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The evolution of nucleobases under asteroidal aqueous alteration

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Abstract:

Nucleobases such as guanine, xanthine, and uracil have been detected in numerous carbonaceous chondrites (CCs), with isotope signatures indicating their extraterrestrial origin. A correlation between nucleobase concentrations and the alteration degree of parent bodies is often reported, highlighting the importance of understanding aqueous alteration influence on nucleobase evolution to decode early solar system organic materials. Therefore, a laboratory investigation of the evolution of guanine, uracil, and xanthine was performed under aqueous alteration conditions typical of carbonaceous chondrites. Given the intimate association of organic molecules with inorganic materials in CC matrices, we also included a set of inorganic phases in this study to discuss the influence of minerals on nucleobases evolution during aqueous alteration. Results showed that guanine and uracil exhibit high stability, while xanthine undergoes decarboxylation. Saponite traps about 25% of xanthine, 53% of uracil and nearly all guanine, promoting nucleobases preservation. The isotope values ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) of nucleobases remained constant through aqueous alteration, suggesting that their isotope signatures are related to synthesis in cold environments in the proto solar nebula or the parent molecular cloud. Guanine relative stability

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during aqueous alteration explains its abundance in meteorites. Nevertheless, other processes such as (geo)chromatographic effect may account for the observed decrease in guanine abundance with increasing degree of alteration in CCs. The reported concentrations of uracil and xanthine in CCs are not correlated with alteration degree, hence differences in relative abundance are either related to different parent body reservoirs or synthesis/migration during aqueous alteration events.

Keywords: Nucleobases; aqueous alteration; Fe-containing minerals; saponite; carbonaceous chondrites; isotope composition

1. Introduction

Asteroids, comets, and their fragments including meteorites, micrometeorites, and interplanetary dust particles (IDPs) could serve as delivery vehicles for organic matter to Earth^{1,2}. Therefore, the organic compounds of chondrites, carbonaceous meteorites, and comets are essential for the decoding of the origin of life on Earth. Among the organic compounds detected in chondrites, nucleobases are of particular interest because they are the building blocks of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Nucleobases such as guanine and xanthine, and pyrimidine nucleobases such as cytosine, uracil and thymine have been detected in several carbonaceous chondrites³⁻⁷. For example, the purines adenine, guanine, hypoxanthine, and xanthine and the pyrimidine uracil have been detected in the Murchison, Murray and Orgueil meteorites^{8,9}. It has been reported that the CM2 meteorites show the most abundant and diverse suite of nucleobases in carbonaceous chondrites.

Compound specific stable isotope analysis (CSIA) is one suitable method to determine the origin and indigenous nature of meteoritic nucleobases. The nucleobases are ¹³C-enriched in Murchison meteorite samples compared to terrestrial counterparts, with $\delta^{13}\text{C}$ values of +44.5‰ and +37.7‰ for uracil and xanthine, respectively⁹. The carbon isotope ratios of uracil and thymine from a soil collected in the proximity of the meteorite fall site ($\delta^{13}\text{C} = -10.6\text{‰}$ and -15.9‰ , respectively) confirmed that uracil and xanthine detected in the Murchison meteorites were indigenous to Murchison meteorite⁹. However, the N isotope was not analyzed in this study. Of note, reports of $\delta^{13}\text{C}$ values of nucleobases in other carbonaceous chondrites are scarce. On the

other hand, the isotopic composition of meteoritic nucleobases by Matins ⁹ were questioned because of the baseline separation on the chromatogram was very poor ⁴.

Generally, the abundances and the isomers distributions of nucleobases in meteorites correlates with the aqueous alteration that chondrites experienced on the parent body ¹⁰. Within the CM class of carbonaceous meteorites, the increasing degree of aqueous alteration was reported accompanied by a decrease in the overall abundance and diversity of nucleobases ⁴. Guanine is the most abundant nucleobase in the type 2 carbonaceous chondrites, followed by xanthine and hypoxanthine. The abundance of guanine decreases with increasing aqueous alteration. Compared to the abundance of nucleobases in CM meteorites, the abundance of nucleobases in CR is very low (<21 ppb). The distribution in the least altered CR3 meteorites tends to favor xanthine, adenine and purine ¹⁰. No clear trend was observed with the increasing of aqueous alteration, maybe also because of the low abundance of those nucleobases in CR meteorites. The different distributions of nucleobases between CM and CR may be due to their distinct parent bodies.

The aqueous alteration affects the mineral phases, which has also been investigated and documented by many authors ¹¹⁻¹⁴. For example, hydrous minerals differ among the different types of chondrites, the matrices of CI chondrites mainly consist of serpentine, saponite, and ferrihydrite while the matrices of CM chondrites mainly consist of serpentine and tochilinite, and the matrices of hydrated CV chondrites contain saponite. The aqueous alteration also affect the composition of the phyllosilicate assemblages among CM chondrites between Fe-rich and Mg-rich endmembers ¹⁵⁻²⁰. Those changes may relate to varying degrees of aqueous alteration of CM2 chondrites and highlights the progression of aqueous alteration involving the transformation from Fe-rich to Mg-rich serpentines ²¹. With increasing aqueous alteration, CIs contain increasingly more ordered serpentine and a larger abundance of saponite ²². Several geochemical indicators, including O isotopes in silicates or isotope compositions of carbonates, have constrained maximum temperature for aqueous alteration on the parent bodies of type 1 and 2 carbonaceous chondrites at around 150°C ²³⁻²⁶.

Phyllosilicates can influence the evolution of organic compounds in meteorites or carbonaceous chondrites. In general, clay minerals are expected to promote the synthesis of nucleobases. Fe-containing catalysts can promote the synthesis of nucleobases ²⁷. Fe-smectites even better promote nucleobase synthesis, while the overall effect of Ni/Fe metal or Fe₂O₃ is negligible ²⁸. However, it has also been shown that the presence of Fe-rich smectites inhibits the

increase of molecular complexity and the production of insoluble organic matter during the reaction of formaldehyde and glycolaldehyde. This could be caused by the interaction of clay minerals with organic molecules²⁹. The Fe-rich smectites can also hamper the formation of amino acids while the Al-rich smectites can stimulate the production of amino acids from the aqueous alteration of hexamethylenetetramine³⁰. However, there have been few studies that reported the influence of aqueous alteration on the evolution of nucleobases. It must also be noted that the presence of organic matter also impact the evolution of the mineral assemblage²⁹.

In this study, the evolution of nucleobases under aqueous alteration and the role of minerals have been investigated. The gaseous, liquid, and solid products of the evolution of nucleobases with and without minerals were analyzed. The carbon and nitrogen isotope evolution in nucleobases under aqueous alteration has also been studied.

2. Materials and methods

2.1 Materials

Guanine (Aldrich, 98%), xanthine (Sigma, purity $\geq 99\%$), and uracil (sigma-Aldrich, purity $\geq 99\%$ (HPLC)) were used in this study. Tetramethylammonium hydroxide (TMAH, 25% by weight in methanol; Sigma-Aldrich) was used as a derivatizing agent in liquid phase. Minerals include Fe-metal (Aldrich, 99.5% trace metals basis), FeS₂(Aldrich, 99.8% trace metal basis), Fe₂O₃(Alfa Aesar, 99.998%), gel of saponite and pure saponite (Na_{0.4}(Si_{3.6}Al_{0.4}) Mg₂O₁₀(OH)₂nH₂O). The gel and the crystallized saponite were synthesized following the protocol of³¹.

