Radiolysis of solid-state nitrogen heterocycles provides clues to their abundance in the early solar system

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Abstract

We studied the radiolysis of a wide variety of N-heterocycles, including many of biological importance, and find that the majority are remarkably stable in the solid-state when subjected to large doses of ionizing gamma radiation from a ^{60}Co source. Degradation of N-heterocycles as a function of dose rate and total dose was measured using high-performance liquid chromatography with UV detection. Many N-heterocycles show little degradation when γ-irradiated up to a total dose of ∼1 MGy, which approximates hundreds of millions of years' worth of radiation emitted in meteorite parent bodies due to slow radionuclide decay. Extrapolation of these results suggests that these N-heterocyclic compounds would be stable in dry parent bodies over solar system timescales. We suggest that the abundance of these N-heterocycles as measured presently in carbonaceous meteorites is largely reflective of their abundance at the time aqueous alteration stopped in their parent bodies and the absence of certain compounds in present-day samples is either due to the formation mechanisms or degradation which occurred during periods of aqueous alteration or thermal metamorphism.

Introduction

Carbonaceous chondrites are meteorites that contain abundant indigenous organic compounds, including many of biological significance such as amino acids and nucleobases (Sephton, 2002; Burton *et al.*, 2012). Meteorites are continuously delivered to the Earth today (Halliday *et al.*, 1989) and were likely delivered at a much higher rate early in its history (Schoenberg *et al.*, 2002; Gomes *et al.*, 2005). Thus, these materials are significant in that they represent major initial inputs of organic materials to early solar system planetary surfaces and may have contributed to the origins of life on Earth (Oró, 1961; Chyba and Sagan, 1992). One generally accepted scheme for the synthesis of these meteoritic organics is that they are derived from the energetic processing of simpler compounds that had condensed on dust grains. Eventually, these grains were incorporated into larger parent bodies such as asteroids. Pre-terrestrial aqueous alteration, which is attributed to radiogenic heating and melting of ice on the parent asteroid shortly after accretion, likely influenced the organics found in meteorites as well (Browning *et al.*, 1996; Wilson *et al.*, 1999).

In modern analyses of meteorites, the distribution and abundance of indigenous organic compounds may not necessarily reflect those originally present billions of years ago when carbonaceous chondrites were delivered to the prebiotic Earth. One potential reason for this is the prolonged radiolysis of organic compounds while in the dry state (after the aqueous alteration phase) since long-lived radionuclides likely contributed significant doses of high-energy radiation within meteorite parent bodies over their entire lifetimes (Urey, 1955, 1956). The early solar system contained a variety of radionuclides, which are well-documented in meteorites (Lee *et al.*, 1976, 1998; McKeegan *et al.*, 2000; Huss *et al.*, 2001). Though ^{26}Al is relatively short-lived ($t_{1/2} \sim 7.2 \times 10^5$ y), it may have been especially abundant in early solar system materials (Diehl *et al.*, 1995; Macpherson *et al.*, 1995; Russell *et al.*, 1996). ^{40}K, ^{235}U, ^{238}U and ^{232}Th have long half-lives and undergo complex decay resulting in the emission of high-energy particles and γ-rays. These γ-rays are of sufficient energy to interact with matter via Compton scattering, effectively transferring photon energy to electrons and creating positive ion radicals, which then could lead to degradation or possibly complexification of organic compounds. Cosmic rays are also prevalent; however, they are not deeply penetrating and the absorbed energy would affect only the surface layers (on the range of meters) in asteroids (Draganic *et al.*, 1984).

There has been a long history of research to understand how organic compounds can be synthesized and survive in harsh cosmic environments through laboratory experiments

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using radiolytic and photolytic processing (Bernstein *et al.*, 1995; Hudson and Moore, 2001). Multiple investigations have examined the effect of ionizing radiation on the survival and racemization of amino acids (Cataldo *et al.*, 2011*b*, 2011*a*, Iglesias-Groth *et al.*, 2011) in an effort to explain the non-racemic mixtures of amino acids observed in meteorites (Cronin and Pizzarello, 1997; Pizzarello and Cronin, 2000; Glavin and Dworkin, 2009).

