SEEDING THE PREGENETIC EARTH: METEORITIC ABUNDANCES OF NUCLEOBASES AND POTENTIAL REACTION PATHWAYS

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ABSTRACT

Carbonaceous chondrites are a class of meteorite known for having high contents of water and organics. In this study, the abundances of the nucleobases, i.e., the building blocks of RNA and DNA, found in carbonaceous chondrites are collated from a variety of published data and compared across various meteorite classes. An extensive review of abiotic chemical reactions producing nucleobases is then performed. These reactions are then reduced to a list of 15 individual reaction pathways that could potentially occur within meteorite parent bodies. The nucleobases guanine, adenine, and uracil are found in carbonaceous chondrites in amounts of 1–500 ppb. It is currently unknown which reaction is responsible for their synthesis within the meteorite parent bodies. One class of carbonaceous meteorite dominates the abundances of both amino acids and nucleobases—the so-called CM2 (e.g., Murchison meteorite). CR2 meteorites (e.g., Graves Nunataks) also dominate the abundances of amino acids, but are the least abundant in nucleobases. The abundances of total nucleobases in these two classes are 330 ± 250 and 16 ± 13 ppb, respectively. Guanine most often has the greatest abundances in carbonaceous chondrites with respect to the other nucleobases, but is 1–2 orders of magnitude less abundant in CM2 meteorites than glycine (the most abundant amino acid). Our survey of the reaction mechanisms for nucleobase formation suggests that Fischer–Tropsch synthesis (i.e., CO, H2, and NH3 gases reacting in the presence of a catalyst such as alumina or silica) is the most likely candidate for conditions that characterize the early states of planetesimals.

Key words: astrobiology – astrochemistry – meteorites, meteors, meteoroids – methods: data analysis – molecular data

1. INTRODUCTION

It has long been proposed that a significant portion of the prebiotic reservoir of biomolecules (including amino acids, fatty acids, and nucleobases) on Earth was synthesized in comets and planetesimals and delivered by meteorites, comets, and interplanetary dust particles (Chamberlin & Chamberlin 1908; Oró 1961a; Chyba & Sagan 1992; Pierazzo & Chyba 1999; Burton et al. 2012). (Planetesimals in this context are solid bodies approximately 1–100 km in diameter, originating from the circumstellar disk.) This theory is substantiated by the high abundances of organics measured in the fragments of planetesimals, i.e., the carbonaceous chondrite meteorites that have fallen on the Earth. Additional support comes from the recent analysis of biomolecules on the surface of Comet 67P/Churyumov–Gerasimenko, which has revealed some evidence of nonvolatile organic macromolecular materials (Capaccioni et al. 2015). Thus, the formation and origin of pregenetic biomolecules for young planets is of particular interest for understanding the steps that led to the appearance of life.

Nucleobases are the nitrogen-containing, characteristic molecules in nucleotides. They come in two varieties: the purines, guanine (G) and adenine (A), and the pyrimidines, cytosine (C), thymine (T), and uracil (U). They are important because the particular ordering of nucleobases in the chain(s) of DNA in organisms (or RNA in some viruses) constitutes the genome. In DNA the base pairs are G–C and A–T, and in RNA the base pairs are G–C and A–U. Since all known organisms and viruses use DNA and/or RNA to replicate, and since DNA or RNA stores the instructions for building proteins, understanding the origin of the nucleobases is essential for understanding the origin of the genetic code.

As part of a long-term project to understand the astrophysical origins of biomolecules and their delivery to forming planets, Cobb & Pudritz (2014) first collated and displayed the abundances of amino acids in carbonaceous chondrites. Theoretical work on the origin of amino acids by means of aqueous Strecker reactions occurring in meteorite parent bodies was then carried out and compared with the meteoritic record (Cobb et al. 2014). In this and subsequent papers, we extend this approach to nucleobases by first presenting the available data on nucleobase abundances within meteorites.