2.2 Laboratory experiments

The ultrapure water (18.2 M Ω) was degassed with argon (>99.999%; Air Liquide, ALPHAGAZ 1) before starting the experiment. Guanine (G, 50 mg), xanthine (X, 49 mg), or uracil (U, 43 mg) were placed in the titanium Parr© reactors filled with 10 mL degassed ultrapure water (without pH adjustments). The titanium reactors (23 mL) were sealed under argon atmosphere (>99.999%; Air Liquide, ALPHAGAZ 1) in a glove box (<0.5 ppm O₂). They are equipped with gas collection tubes for gas sampling. The experiments in the presence of minerals share the same procedure except that we added 100 mg of minerals in each reactor. For each experiment, the Parr© reactors were placed in an oven with temperature accurately regulated at 150 °C for 10 days. This temperature was chosen as it is considered by several authors as the maximum temperature

of aqueous alteration recorded in type 1 and 2 carbonaceous chondrites^{23–26}. After 10 days, the gas was collected into the gas sampling tubes and analyzed by GC-TCD. The liquid and solid phase products of nucleobases and water were collected and placed in a 15 mL polypropylene centrifuge tube, followed by the centrifuge process (30 min at 10000 rpm). The liquid phases were transferred to a new falcon tube and stored in a refrigerator. The solid phases were dried in an oven at 50 °C. The dried solid phase residues were then ground using an agate mortar and pestle and stored for later characterizations. In addition, the liquid phase recovered from xanthine and uracil experiments were also dried in an oven at 50 °C for later characterizations. The workflow can be seen in Figure 1. Control experiments were also performed in this study, including with only H₂O, gel-saponite in H₂O, saponite in H₂O. The contamination of water and titanium reactor was ruled out by GC-MS. The liquid water sample after 10 days experiments was derivatized with TMAH, and no peaks were detected by GC-MS (figure S1). No unexpected or unusually high safety hazards were encountered during the experiments.

The experimental products were afterwards analyzed using a set of analytical techniques (figure 1) to characterize gas (GC-TCD), liquid (GC-MS) and solid phases (XRD, EA-irMS, FT-IR and EA). The analytical methods are detailed in the supplementary information (SI).

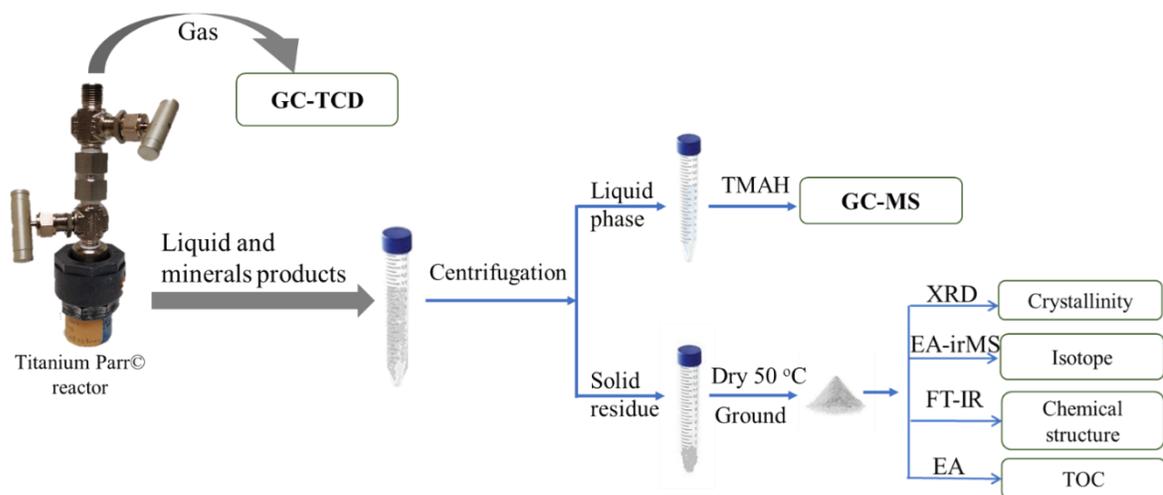


Figure 1. Schematic diagram of the analytical strategy followed in this study. GC-MS: Gas chromatography and mass spectrometry; EA-irMS: Elemental analyzer isotope ratio mass spectrometry; GC-TCD: Gas chromatography thermal conductivity detector; FT-IR: Fourier-transform infrared spectroscopy; XRD: X-Ray Diffraction; TMAH: Tetramethylammonium hydroxide; EA: elemental analysis. TOC: total organic carbon analysis.

3. Results

3.1 Gas products of nucleobases under aqueous alteration

The gas produced by nucleobases after the aqueous alteration are reported in Figure 2 which shows the relative abundance of CO₂ and H₂ released from nucleobases after the aqueous alteration at 150 °C for 10 days, with and without minerals. CO₂ is one of the main gases produced by guanine, uracil and especially xanthine, which releases the highest amount of CO₂. When xanthine is mixed with pure Fe, the CO₂ yield is much lower, about 23 times lower than the experiment without minerals. The addition of Fe₂O₃ and FeS₂ slightly reduced the release of CO₂ from xanthine. For guanine and uracil, the presence of gel-saponite and saponite increased the yield of CO₂. Otherwise, the presence of Fe and Fe₂O₃ did not influence the release of CO₂. No CO₂ was detected in the presence of gel-saponite and xanthine. The presence of pure Fe facilitates the release of H₂ during the aqueous alteration of nucleobases, likely due to oxidation reactions that produce H₂ from water. Less H₂ was released from the aqueous alteration of xanthine and uracil, indicating that the interaction of xanthine and Fe mineral may occur during the aqueous alteration.

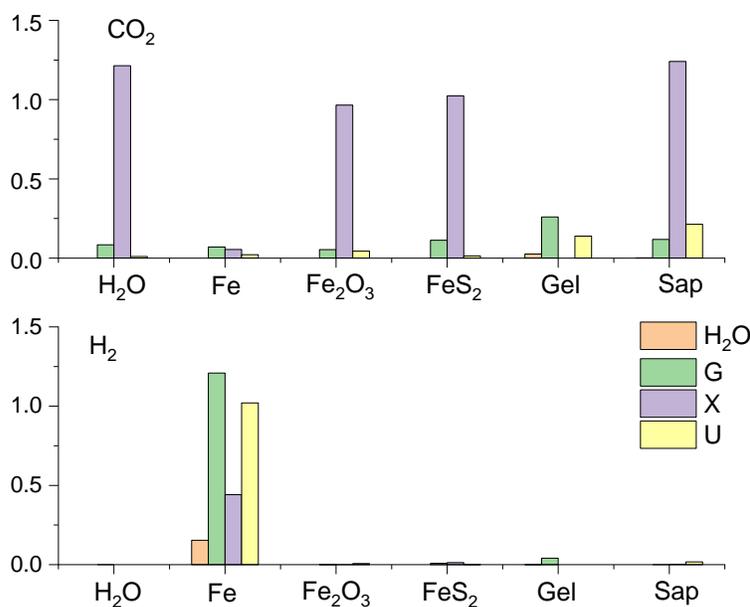


Figure 2. The abundance of CO₂ and H₂ formed during the aqueous alteration of nucleobases at 150 °C for 10 days. G: guanine, X: xanthine, U: uracil.