Here, various nitrogen heterocycles in the solid-state were exposed to γ-radiation from a ^{60}Co source to investigate the stability of these compounds with respect to total radiation dose and dose rate. The nitrogen heterocycles studied (see Fig. 1) included the canonical nucleobases, which are universal to nucleic acids and closely related purines and pyrimidines that have been identified in cyanide reactions (Sanchez *et al.*, 1967; Ferris *et al.*, 1978; Ferris and Hagan, 1984; Miyakawa *et al.*, 2002) and/or extraterrestrial meteorites (Vandervelden and Schwartz, 1977; Stoks and Schwartz, 1979, 1981, 1982; Martins *et al.*, 2008; Callahan *et al.*, 2011) and thought to be important for prebiotic chemistry and the origin of life on early Earth. Simulating hundreds of millions of years of radiation over the course of a few months raises reasonable questions about the realism of such simulations. As it is impossible to carry out such experiments on solar system timescales, we have designed our experiments as efficiently and practically as possible to investigate the radiolytic stability of nitrogen heterocycles and to better understand what the distribution and abundance of these compounds may have been in meteorites delivered to Earth approximately 4 billion years ago.

Methods

Sample preparation of γ-irradiated samples and controls

All glassware used in these experiments was wrapped in aluminum foil and baked at 500 °C for 24 h under air to remove organic contaminants. Ultrapure water (18.2 MΩ·cm) produced by a water purification system was used for this study.

Individual solutions of nitrogen heterocycles were prepared by dissolving the reference standard with 0.1 M NH_4OH to a concentration in the low millimolar range. 400 µl of each nitrogen heterocycle solution was added to individual glass ampoules and heated to dryness at 60 °C using an oven. Once dry, these ampoules were sealed under vacuum on a glass Schlenk line using a hand-held butane torch. For each nitrogen heterocycle, 11 ampoules were prepared: four non-irradiated controls and seven samples for radiolysis.

A ^{60}Co source at the Research Laboratory for Nuclear Reactors at the Tokyo Institute of Technology was used to provide γ-radiation for this study. One set of ampoules for each heterocycle was placed at a distance of 30 cm from a ^{60}Co source in order to receive a dose rate of ~350 Gy h^{-1}. These ampoules were placed around the γ-radiation source (Fig. 2) and one ampoule from each set was removed from the source at ~17-day intervals in order to produce sets of samples with increasing doses of γ-radiation (see Table 1). The maximum total dose was ~0.992 MGy, which took 119 days to complete. Additionally, sets of canonical nucleobases were placed at varying distances from the radiation source (Fig. 2) in order to receive a total dose of ~250 kGy, but with different dose rates (see Table 2). A slower dose rate, corresponding to a sample placed further away from the ^{60}Co source, means a longer time on the source in order for the samples to receive the same total dose of

~250 kGy. Irradiation experiments took place at room temperature. After irradiation of samples was complete, samples and non-irradiated controls were carefully packaged and shipped to Boise State University for work-up and sample analysis.

To prepare samples for high-performance liquid chromatography (HPLC) analysis, sealed ampoules were cracked open using disposable ampoule openers (a popping sound was observed upon opening ampoules, which indicated that the vacuum seal had not been compromised). 400 µl 0.1 M NH_4OH was placed inside each ampoule and mixed using a vortex mixer on low setting for 30 s. The ampoules were then allowed to stand for 20 min in order to dissolve the individual nitrogen heterocycle before transferring to an HPLC vial. An additional 400 µl 0.1 M NH_4OH was added to the ampoule and the process was repeated: vortex mix, let stand for 20 min, rinse the sides and then solution transfer. A final volume of 200 µl 0.1 M NH_4OH was added and the procedure was performed one last time to ensure quantitative transfer. These steps provided a 1 ml sample. Typically, a 100-fold dilution for nitrogen heterocycle sample solutions was performed before HPLC analysis for accurate quantitation using a standard concentration curve.

Guanine does not readily dissolve in 0.1 M NH_4OH; therefore, guanine samples were dissolved in 1 M NH_4OH according to a slightly modified procedure from that used for the above samples. Two 400 µl and one 200 µl aliquots of 1 M NH_4OH were used as outlined above. After this, nine successive 1 ml volumes of 1 M NH_4OH were used to quantitatively rinse the ampoules for sample transfer into a 25 ml glass vial. From this guanine in 1 M NH_4OH solution (10 ml), a 1:10 dilution using ultrapure water was performed, which resulted in the same 100-fold dilution as described earlier. Sample solutions were analysed immediately by HPLC.

