le Postollec:** Writing – review & editing, Validation. **Michel Dobrijevic:** Writing – review & editing, Validation. **Guillaume Rioland:** Project

administration, Funding acquisition. **Brian Gregoire**: Writing – review & editing, Validation, Methodology. **Pauline Poinot**: Writing – review & editing, Validation, Methodology. **Claude Geffroy Rodier**: Writing – review & editing, Validation, Supervision, Conceptualization.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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