3.2 Organic compounds in the liquid phase

Figure 3 reports chromatograms of starting nucleobases and the products of nucleobases after aqueous alteration with and without minerals. The mass spectra of each analysis are reported in Figure S2 in the supplementary material. The main compounds detected after TMAH methylation of the starting water solution of guanine are dimethyl-guanine, trimethyl-guanine, tetramethyl-guanine, and caffeine. However, only caffeine was detected from the liquid products of guanine after aqueous alteration with and without minerals at 150 °C for 10 days, in low amount. This may be caused by the low solubility of guanine in water. Only caffeine was detected because it is one of the most soluble derivates of guanine. It may also be because a few amounts of guanine react into xanthine through deamination, which is then detected as caffeine after TMAH methylation.

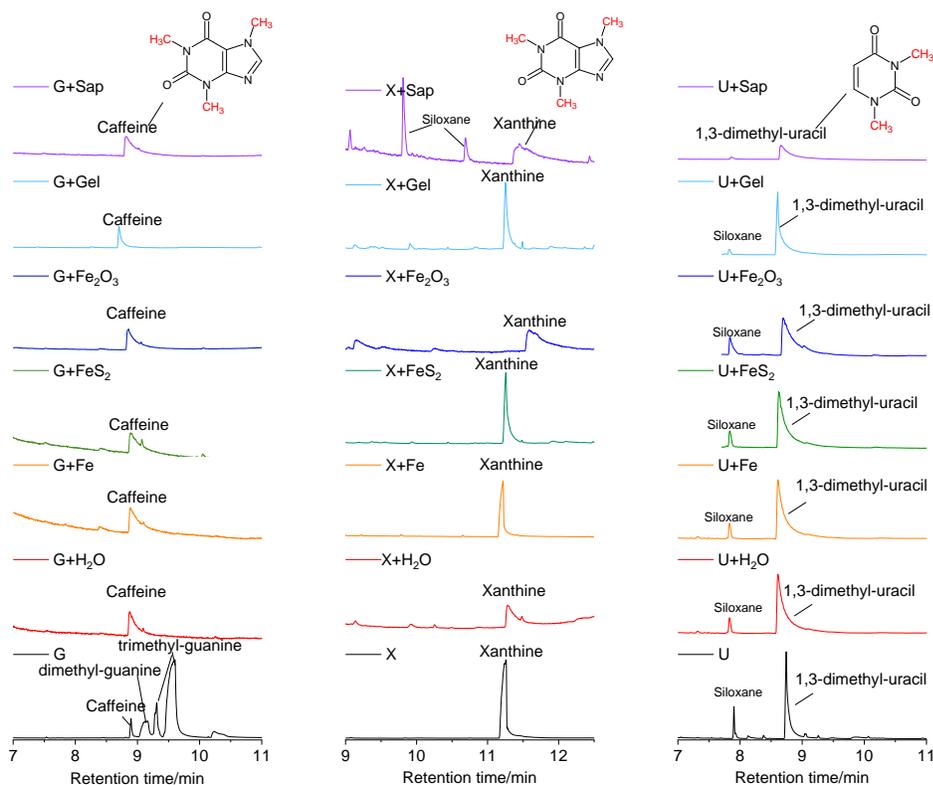


Figure 3. The GC-MS chromatogram of nucleobases before and after the aqueous alteration at 150 °C for 10 days with and without the presence of minerals. G: guanine, X: xanthine, U: uracil. Note: Caffeine (1, 3, 7-trimethyl-xanthine). The MS spectra of each nucleobase have been compared with nucleobases' standards (in the supplementary figure S2.).

The 1,3-dimethyl-uracil is the main derivatized form of uracil through TMAH methylation. No new products were detected in the liquid phase of uracil after the aqueous alteration with and without minerals. For Xanthine, only caffeine (i.e. methylated xanthine) was detected in liquid phase before and after experiment, and there are no new products from the aqueous alteration of xanthine. Fe, Fe₂O₃, and FeS₂, gel-saponite and the well crystallized saponite did not affect the aqueous alteration of xanthine. However, the broad peaks in the chromatogram of xanthine and saponite as well as Fe₂O₃ may be because of the effect of salts, resulting from the dissolution of minerals during the experiments, on the separation efficiency of the column.

3.3 Characterizations of solid phases

3.3.1 Elemental analysis

To determine the content of organic compounds after the aqueous alteration of nucleobases with and without minerals, elemental analyses of the solid phase and dried liquid phase were performed. The N and C concentrations of products in liquid and solid phase compared with their starting materials are shown in Figure 4. Guanine, being poorly soluble in water, remained mostly in the solid phase, with its carbon content matching the initial amount. Uracil, highly soluble in water, was predominantly in the liquid phase, with its carbon content unchanged. Xanthine, also soluble, was mainly found in the liquid phase, containing 82.9% of the initial carbon content, with no solid residue observed. The results slightly differ when minerals are involved.

The starting mixtures of guanine and minerals result in a TOC (total organic carbon) of 13.3%. After the experiments, the TOC in the solid residues ranged from 10.9% to 12.3%, which implies that 82% to 92% of the organic carbon from guanine is recovered in the solid phase associated with minerals (consistent with the XRD analysis in the supplementary information, Figure S4-S9). The N content in solid residues without mineral is the same as that of the starting material. With minerals, N recovery rates were 78% to 86%, there is no N in the dried liquid phase. The highest TOC was observed with saponite. The presence of Fe₂O₃ during the aqueous alteration of guanine shows that about 91% C and 85% N remains associated with Fe₂O₃. In contrast, with Fe metal, only 82% of C and 78% N were detected, possibly due to guanine reacting with H₂O in presence of Fe. However, the N/C ratios of guanine residues with minerals before and after the

aqueous alteration at 150 °C remain at 1.1, similar to the starting material guanine, of, suggesting the presence of unreacted guanine.

In uracil experiments, the C recovery rate in the dried liquid phase exceeded 99%. However, it appears lower (about 10% relative less) when uracil is mixed with gel-saponite (90.5%) and crystallized saponite (92.1%), indicating that the silicate mineral traps organic material more efficiently than metal and oxides. This is consistent with the XRD results in figure S9. Non-silicate minerals showed minimal organic compound detection in solid products (TOC between 0.2% and 0.4%), contrasting with 6.9% in saponite experiments. Fe and Fe₂O₃, and FeS₂ had no noticeable influence on uracil during aqueous alteration. Uracil in the dried liquid phase showed consistent N content without minerals. Introducing Fe and Fe₂O₃ does not influence the N content of the organic products of uracil in the liquid phase after experiment. The N/C ratio of uracil products does not change significantly with and without minerals, confirming uracil dominance in the liquid phase.