High performance liquid chromatography

Irradiated samples, non-irradiated controls and reference standard solutions were analyzed using a Thermo Scientific Accela HPLC/UHPLC coupled to an Accela photodiode array detector (PDA). Nitrogen heterocycle separation was achieved by injecting 10 µl sample solution onto a Phenomenex Synergi 4 µ Fusion reverse phase column (2 mm × 150 mm; 80 Å pore size). The flow rate was 200 µl min^{-1} and the column temperature was maintained at 30 °C. Mobile phase A was composed of 20 mM ammonium acetate buffer at pH 4.5 and mobile phase B was acetonitrile. The ammonium acetate buffer was prepared via NH_4OH titration of 20 mM acetic acid solution to pH 4.5. The following HPLC gradient was used: 0–10 min 0–45% B, 10–12 min 45–100% B, 12–17 min 100% B, 17–19 min 100–0% B and 19–29 min 0% B (equilibration of column). The PDA detector recorded the UV spectrum from 200–400 nm, although 260 nm was typically used for nitrogen heterocycle analysis. All samples were analysed in triplicate.

To prepare reference standard solutions, nitrogen heterocycles were dissolved in 0.1 M NH_4OH to produce ~3 mM stock solutions. Serial dilutions were then performed to prepare 1, 10, 50 and 100 µM working solutions. Four-point calibration curves for each nitrogen heterocycle were measured and determined to be linear ($R^2 > 0.99$) in this concentration range.

Recovery of irradiated nitrogen heterocycles was calculated in two ways: (1) HPLC peak area of the irradiated nitrogen heterocycle compared with HPLC peak area of the non-irradiated control and (2) mole ratio of the irradiated nitrogen heterocycle to the non-irradiated control using the corresponding calibration curve. These two methods gave nearly identical results. Per cent
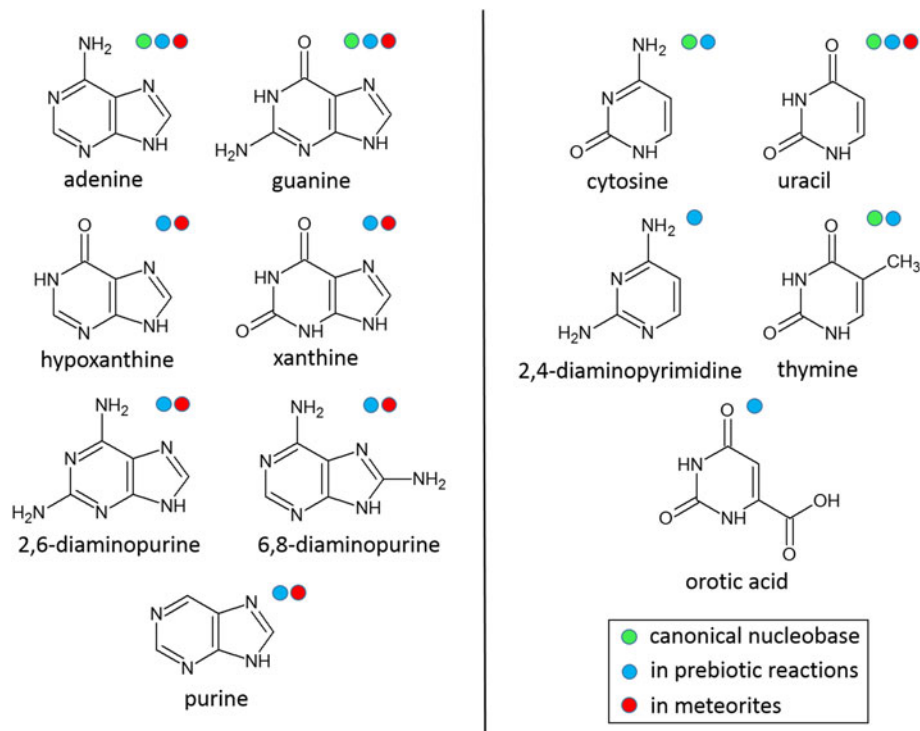
Fig. 1. Structures of nitrogen heterocycles that underwent γ-irradiation studies. These nitrogen heterocycles are considered important for prebiotic chemistry leading to the origin of life (i.e. they are identified in plausible prebiotic reactions and/or extraterrestrial meteorites) or are essential for biology.
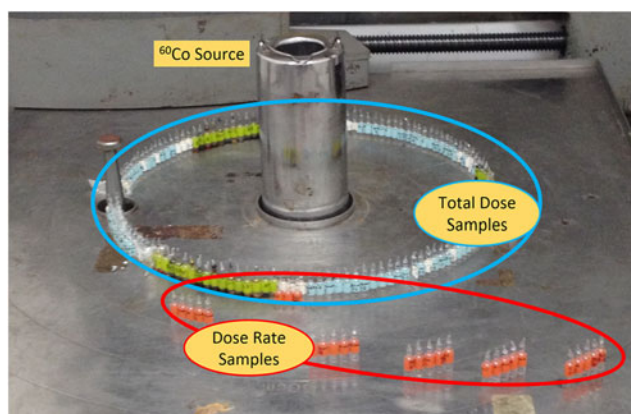

Fig. 2. Photograph of sample placement around the ^{60}Co source. Samples of solid-state nitrogen heterocycles in vacuum-sealed glass ampoules are specifically placed for two separate studies: the effect of total dose (in blue circle) and dose rate (in red circle).