There are three components to the nucleotide: one nucleobase (G, A, C, T, or U), one sugar (ribose or deoxyribose), and at least one phosphate group (PO43−). Three of the five nucleobases in DNA or RNA (G, A, and U) have been discovered in CM2, CR2, CI1, CM1, CR1, and CR3 type meteorites (Hayatsu 1964; Hayatsu et al. 1968, 1975; van der Velden & Schwartz 1977; Stoks & Schwartz 1979, 1981; Shimoyama et al. 1990; Martins et al. 2008; Callahan et al. 2011), along with some nucleobase analogs (purine, 2,6-diaminopurine, 6,8-diaminopurine) and nucleobase catabolic intermediates (hypoxanthine and xanthine). Ribose and deoxyribose have not been identified in meteorites (although the sugar dihydroxyacetone has; Cooper et al. 2001). Phosphates have been found as minerals in many meteorites, typically as Ca-phosphates or Fe-phosphate (Ebihara & Honda 1987). For informative reviews about carbonaceous chondrite meteorites and their classification, please see Cobb &
Pudritz (2014), Weisberg et al. (2006), Botta & Bada (2002), and Hayes (1967).

In this paper we begin by compiling a comprehensive list of the observed abundances of nucleobases in carbonaceous chondrites as reported in the scientific literature. We then collate and display the data from these studies, emphasizing the trends in abundances and frequencies of these molecules by meteoritic type—and hence formation conditions. The data is first displayed by the individual nucleobase abundance for each meteorite sample, then by the total nucleobase abundance for each meteorite sample, and finally by the average relative nucleobase abundance to G ratio for CM2 meteorites. The potential for nucleobase contaminant in the samples of each study are also reviewed.

We then perform an extensive survey of all of the published chemical methods that have been employed or suggested as pathways for the abiotic formation of nucleobases. This survey is presented as a starting point in order to understand the reaction pathway(s) that could occur within planetesimals. The comprehensive list is reduced by disregarding reactions that are unlikely to occur in such environments. A final list of candidate nucleobase reaction pathways within planetesimals is then proposed.

In a subsequent paper, we will use this candidate list to investigate the synthesis of nucleobases in planetesimal interiors.

2. METEORITIC DATA

The two fundamental techniques for measuring meteoritic nucleobases in the laboratory are chromatography and mass spectrometry (MS). Chromatography separates a mixture by dissolving it in a fluid, a.k.a. the mobile phase, and sending it through a structure, e.g., a column, holding a stationary phase, e.g., a silica layer. The molecules in the mixture travel at different speeds through the structure, causing them to separate for detection. MS separates a mixture by ionizing its constituents (e.g., by bombarding them with electrons) and then accelerating them through an electric or magnetic field. The ions are deflected as they pass through the field, and separated according to their mass-to-charge ratio.

The specific analytical techniques used to detect nucleobases in carbonaceous chondrites have improved significantly over time. The first analyses of nucleobases applied paper and thin-layer chromatography (PC, TLC, respectively; Hayatsu 1964; Hayatsu et al. 1968) and MS (Hayatsu et al. 1975). (PC and TLC are very similar, with the only difference being that PC has its stationary phase within a tube and TLC has its stationary phase on a plane.) These studies found extraordinarily high concentrations of G and A in the Murchison and Orgueil meteorites, with abundances ranging from 5000 to 20,000 ppb. Analytical techniques then moved toward ion-exclusion chromatography (IEC, IEC-MS; van der Velden & Schwartz 1977; Stoks & Schwartz 1979, 1981) and high performance liquid chromatography (HPLC, HPLC-MS; Shimoyama et al. 1990; Callahan et al. 2011). These studies yielded nucleobase abundances in the 1–500 ppb range. IEC uses an aqueous mobile phase and separates the ionized compounds from the non-ionized compounds of a mixture by excluding the former. After the mixture is separated by the chromatograph, it is sometimes sent into a mass spectrometer for further separation. HPLC has a liquid mobile phase and improves chromatographic resolution by applying pressure to the dissolved mixture, allowing the mixture to flow at a much higher speed through the column. The use of a higher pressure allows for smaller particles to be used for the column packing material, which creates a greater surface area for interaction between the stationary phase and the flowing molecules. This allows for a better separation of molecules. MS is also sometimes used in tandem with HPLC for further separation.