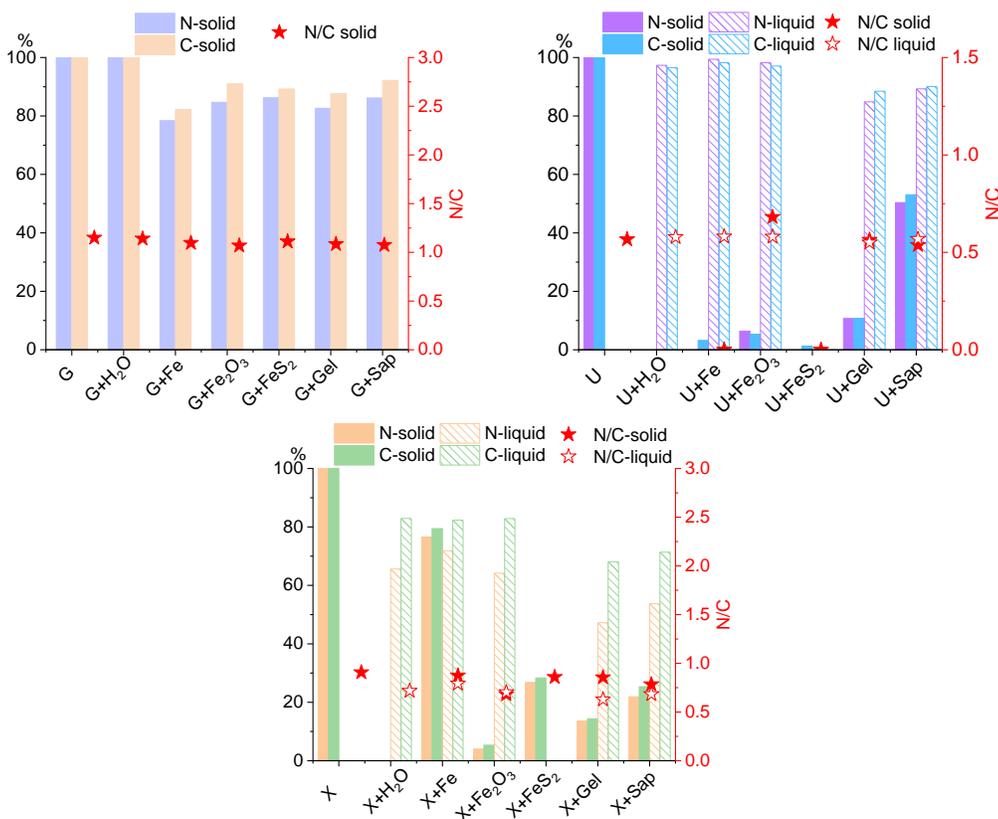


Figure 4 Elemental contents in carbon and nitrogen of solid and liquid phases before and at the end of experiments. G: guanine, X: xanthine, U: uracil. Gel: non crystalized saponite, Sap: saponite. (Note: no data of

dried liquid phase of xanthine with FeS₂ and uracil with FeS₂, because of the technical limitation with the instruments.) Data is in SI Table S1.

The C recovery rate after experiments with xanthine varies with the nature of the inorganic component. Fe and Fe₂O₃ had minimal influence on xanthine liquid phase during the aqueous alteration, as indicated by the C and N content of the dried liquid products. With Fe and Fe₂O₃, the dried liquid phase contains about 32.7% C, corresponding to 82.9% recovery rate from the initial xanthine. Similar trends were observed with gel-saponite and saponite, suggesting organic carbon trapping in the mineral phase, which is consistent with the XRD results in Figure S9. Overall, experiments with xanthine showed lower carbon recovery rates (72.8% to 79.7%) compared to guanine and uracil under similar conditions (see Figure 4). The N content of the xanthine product in dried liquid phase after experiment in pure water is lower than the starting material, and the N/C ratios also decreased. The N/C ratios of xanthine residues of Fe, FeS₂ and gel-saponite are similar with the starting xanthine, while those with Fe₂O₃ and saponite are about 25% and 14% lower, possibly due to the aqueous alteration, though drying process may have contributed.

3.3.2 FTIR

Pure starting minerals, nucleobases and the mixtures of nucleobase with minerals after experiments were analyzed by Mid-IR within the wavelength of 400-4000 cm⁻¹ to investigate their chemical bonds. The ATR-MIR spectra of the minerals before and after experiments in Figure S3 in the supplementary information indicate no obvious change.

Guanine and the experimental products of guanine and minerals have the same mid-IR spectra but with different peaks width and shape (Figure 5); this is consistent with guanine remaining associated by the minerals in the solid products. Detailed identification of these peaks is provided in Supplementary Information.

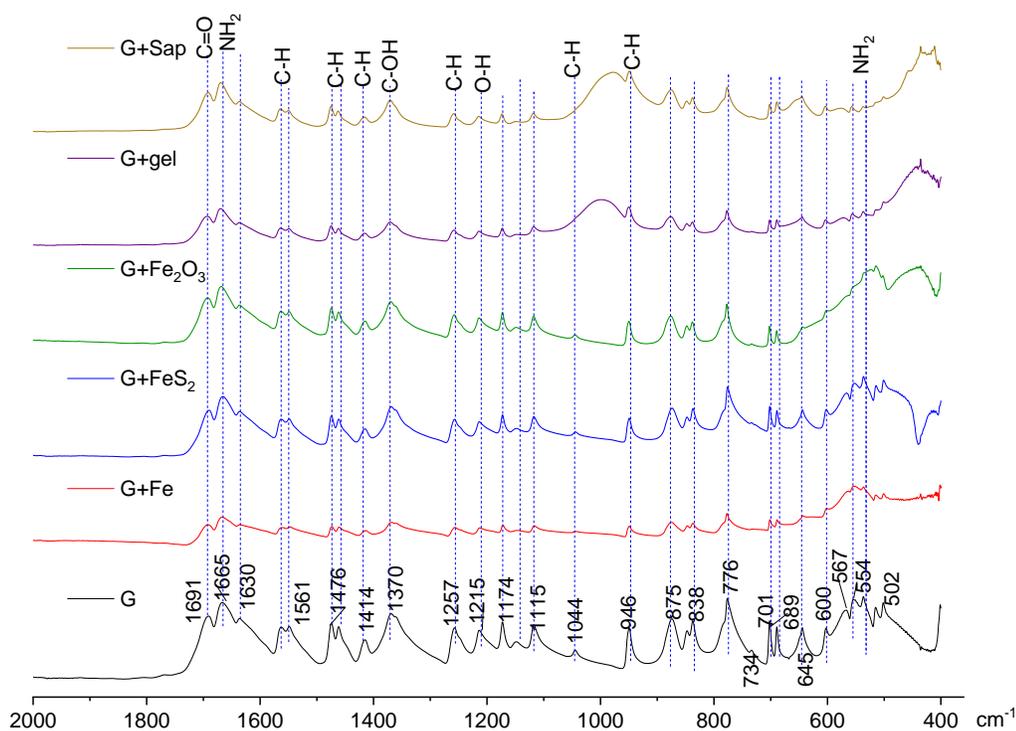


Figure 5 ATR-MIR spectra of guanine and residue of the guanine and minerals after aqueous alteration. Peak assignment can be found in SI.

Figure 6 is the mid-IR spectra of starting uracil and the experimental solid products of uracil and minerals at 150 °C for 10 days. Comparing the IR bands of solid products of uracil with minerals and the initial uracil, we found that some bands of organic functional groups such as C=O, C-H, and N-H have been observed in uracil with saponite and, to a lower extent, gel saponite. This demonstrates that the small amount of organic matter that we detected by EA in the solid products of experiments with saponite and gel saponite (see section 3.3.1) corresponds to unreacted uracil. No mid-IR band was detected in the residues of uracil and Fe, Fe₂O₃, and FeS₂ mixtures.