Table 1. Total dose and irradiation time for N-heterocycles

Sample set	Days (h)	Total dose (Gy)
1	17 (408)	141 739
2	34 (816)	283 478
3	51 (1224)	425 218
4	68 (1632)	566 957
5	85 (2040)	708 696
6	102 (2448)	850 435
7	119 (2856)	992 174

Table 2. Dose rate data

Sample set	Days (h)	Distance (cm)	Dose rate (Gyh^{-1})	Total dose (Gy)
1	34 (816)	32	304	241 252
2	51 (1224)	39	207	249 533
3	68 (1632)	45.5	154	249 043
4	85 (2040)	51	123	251 225
5	102 (2448)	56	103	252 886
6	119 (2856)	61	87	251 236

recoveries shown in Tables 3–5 are based on the first method using the equation below:

$$\% \, \text{Recovery} = \frac{\text{HPLC Peak Area (Irradiated Sample)}}{\text{HPLC Peak Area (Control)}} \times 100$$

Results and discussion

For all irradiated samples, only one peak was detected in the UV chromatogram, which corresponded to the nitrogen heterocycle of interest. Furthermore, no degradation products were detected in UV chromatograms using the full spectral range from 200 to 400 nm. This may be due to non-volatile degradation products lacking a chromophore in this UV detection range or that,

more likely, degradation products were volatile and lost during the sample work-up. As an example, UV chromatograms of irradiated adenine and guanine along with their controls (non-irradiated adenine and guanine) are shown in Fig. 3.

In the solid state, most of the purines and pyrimidines in this study appear to be remarkably stable to γ-radiation up to doses of

Table 3. Percent recovery of γ-irradiated purines

Dose (kGy)	Purine	Adenine	Hypoxanthine	Guanine	Xanthine	2,6-diaminopurine	6,8-diaminopurine
142	98 ± 3	102 ± 1	99.6 ± 0.6	108.0 ± 0.9	98.6 ± 0.9	103 ± 1	98.3 ± 0.2
283	93 ± 2	102 ± 1	96.7 ± 0.6	91.1 ± 0.1	94 ± 1	95 ± 2	101.1 ± 0.9
425	94 ± 3	102 ± 1	98.2 ± 0.4	89 ± 1	94 ± 1	98 ± 3	100 ± 1
567	93 ± 5	95.7 ± 5	98 ± 1	87 ± 1	99 ± 2	98 ± 2	94 ± 2
709	96 ± 2	97.1 ± 0.9	95.8 ± 0.8	83.6 ± 0.9	99 ± 2	99 ± 4	97.1 ± 0.7
850	94 ± 3	96 ± 3	100.4 ± 0.3	76 ± 1	97 ± 2	99 ± 3	89.3 ± 0.6
992	94 ± 2	102 ± 3	102.5 ± 0.7	47 ± 3	69 ± 3	102 ± 3	99 ± 2

Table 4. Percent recovery of γ-irradiated pyrimidines

Dose (kGy)	Cytosine	Uracil	Thymine	Orotic acid	2,4-diaminopyrimidine
142	104 ± 2	96 ± 1	105 ± 3	99.9 ± 0.8	102 ± 0.4
283	99 ± 5	97.5 ± 0.8	100 ± 3	93 ± 2	100 ± 1
425	108 ± 4	98.0 ± 0.9	100 ± 6	98 ± 1	103 ± 1
567	94 ± 2	92.8 ± 0.9	101 ± 5	87.6 ± 0.2	99.6 ± 0.5
709	100 ± 1	97 ± 1	99 ± 5	99.3 ± 0.3	99.5 ± 1
850	106 ± 3	97 ± 1	99 ± 3	95 ± 1	96.1 ± 0.5
992	97 ± 8	91 ± 1	101 ± 7	97.9 ± 0.5	NS

NS indicates no sample (ampoule was broken during shipping).

Table 5. Percent recovery of γ-irradiated nucleobases using different dose rates. Total dose was ∼250 kGy

Dose rate (Gy h^{-1})	Adenine	Guanine	Cytosine	Thymine	Uracil
87	91 ± 5	98 ± 1	99 ± 3	96 ± 6	99 ± 1
103	97 ± 3	85.2 ± 0.8	96 ± 3	101 ± 6	98.2 ± 0.5
123	98 ± 1	83.9 ± 0.7	96 ± 4	103 ± 9	98.8 ± 0.2
154	99 ± 1	80 ± 1	100 ± 3	90 ± 5	97.2 ± 0.8
207	98 ± 2	71 ± 0.5	99 ± 2	101 ± 5	96 ± 1
304	NS	82 ± 1	NS	109 ± 3	96.0 ± 0.9

NS indicates no sample at this dose rate.

1 MGy (see Tables 3 and 4). All of the canonical nucleobases, with the exception of guanine, were extremely stable to γ-radiation, which always showed >90% recoveries. Similar stability of nucleobases was also observed by Pilling *et al.* who used soft X-rays at 150 eV to irradiate solid-state adenine and uracil and concluded that only small reductions were measured by *in situ* Fourier transform infrared spectroscopy (Pilling *et al.*, 2011). Past studies have also shown that nucleobases are much more resistant to ionizing radiation than amino acids, another class of organic compounds necessary for life as we know it (Pilling *et al.*, 2011; Cataldo *et al.*, 2011*a*, 2011*b*; Iglesias-Groth *et al.*, 2011; Cherubini *et al.*, 2014).

Purine is very stable to γ-radiation. Adenine (6-aminopurine), 2,6-diaminopurine and 6,8-diaminopurine are also very stable to γ-radiation, which demonstrates that adding basic amine groups in different positions to purine does not reduce or enhance resistance to γ-irradiative decomposition. Hypoxanthine, a deamination product (replacement of an amino group with a carbonyl group) of adenine, was extremely stable to γ-radiation, which suggests that purines substituted at the 6-position are also relatively stable.

The recovery of guanine decreases as the radiation dose increases. Also, guanine displays the highest decomposition of all the compounds studied here, a reduction of 53% at ∼1 MGy. Xanthine remained very stable to γ-radiation with the exception of the last data point (992 kGy), which showed a 31% decrease compared with its control. The exact reason for this decrease is unknown, although we may draw some insight by comparing xanthine to guanine. Xanthine is a deamination product of guanine and their structural similarity may explain their response to γ-radiation; guanine and xanthine were the two nitrogen heterocycles with the highest degree of decomposition. Methylation of xanthine does not alter its high radiolytic stability. In a previous study, theobromine (3,7-dimethylxanthine), theophylline (1,3-dimethylxanthine) and caffeine (1,3,7-trimethylxanthine) showed very little degradation to ionizing radiation (9.96 MeV electron beam) up to doses of 400 kGy (Marciniec *et al.*, 2013).
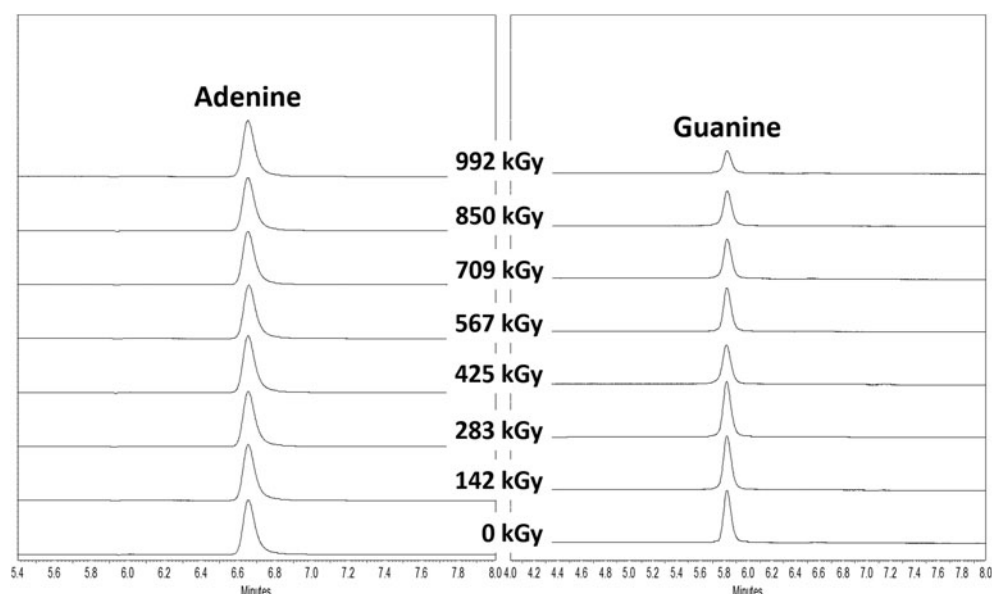
Fig. 3. UV chromatograms at 260 nm of γ-irradiated adenine and guanine at increasing doses along with their control samples (0 kGy).