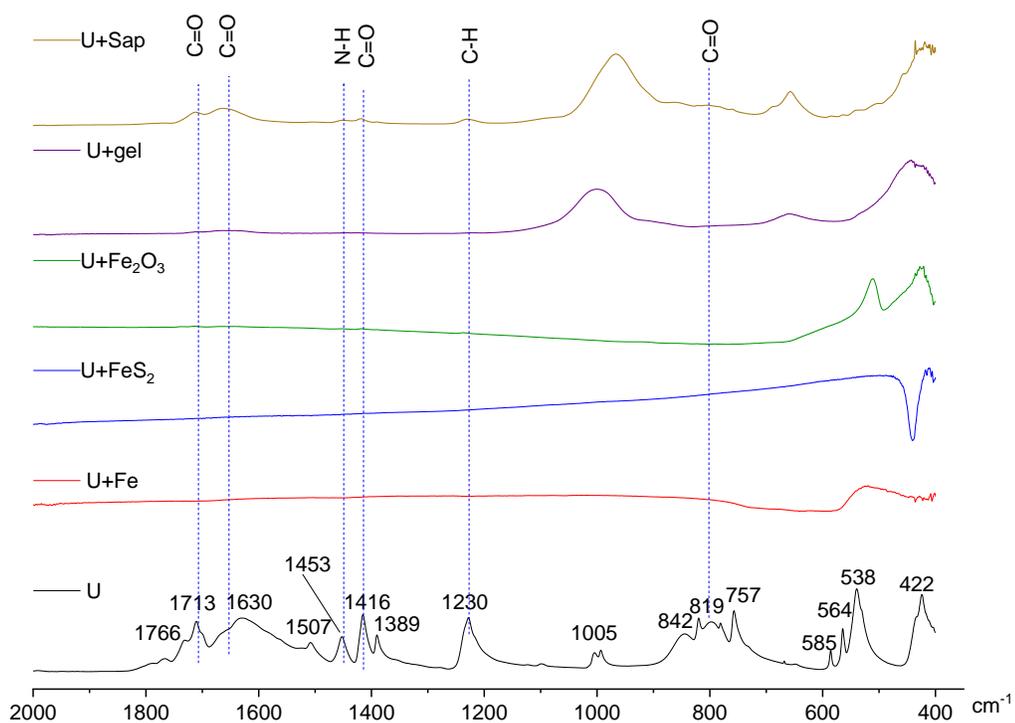


Figure 6 ATR-MIR spectra of uracil and residue of the uracil and minerals after aqueous alteration. Peak assignment can be found in SI.

Figure 7 is the mid-IR spectra of starting xanthine and the experimental solid products of xanthine and minerals at 150 °C for 10 days. Only the solid products of experiments with FeS₂ and Fe exhibit the fingerprint peaks of xanthine. In addition, some peaks of C=O and C-C bond have been detected in the products of experiments with gel-saponite and saponite. Mid-IR results are consistent with elemental analysis (section 3.3.1), showing the presence of a small amount of organic compounds in the solid products, likely being xanthine.

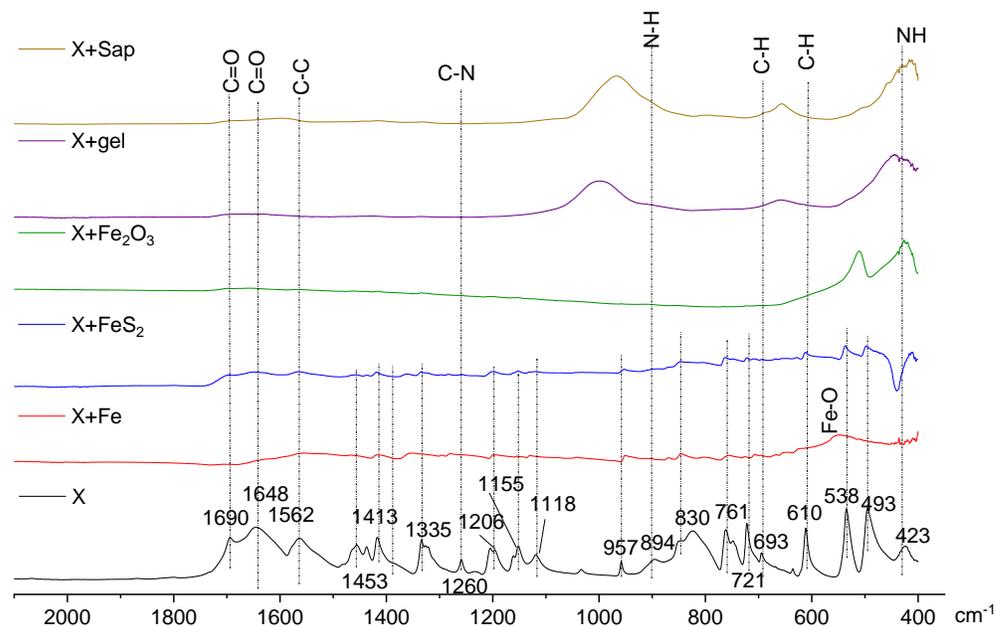


Figure 7 ATR-MIR spectra of xanthine and residue of the xanthine and minerals after aqueous alteration. Peak assignment can be found in SI.

3.3.3 Carbon and nitrogen isotope compositions

The C and N-isotope ratios of organic products have been determined by EA-irMS (Figure 8). The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of guanine and uracil do not show any variation during the experiments with and without minerals. However, the $\delta^{13}\text{C}$ value of xanthine slightly increased from -26.6 ‰ to -25.1 ‰ which may be due to the degradation of xanthine during the aqueous alteration (Figure 2). The $\delta^{13}\text{C}$ value of xanthine after the experiment with and without minerals is constant; this is consistent with a similar CO_2 production in each experiment. For xanthine, there are about 17.1% of C and 34.4% of N atoms lost after 10 days. The $\delta^{15}\text{N}$ value of xanthine after experiment increased from -5.3 ‰ to -1.4 ‰, and the value is the same whatever the mineral present in the experiment.

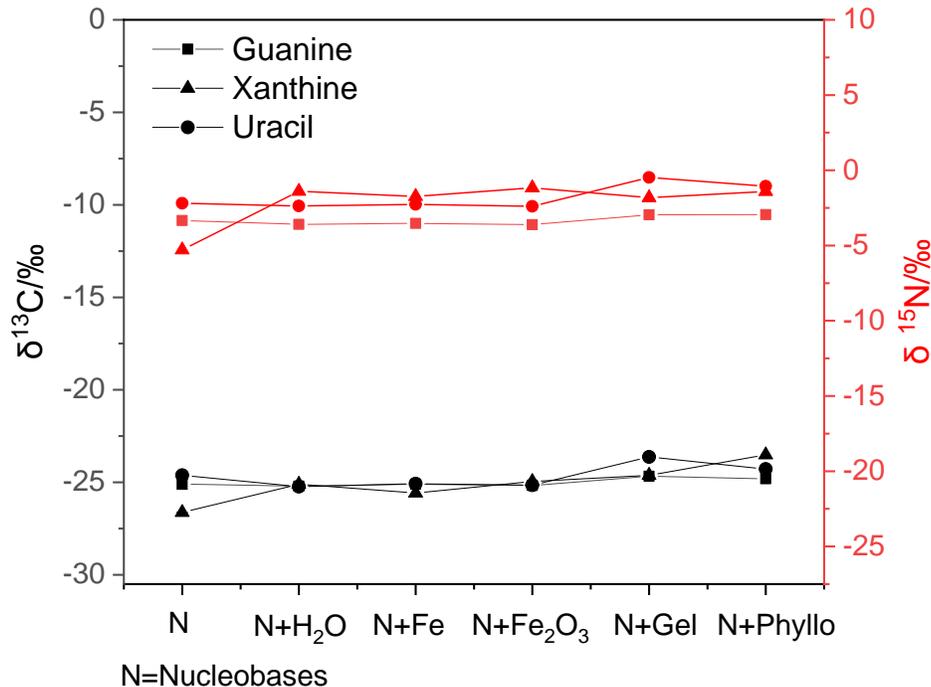


Figure 8 Stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotope analysis of experimental products along with initial compositions. Note: guanine in solid phase, xanthine, and uracil from the dried liquid phase. Data in Table S2.