All five pyrimidines studied here were also very stable to γ-radiation and methyl, amine and carboxylic acid substitutions did little to alter this stability.

The second part of our study investigated the effect of dose rate on the degradation of the canonical nucleobases. Percent recoveries of γ-irradiated nucleobases were determined at different dose rates (between 87 and 304 Gy h^{-1}) while the total dose remained constant (~250 kGy), which is shown in Table 5. For adenine, cytosine, thymine and uracil, the percent recoveries of γ-irradiated nucleobases were relatively high, ranging from 91 to 109%, which suggested that the radiolysis of these canonical nucleobases in the solid-state did not significantly depend on the dose rate. The lower recovery of adenine at a dose rate of ~87 Gy h^{-1} is calculated as an outlier at 95% confidence using a Dixon's Q-test; however, we cannot completely rule out that a lower dose rate does not have an effect on adenine.

Guanine is a different story. At a total dose of ~250 kGy, the recovery of guanine steadily declines from 98% to 71% as the dose rate increases from 87 to 207 Gy h^{-1}; however, at the highest dose rate of 304 Gy h^{-1}, the recovery of guanine is around 82%. Nonetheless, the effect of dose rate on guanine is readily apparent when compared with the other canonical nucleobases. It is also interesting to note that the canonical nucleobases (adenine, cytosine, thymine and uracil) that were most stable to the highest doses of γ-radiation seemed to be the least affected by different dose rates. For guanine, appreciable decomposition due to γ-radiation may indicate greater sensitivity to dose rate. Further investigation of more nitrogen heterocycles would be necessary to see if these trends are consistent. Finally, these results suggest that both total dose and dose rate should be examined with each particular compound for a full understanding of its radiation chemistry.

Comparison of results with estimated cosmic radiation doses

Draganic *et al.* have estimated that a cometary nucleus of 10 km radius would contain radionuclides that would emit ~14 MGy of radiation over 4.5 billion years (the age of the Solar System); the majority of this radiation (11 MGy) occurring in the first

tens of millions of years due to ^{26}Al decay (Draganic *et al.*, 1984). Many other studies investigating the radiolysis of organic compounds have adopted this dose of 14 MGy for asteroids and comets in general (Cataldo *et al.*, 2011*a*, 2011*b*; Iglesias-Groth *et al.*, 2011; Cherubini *et al.*, 2014). Our total dose of ~1 MGy approximates hundreds of million years' worth of γ-radiation emitted in meteorite parent bodies due to slow radionuclide decay. Linear extrapolation of our results suggests that there would be only small differences, less than an order of magnitude, between the purine nitrogen heterocycle abundances measured in carbonaceous chondrites today with those from the early solar system (with the exception of guanine). It is important to point out that our experiments involve the radiolysis of pure nitrogen heterocycles only and do not take into account other organics and mineral matrices that co-exist within asteroids. Therefore, we would consider any extrapolation to organic abundance as a first approximation only. Nonetheless, we conclude that nitrogen heterocycles would be very stable in dry parent bodies and persist for billions of years, hence their detection in carbonaceous chondrites today (Callahan *et al.*, 2011; Smith *et al.*, 2014).

Conclusions

Many purine and pyrimidine nitrogen heterocycles in the solid state are remarkably stable when γ-irradiated to ~1 MGy, which is the dose equivalent of γ-radiation released by radionuclide decay in asteroids in ~350 million years (assuming a total radiation dose of 14 MGy and simple linear decay only). The effect of dose rate on the survival of nitrogen heterocycles may be compound dependent; however, we observed that different dose rates influenced the recovery of guanine, which turned out to be the nitrogen heterocycle most prone to decomposition. From our radiolysis data, we suggest that the abundance of these purine nitrogen heterocycles, with the exception of guanine, as measured presently in CM2 carbonaceous chondrites is largely reflective of their abundance at the time aqueous alteration stopped in the parent bodies. The absence of other nitrogen heterocycles (derived from NH_4CN chemistry) in carbonaceous chondrites may be

due to degradation that occurred during the period of aqueous alteration. Finally, we suggest that guanine may have been more abundant in young parent bodies of carbonaceous chondrites (compared with guanine found in carbonaceous chondrites today) and that increased abundances may have made this nucleobase particularly favourable for prebiotic chemistry leading to a primitive genetic material.