4. Discussion

4.1 The effect of aqueous alteration on nucleobases

Compared to uracil and xanthine, guanine is the most stable nucleobase after aqueous alteration experiments; the C and N content and the N/C ratio remain unchanged through experiments. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values do not show variation upon aqueous alteration (Figure 8), indicating that isotope signature of guanine or its pre-accretion precursors was preserved during aqueous alteration on parent bodies. The high stability of guanine under aqueous alteration may relate to its insolubility in water. Guanine may remain solid throughout the entire experiment, hence reducing its reactivity.

Guanine is a bicyclic molecule comprising a fused pyrimidine-imidazole ring system, which can exist in several isomeric forms. In the solid state, guanine can exist either in the hydrated

or in the anhydrous form. Interestingly, the guanine monohydrate crystal reveals a preference for the 9H-keto-amino tautomer, while the anhydrous base favors the 7H-keto-amino species³²⁻³⁴. The crystal structure of guanine monohydrate follows a hexagonal fashion with a ring-like plane composed of six molecules. A column of water molecules passes through the interstices of these hexagonal arrays, stabilizing the layered crystals³⁵. Molecules are linked to each other by weak N-H...N and N-H...O hydrogen bonds to form sheets, between which there are $\pi - \pi$ stacking interactions. In the absence of any solvent or other molecules, guanine exists as the amino-keto tautomer in the solid state³⁶. The highly ordered structure arose from the assembly of guanine bases into square-planar groups that resemble macrocycles, in which the bases interact via hydrogen bonds³⁷. The occurrence of such a crystallized structure in our experiments is confirmed by XRD data and may explain that guanine remains insensitive to water throughout the experiment.

In addition, the solubility of guanine is pH dependent. The solubility of guanine shows a sudden decrease at pH 3.3, meaning that guanine becomes almost insoluble at pH 4 to 7³⁸. The solubility of guanine increased from pH 8 to 9, which may be due to the presence of its protonated form³⁹. In our experiments, the pH values of the liquid products from guanine after aqueous alteration, with and without minerals, varies from 6-9. Therefore, a very low content of guanine could be dissolved in the aqueous solution. In addition, the decomposition rate of guanine has been proven to exhibit a relatively flat region from pH 5-10 at 100, 120, and 145 °C⁴⁰. This is consistent with our result that guanine did not show obvious degradation at the pH range of 6-9 at 150 °C.

The stability of uracil after aqueous alteration ranks second among the three nucleobases. Uracil could be dissolved in water and its solubility is pH independent³⁸, thus most of the uracil is in liquid phase at the end of the experiment. Uracil is soluble in hot water but it has a low solubility in cold water and alcohol⁴¹. Solvent polarity is important for the reactivity of uracil. The coordination of solvent molecules significantly affects the energy of carbonyl oxygen lone pair orbitals, while their influence on the diffuse π and π^* orbitals is much more limited⁴². In aqueous solution, the molecule of uracil creates two hydrogen bonds and shows stability from layer interaction, and a change in substituents disturbs the network of the hydrogen bonds, which causes a change in the crystal lattice⁴¹. In addition, water molecule H-bonded to amide sites are mostly localized in the plane of uracil, or at least not very far from it. The H bond between water and uracil favored the preservation of uracil during the aqueous alteration.

In contrast, xanthine shows a different behavior upon aqueous alteration. The decrease of C and N content, the N/C ratios, and the detection of CO₂ gaseous products suggest that degradation occurs. A large amount of organic carbon from xanthine remains after the aqueous alteration at 150 °C. This results in a small increase in δ¹³C and δ¹⁵N during the aqueous alteration of xanthine. Xanthine is a purine base and can be formed by oxidation of hypoxanthine. Known to be bi-cyclical heterocyclic ampholyte, it has both acidic and alkaline tendency. The solubility of xanthine is influenced by strong inter-base hydrogen bonds and base stacking. The existence of relatively strong intermolecular bonds between N-H groups could be another factor for the poor solubility of xanthine. Higher temperature increases the solubility of xanthine. In addition, the solubility of xanthine also depends on the pH value of the solutions, the pH range 5.0-8.0 xanthine solubility changes drastically and it increases as pH rises due to the increasing presence of the much more soluble anionic form⁴³. The final pH of xanthine solutions after aqueous alteration are about 9, which could favor the dissolution of xanthine at 150 °C. In addition, xanthine could be oxidized into uric acid, which may be decomposed during the aqueous alteration leading to the release of CO₂⁴⁴.

Nucleobases dissolve in pure water due to hydrogen bonding interactions between polar sites of nucleobases and solvent. The polar sites of all nucleobases include NH₂, NH, and C=O groups. Xanthine is the intermediate product of guanine deamination; therefore, xanthine contains one more C=O compared with guanine⁴⁵. There are two types of amine groups: primary amine (exocyclic NH₂ group) and secondary amine (ring NH group). Both can undergo hydrogen bonding with water but in different ways. The hydrogen bonding of water with the amine group of methylated guanine corresponds to the Coulombic contribution of the solvent free energy in pure water. The stacking of cations with nucleobases corresponds to the excess solvation free energy in the form of van der Waals interaction⁴⁵. In addition, the intermolecular bonding between the oxo and amino groups in the molecules in the guanine crystal may lead to its insolubility in water^{35,37,46}, and may also help to avoid the degradation during aqueous alteration. For Xanthine, there are two C=O groups able to interact with water molecules, which may increase the solubility of Xanthine in aqueous solvent.

4.2 The possible interactions of nucleobases and minerals

4.2.1 Corrosion of Fe-metal

The production of H₂ during the reaction of Fe, H₂O, and organic compounds is linked to Fe corrosion in water. Key surface properties influence this process, where H atoms can form H₂ or diffuse into the metal⁴⁷. Fe oxidation involves Fe dissolution and the creation of H₂ and H₃O⁺. Water dissociates into H⁺ and OH⁻, with H⁺ quickly picking up electrons. Some H⁺ forms H₃O⁺, leading to H₂⁴⁸. Hydroxyl ions can undergo dismutation, forming O²⁻ ions, which attack Fe, causing defects and accelerating oxide growth. Dissolved Fe and OH⁻ ions precipitate, forming a porous outer oxidation layer⁴⁹ that traps organic compounds like xanthine.

The interaction of xanthine and Fe may include 3 processes, the adsorption of xanthine on the surface of Fe, the redox reaction of Fe (0) and water; the interaction of xanthine and Fe. The adsorption of xanthine may happen on the clay mineral. During the xanthine adsorption process, the balance between repulsive forces (i.e. electrostatic repulsion) and attractive forces (i.e. electron-donor-acceptor) can be decided by the isoelectric point of the adsorbents and the unique physicochemical properties of pollutant⁵⁰. The reduction plays a prominent role in the removal of organic pollutants by NZVI and its based materials. The strong reducing properties of Fe⁰ and Fe²⁺ are suitable for electron donors to organic pollutants in the reduction process⁵⁰. Therefore, xanthine could have been the electron acceptor so that the oxidation and decarboxylation of xanthine has been suppressed, leading to lower release of gaseous CO₂ and H₂ during the aqueous alteration of xanthine and Fe.

4.2.2 Influence of sulfides

Pyrites can act as an attractive substrate for the adsorption of organic matter⁵¹. Previous studies have shown that anionic, zwitterionic, cationic and non-ionic molecules interact with the pyrite surface through the formation of weak chemical bonds. No organic compounds have been detected in the residues of uracil and pyrite. For the residues of guanine and FeS₂, the N/C ratio is very close to the starting guanine, which indicates that pyrites do not have a significant effect on guanine. The detection of C and of N in the residues of FeS₂ and Xanthine may be caused by organic matter interaction with iron sulfide (Figure S5). The adsorbate-pyrite interaction is not

limited to simple overall electrostatic attraction or repulsion but must include specific chemical interactions that are governed by localized forces. Pyrites have multiple-site surfaces, which can offer the possibility to bind species that are chemically different. The thiol and iron surface group of pyrite are both available for chemical bonding. In addition, the pyrite surface may also contain uncharged, non-hydrolyzed sites, which cannot contribute to the surface charge of pyrite but may interact with molecular species via non-electrostatic modes of interaction ⁵².

Purine can have delocalized electronic structure which could favor interaction with multiple surface sites on the mineral surface. The interaction of heterocyclic compounds, such as adenine and purine, may involve interaction with one or more surface sites via induced dipole-dipole interaction ⁵³. For example, adenine may interact with several iron sites at once by laying on the pyrite surface ⁵². Xanthine, as one of the purine compounds have a similar characteristic as adenine, thus it may also interact with several iron sites at once by lying flat on the pyrite surface. Mateo-Martí et al ⁵⁴ proved that the bonding takes place through N-Fe interaction involving essentially nitrogen groups of nucleobases, but do not lie completely flat on the surface of pyrite. And the pyrite surface has a very high reactivity and could act as a nitrogen-molecule trap. Therefore, chemical bonds between N-atoms and Fe-atoms in pyrite seem to play an important role for the interactions between nucleobases and iron sulfide minerals ⁵⁵⁻⁵⁷. Hence, the high abundance of N in the solid residues of guanine and xanthine with pyrite may be due to the N-Fe interactions during the aqueous alteration.

4.2.3 Influence of Fe₂O₃

No obvious interaction has been detected between nucleobases and Fe₂O₃ during aqueous alteration. The residues of guanine and Fe₂O₃ also indicates that Fe₂O₃ does not influence the behavior of guanine under aqueous alteration. Guanosine monophosphate was the highest among the other nucleotides when they adsorbed on iron oxides ⁵⁸, which may be a side evidence that iron oxide has little effect on nitrogen-containing bases.

4.2.4 Nucleobase interactions with silicates

Clay minerals are often expected to adsorb organic compounds due to their large available surface ⁵⁹. Saponite shows a better ability to trap organics than that of gel-saponite. This may be caused by the different structure of gel-saponite, considered amorphous, and the well crystallized saponite. The absorption of organic compounds with gel-saponite and crystalline saponite relate

to the physical absorption and chemical bonding. Chemical adsorption controlled the process of the adsorption of caffeine from aqueous alteration by saponite⁶⁰. Okada et al.⁶¹ indicated that saponite based materials are promising candidates for the selective adsorption. The presence of nucleobases decreased the crystallinity of saponite while barely influencing the crystallinity of gel-saponite, which may be due to the pH variations of the liquid solution (Figure S7 and S8). The presence of organic materials disturbs the crystallization of Fe-rich smectites possibly as observed with (Al, Mg)-rich smectites in the presence of RNA or via complexation and affects their permanent charge via the production of organic acids preventing/impacting tetrahedral substitutions²⁹. The poorly crystalline smectites of the residues have retained organic compounds, both within their interlayer spaces and on their surface. Previous studies showed that the smectite trapped more organic compounds than the gel-smectite, which may be due to the highly variable permanent charge in the well crystalline smectite²⁹.

The interaction of nucleobases also depends on the chemical properties of different nucleobases. For instance, in this study, the presence of minerals does not show obvious influence on guanine during the aqueous alteration. Uracil was only detected in the residues of saponite, which could be explained by the high solubility of uracil in water and the water swelling properties. Phyllosilicate particles exhibit three very distinct surfaces, basal, lateral, and interlayer-in the case of swelling clays. The interaction of nucleobases and montmorillonite could be the electrostatic forces, ionic exchange, hydrogen bonding and van der Waals forces at pH 2.00 and 7.20⁶². Uracil does not respond to pH changes, its adsorption can remain almost constant across a wide pH range⁶³. Structural analysis indicates that pairs of hydrogen bonds could form between uracil just as effectively as between purines. Therefore, the interactions between clay-bound pyrimidines or urines result from hydrogen bonds⁶³. In addition, C=O bonds of uracil may play an important role with the interaction of saponite since C=O have been detected from the residues of uracil and saponite (Figure 6).

In this study, organic compounds were detected trapped within saponite layers (Figure S9), while there is less organic matter in gel-saponite residues. The distribution of permanent charge of gel-saponite and crystalline saponite may be different, a higher variable permanent charge of saponite may lead to the higher abundance of organic compounds in the residue of saponite and nucleobases. The presence of saponite and gel-saponite lead to the decrease in the C and N content in the liquid phase. This may be because of the interaction of nucleobase and saponite and gel-

saponite. In saponite layers, isomorphous substitution of some Si(IV) by Al(III) in the tetrahedral sheet not only makes the layer to be negatively charged but also creates Lewis acidity. Many studies have proved that Al in the tetrahedral sheet exhibits Lewis acidity. The exchangeable cations in the interlayer space of saponite, typically Na⁺, K⁺, and Ca²⁺, which compensate the layer charge, can be exchanged with H⁺, thereby creating Brønsted acidity. In addition, more Brønsted acid sites can be created through H⁺ coordination or silanol group –Si-O-H⁺. The presence of acid sites on saponite may catalyze the degradation of xanthine in liquid phase. It must be noted that the starting concentrations of nucleobases in our experiments are below the saturation concentrations of the saponite surface area.

4.3 Implications for carbonaceous chondrites

4.3.1 Nucleobases in carbonaceous meteorites

A wide variety of extraterrestrial nucleobases have been identified in carbonaceous chondrites^{4,6,64}. It has been proposed that the distribution of nucleobases in the most altered carbonaceous chondrites (Type 1 and 2) was dominated by guanine relative to the other bases, while in the least altered meteorites (Type 3) the distribution is balanced between xanthine, adenine and purine¹⁰. The dominance of guanine within nucleobases in type 1 and 2 chondrites is consistent with its stability during our experiments. Xanthine is not as stable as guanine and uracil under aqueous alteration, hence its relative concentration decreases with aqueous alteration.

Uracil is the only pyrimidine nucleobases previously quantified in the Murray and Murchison meteorites, at about 30 to 37 ppb in a water extract⁸. However, Oba et al.⁶⁴ reported that the weighted average of the uracil concentration was about 7 ppb without hydrolysis, which is four time lower than previously reported. This may be related to the heterogeneity of the Murchison sample. Uracil was also detected in the Orgueil CI meteorite and in samples from asteroid Ryugu, in hydrolyzed extract (at about 30 ppb in Ryugu vs 140 in Orgueil)⁵. Such large variations appear inconsistent with our experimental results showing a quite good stability of uracil under aqueous alteration. Transportation within the alteration fluid may account for the variable concentrations of uracil, as it exhibits the highest solubility in water among the three nucleobases investigated here. It must be noted that the difference in uracil concentration between Ryugu and

Orgueil may be related to irradiation processes occurring at the asteroid surface, that would have affected uracil in Ryugu samples but not in Orgueil ⁵.

The simulated aqueous alteration experiments were performed in a closed system, whereas the parent body conditions may occur in a partially open system, where the gas products could have been lost. Transportation within the alteration fluid as well as pH changes in the course of the alteration process may redistribute nucleobases within asteroidal parent bodies. Hence, the (geo) chromatographic effect (e.g., chemical fractionation due to differential transport in the fluid) may explain why the absolute concentration of guanine, despite being stable under aqueous alteration, decreases with increasing alteration degree in CM chondrites ¹⁰.