References

Bernstein MP, Sandford SA, Allamandola LJ, Chang S and Scharberg MA (1995) Organic-compounds produced by photolysis of realistic interstellar and cometary ice analogs containing methanol. *Astrophysical Journal* **454**, 327–344.

Browning LB, McSween HY and Zolensky ME (1996) Correlated alteration effects in CM carbonaceous chondrites. *Geochimica Et Cosmochimica Acta* **60**, 2621–2633.

Burton AS, Stern JC, Elsila JE, Glavin DP and Dworkin JP (2012) Understanding prebiotic chemistry through the analysis of extraterrestrial amino acids and nucleobases in meteorites. *Chemical Society Reviews* **41**, 5459–5472.

Callahan MP, Smith KE, Cleaves II HJ, Ruzicka J, Stern JC, Glavin DP, House CH and Dworkin JP (2011) Carbonaceous meteorites contain a wide range of extraterrestrial nucleobases. *Proceedings of the National Academy of Sciences of the United States of America* **108**, 13995–13998.

Cataldo F, Angelini G, Iglesias-Groth S and Manchado A (2011*a*) Solid state radiolysis of amino acids in an astrochemical perspective. *Radiation Physics and Chemistry* **80**, 57–65.

Cataldo F, Ragni P, Iglesias-Groth S and Manchado A (2011*b*) A detailed analysis of the properties of radiolyzed proteinaceous amino acids. *Journal of Radioanalytical and Nuclear Chemistry* **287**, 903–911.

Cherubini C, Ursini O, Cataldo F, Iglesias-Groth S and Crestoni ME (2014) Mass spectrometric analysis of selected radiolyzed amino acids in an astrochemical context. *Journal of Radioanalytical and Nuclear Chemistry* **300**, 1061–1073.

Chyba C and Sagan C (1992) Endogenous production, exogenous delivery and impact-shock synthesis of organic molecules: an inventory for the origins of life. *Nature* **355**, 125–132.

Cronin JR and Pizzarello S (1997) Enantiomeric excesses in meteoritic amino acids. *Science* **275**, 951–955.

Diehl R, Dupraz C, Bennett K, Bloemen H, Hermsen W, Knodlseder J, Lichti G, Morris D, Ryan J, Schonfelder V, Steinle H, Strong A, Swanenburg B, Varendorff M and Winkler C (1995) COMPTEL observations of Galactic ^{26}Al emission. *Astronomy & Astrophysics* **298**, 445–460.

Draganic IG, Draganic ZD and Vujosevic S (1984) Some radiation-chemical aspects of chemistry in cometary nuclei. *Icarus* **60**, 464–475.

Ferris JP and Hagan WJ (1984) HCN and chemical evolution: the possible role of cyano compounds in prebiotic synthesis. *Tetrahedron* **40**, 1093–1120.

Ferris JP, Joshi PC, Edelson EH and Lawless JG (1978) HCN: a plausible source of purines, pyrimidines and amino acids on the primitive Earth. *Journal of Molecular Evolution* **11**, 293–311.

Glavin DP and Dworkin JP (2009) Enrichment of the amino acid L-isovaline by aqueous alteration on CI and CM meteorite parent bodies. *Proceedings of the National Academy of Sciences of the United States of America* **106**, 5487–5492.

Gomes R, Levison HF, Tsiganis K and Morbidelli A (2005) Origin of the cataclysmic Late Heavy Bombardment period of the terrestrial planets. *Nature* **435**, 466–469.

Halliday I, Blackwell AT and Griffin AA (1989) The flux of meteorites on the Earth's surface. *Meteoritics* **24**, 173–178.

Hudson RL and Moore MH (2001) Radiation chemical alterations in solar system ices: an overview. *Journal of Geophysical Research-Planets* **106** (E12), 33275–33284.

Huss GR, MacPherson GJ, Wasserburg GJ, Russell SS and Srinivasan G (2001) Aluminum-26 in calcium-aluminum-rich inclusions and chondrules from unequilibrated ordinary chondrites. *Meteoritics & Planetary Science* **36**, 975–997.

Iglesias-Groth S, Cataldo F, Ursini O and Manchado A (2011) Amino acids in comets and meteorites: stability under gamma radiation and preservation of the enantiomeric excess. *Monthly Notices of the Royal Astronomical Society* **410**, 1447–1453.

Lee T, Papanastassiou DA and Wasserburg GJ (1976) Demonstration of ^{26}Mg excess in Allende and evidence for ^{26}Al. *Geophysical Research Letters* **3**, 109–112.