Our experiment rationale assumed that nucleobases were accreted along with other organic molecules, mineral components and ice. Then aqueous alteration would have started with ice melting inducing mineralogical and chemical evolution. The aforementioned hypotheses, nevertheless, remain valid if nucleobases were synthesized during the early stages of aqueous alteration on the parent bodies from accreted organic precursors. This early synthesis on the parent body may account for the low abundance of uracil whereas it is expected to be stable during alteration. Indeed, pyridine nucleobase synthetic route may be less efficient than purine ones under asteroidal conditions⁶⁴. Finally, geoelectrochemical alteration processes, recently proposed by Li et al., may have influenced the abundance and distribution of nucleobases in carbonaceous chondrites ^{65,66}.

4.3.2 The isotope characteristics of nucleobases

Compound specific stable isotope compositions of hydrogen, carbon and nitrogen can be a powerful discriminator of the origin of organic compounds in meteorites. The $\delta^{13}\text{C}$ value of xanthine (+37.7 ‰) and uracil (+44.5 ‰) in Murchison meteorites signed their extraterrestrial origin ⁹. In this study, the C-isotope values of nucleobases do not change after the aqueous alteration at 150 °C for 10 days with and without the presence of minerals for Uracil and Guanine and show minor increase (around 1‰) for Xanthine. Hence isotope composition can be used as a record of the synthesis environments of nucleobases or their precursors in the prebiotic conditions. Interestingly, xanthine was found to be slightly depleted in ¹³C relative to uracil. Such a difference between uracil and xanthine cannot be explained by aqueous alteration. It rather indicates that they formed from different precursors, and in particular the C atom in the 5-atom ring has a distinct

isotope composition than the other ones, assuming a common origin of the 6 atom rings for both nucleobases.

The origin of nucleobase in chondrites has been studied since the early 1960s when the first report of purine and pyrimidine bases in extracts of carbonaceous meteorites were published ⁶⁷. The $\delta^{13}\text{C}$ in nucleobases is even larger than in amino acids ^{9,68}. Several synthesis mechanisms of nucleobases in the early solar system have been proposed based on laboratory experiments, including reaction of hydrogen cyanide and ammonia ⁶⁹, and the dehydration and condensation of formamide ⁷⁰. In addition, some nucleobases such as uracil and thymine can be formed by UV photoirradiation of astrophysical ice analogues containing pyrimidine ^{71,72}. Large ^{13}C content in nucleobases may indicate ^{13}C -rich interstellar precursors or formed by photochemical reactions within the protosolar nebula, where heavy isotope enrichments can occur as a result of processes like self-shielding ⁷³.

4.3.3 The preservation of nucleobases in prebiotic environments

Phyllosilicate may have played an important role in organic matter evolution in meteorites. In the Orgueil and Murchison meteorites, and the Ryugu asteroid ⁵, organic matter is systematically interspersed within phyllosilicates at the nanometer scale ⁷⁴. This may be caused by different reasons, as (1) spatial redistribution followed by encapsulation of organic matter into nanoscale porosity between phyllosilicates grains during aqueous alteration, (2) absorption of soluble organics onto the surfaces of phyllosilicates or (3) intercalation of some organic molecules into the interlayer sites of smectite-like clays such as saponite ¹³. The detection of organic matter associated with saponite in this study also proves that phyllosilicate could trap nucleobases efficiently. The solubility of nucleobases may play a role in their spatial distribution. In the Murchison meteorite, it was shown that organic grains appear chemically heterogenous as illustrated by variations in width and intensity of the aromatic and C=O peak ¹³. The C=O bond from nucleobases within the interlayers of saponite may also contribute to the C=O peak (Figure 6,7 and 8). Our study shows that saponite trapped more organic compounds from uracil solution than other minerals used herein. This maybe also relate to the stereoscopic structure and geometric size of organic cations and the types of arrangements in the interlayer space of saponite ⁷⁵. The smaller the organic compounds, the easier it is to get into the interlayer spaces of phyllosilicate.

The caveat for this intimate association is that nucleobases could be difficult to extract. Moreover, their variable affinity with mineral surfaces may result in fractioning during analytical extraction e.g. measured concentrations may be biased by extraction efficiency that is variable from one nucleobase to the other. Hence, new effective extraction methods for meteoritic nucleobases should be developed in future studies. Factors influencing extraction efficiency, such as the temperature and pH of the extraction solvent for the target nucleobase and the influence of saponite or other clay minerals, should be considered.

5. Conclusions

The influence of minerals on the evolution of nucleobases under aqueous alteration at 150 °C for 10 days has been investigated. Guanine and uracil appear to be insensitive to aqueous alteration in asteroidal conditions. Xanthine appears to undergo decarboxylation as attested by the release of CO₂ and the decrease in C and N contents in the solid and liquid products of experiments with and without minerals. About 25% of xanthine and 53% of uracil may be trapped or adsorbed by phyllosilicates after the experiment. However, the presence of iron containing minerals does not influence the preservation of nucleobases under similar aqueous alteration conditions, which contrasts with previous studies. The isotope composition of nucleobases during aqueous alteration remains constant for uracil and guanine, indicating that the pre-accretion isotope signature of nucleobases or their precursors has been preserved. Xanthine gets slightly enriched in heavy isotopes of C and N. Therefore, the isotope compositions of uracil and guanine detected in carbonaceous chondrites have been directly inherited from their synthesis environment in the protosolar nebula or the molecular cloud. The isotope composition of xanthine may have slightly increased during aqueous alteration hence reported values are upper estimates of the composition of accreted xanthine.

Nucleobase abundance in meteorites can be discussed in the light of our experiments. Guanine is the most abundant while it is shown to be the most stable upon aqueous alteration. Uracil has a higher solubility in water and appears to dominate the nucleobase content of heavily altered chondrites like Orgueil, maybe as the result of water transport during aqueous alteration. Differences between meteorites within the same class, but showing different alteration degrees, may result from fluid transport of organics that induces redistribution within parent bodies.

Xanthine, the less stable nucleobase in this study, is undetected in type 1 chondrites but rather abundant in type 2; it may result from its degradation during aqueous alteration on the parent body. This study improves our understanding of the evolution of nucleobases in the context of aqueous alteration. It confirms that the isotope characteristics of extraterrestrial nucleobases in carbonaceous chondrites result from the conditions of their pre-accretion synthesis conditions (or those of their precursors).

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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Supporting information:

Page 2-4: The characterization methods of gas (GC-TCD), liquid (GC-MS) and solid phase

Figure S1: The chromatogram of H₂O after 10 days experiment (control experiment) with TMAH. (XRD, EA-irMS, FT-IR and EA) of amino acids are in the supplementary information (SI).

Figure S2: the comparison of mass spectra of methylated nucleobases before and after the experiments (correspond to Figure 3).

Table S1: Elemental analysis of nucleobases before and after aqueous alteration (correspond to Figure 4).

Figure S3: ATR-MIR spectra of the initial minerals.

Page 11: FT-IR analysis of nucleobases and the residues of nucleobases and minerals after experiments.

Table S2: Stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotope analysis of experimental products along with initial compositions, corresponding to the data of Figure 8.

Page 13: XRD analysis minerals and the residues of nucleobases and minerals after experiments.

Figure S4-S8: XRD patterns of initial minerals and the residues of minerals with and without nucleobase after aqueous alteration at 150 °C for 10 days.

Figure S9: XRD patterns ambient pressure and under vacuum of initial gel-saponite (Gel) and saponite (Sap), and their residues of after aqueous alteration at 150 °C for 10 days with and without nucleobase.

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