Lee T, Shu FH, Shang H, Glassgold AE and Rehm KE (1998) Protostellar cosmic rays and extinct radioactivities in meteorites. *Astrophysical Journal* **506**, 898–912.

Macpherson GJ, Davis AM and Zinner EK (1995) The distribution of aluminum-26 in the early Solar System–a reappraisal. *Meteoritics* **30**, 365–386.

Marciniec B, Stawny M, Olszewski K, Kozak M and Naskrent M (2013) Analytical study on irradiated methylxanthine derivatives. *Journal of Thermal Analysis and Calorimetry* **111**, 2165–2170.

Martins Z, Botta O, Fogel ML, Sephton MA, Glavin DP, Watson JS, Dworkin JP, Schwartz AW and Ehrenfreund P (2008) Extraterrestrial nucleobases in the Murchison meteorite. *Earth and Planetary Science Letters* **270**, 130–136.

McKeegan KD, Chaussidon M and Robert F (2000) Incorporation of short-lived ^{10}Be in a calcium-aluminum-rich inclusion from the Allende meteorite. *Science* **289**, 1334–1337.

Miyakawa S, Cleaves HJ and Miller SL (2002) The cold origin of life: B. Implications based on pyrimidines and purines produced from frozen ammonium cyanide solutions. *Origins of Life and Evolution of the Biospheres* **32**, 209–218.

Oró J (1961) Comets and formation of biochemical compounds on primitive Earth. *Nature* **190**, 389–390.

Pilling S, Andrade DPP, do Nascimento EM, Marinho RRT, Boechat-Roberty HM, de Coutinho LH, de Souza GGB, de Castilho RB, Cavasso RL, Lago AF and de Brito AN (2011) Photostability of gas- and solid-phase biomolecules within dense molecular clouds due to soft X-rays. *Monthly Notices of the Royal Astronomical Society* **411**, 2214–2222.

Pizzarello S and Cronin JR (2000) Non-racemic amino acids in the Murray and Murchison meteorites. *Geochimica Et Cosmochimica Acta* **64**, 329–338.

Russell SS, Srinivasan G, Huss GR, Wasserburg GJ and MacPherson GJ (1996) Evidence for widespread ^{26}Al in the solar nebula and constraints for nebula time scales. *Science* **273**, 757–762.

Sanchez RA, Ferris JP and Orgel LE (1967) Studies in prebiotic synthesis: II. Synthesis of purine precursors and amino acids from aqueous hydrogen cyanide. *Journal of Molecular Biology* **30**, 223–253.

Schoenberg R, Kamber BS, Collerson KD and Moorbath S (2002) Tungsten isotope evidence from ~3.8-Gyr metamorphosed sediments for early meteorite bombardment of the Earth. *Nature* **418**, 403–405.

Sephton MA (2002) Organic compounds in carbonaceous meteorites. *Natural Product Reports* **19**, 292–311.

Smith KE, Callahan MP, Gerakines PA, Dworkin JP and House CH (2014) Investigation of pyridine carboxylic acids in CM2 carbonaceous chondrites: potential precursor molecules for ancient coenzymes. *Geochimica Et Cosmochimica Acta* **136**, 1–12.

Stoks PG and Schwartz AW (1979) Uracil in carbonaceous meteorites. *Nature* **282**, 709–710.

Stoks PG and Schwartz AW (1981) Nitrogen-heterocyclic compounds in meteorites: significance and mechanisms of formation. *Geochimica Et Cosmochimica Acta* **45**, 563–569.

Stoks PG and Schwartz AW (1982) Basic nitrogen-heterocyclic compounds in the Murchison meteorite. *Geochimica Et Cosmochimica Acta* **46**, 309–315.

Urey HC (1955) The cosmic abundances of potassium, uranium, and thorium and the heat balances of the Earth, the Moon, and Mars. *Proceedings of the National Academy of Sciences of the United States of America* **41**, 127–144.

Urey HC (1956) The cosmic abundances of potassium, uranium, and thorium and the heat balances of the Earth, the Moon, and Mars. *Proceedings of the National Academy of Sciences of the United States of America* **42**, 889–891.

Vandervelden W and Schwartz AW (1977) Search for purines and pyrimidines in Murchison meteorite. *Geochimica Et Cosmochimica Acta* **41**, 961–968.

Wilson L, Keil K, Browning LB, Krot AN and Bourcier W (1999) Early aqueous alteration, explosive disruption, and reprocessing of asteroids. *Meteoritics & Planetary Science* **34**, 541–557.