TLC has been found to be less sensitive and gives worse separation than HPLC (Choma 2005). Stoks & Schwartz (1981) also note that the analytical techniques applied in the earliest studies (PC, MS) are not very suitable for quantitative purposes. Therefore due to their lower accuracy and sensitivity, we do not consider the studies that used PC, TLC, or MS in the quantitative analysis in this paper (i.e., Hayatsu et al. 1968, 1975 and Hayatsu 1964).

Table 1 lists the data sources for the nucleobases, nucleobase intermediates, and nucleobase analogs in each carbonaceous chondrite in this analysis. Carbonaceous chondrites are classified into types based primarily on composition and secondarily on amounts of aqueous and thermal processing (see Cobb & Pudritz 2014 for an overview). For instance, the character “R” in CR1 meteorites signifies that the meteorite is of Renazzo-like composition. The Renazzo meteorite is a meteorite that fell in Renazzo, Italy in 1824. The number “1” in CR1 meteorites signifies that the meteorite is of petrologic type 1 and therefore underwent the highest amount of aqueous alteration. The level of aqueous alteration is determined by the degree the chondrules (round grains) in the meteorite have been changed by the presence of water. Petrologic type 1 signifies the complete obliteration of chondrules in the meteorite, whereas petrologic type 3 signifies the chondrules in the meteorite have not been altered. The majority of meteorite samples with reported nucleobase abundances are CM2 type (Mighei-like composition with an average level of aqueous alteration).

2.1. Contamination Possibility

There is always a concern about terrestrial contamination when analyzing meteorites for organics. Callahan et al. (2011) addressed this by analyzing the content of the terrestrial environment around which the meteorites were retrieved. In the case of Antarctic meteorites they analyzed dried residue from an ice sample collected in 2006 from the Graves Nunataks region, and in the case of the Murchison meteorite they analyzed a soil sample collected in 1999 from near the original Murchison meteorite fall site. In the Antarctic residue sample, less than 5 pppt (parts-per-trillion) of G and A were measured, strongly suggesting that the meteorite nucleobases were of extraterrestrial origin. Interestingly, 1380 ppb of C was measured in the soil sample from near the Murchison fall site, but no abundance of C was measured in the Murchison meteorite sample. Also, several nucleobase analogs were measured in the Murchison meteorite that were either rare or absent on Earth (purine, 2, 6-diaminopurine, and 6, 8-diaminopurine). The conjunction of these findings strongly suggests an extraterrestrial origin for these meteorite nucleobases.

Shimoyama et al. (1990) argued that because the amino acid mixtures measured in the analyzed meteorite were racemic, i.e., composed of equal amounts of D and L enantiomers, it is unlikely that the sample (also containing nucleobases) was subjected to much contamination. Other studies took the high
uracil-to-thymine ratios in the sample (e.g., 21 in a sample of the Murchison meteorite) as evidence that the nucleobases are extraterrestrial in origin (van der Velden & Schwartz 1977; Stoks & Schwartz 1979, 1981). A high uracil-to-thymine ratio is suggestive of an extraterrestrial origin of nucleobases because studies of biogenic nucleobases in various soils and recent sediments have measured little uracil with respect to the other nucleobases (Stoks & Schwartz 1979).

3. RESULTS: NUCLEOBASE ABUNDANCES AND RELATIVE FREQUENCIES

3.1. Nucleobase Abundances in Meteorites

We display the individual nucleobase abundance data grouped by carbonaceous chondrite type. The CM meteorites are displayed in one plot, and the CI and CR meteorites are grouped together in another plot due to the limited nucleobase data of the latter group. The ordering of meteorite samples for both plots is the same as the ordering defined by Cobb & Pudritz (2014) for amino acid abundances. This order was chosen by Cobb & Pudritz (2014) to give a smooth monotonic sequence for the most abundant amino acid: glycine. In Figure 1, we illustrate the ppb (parts-per-billion) abundances of the purines G and A and the pyrimidine U in CM meteorites compared with the abundances of glycine, valine, and aspartic acid found in the same meteorites from Cobb & Pudritz (2014) and (in the case of Yamato 74662) Shimoyama et al. (1979). G is typically the most abundant nucleobase in these samples, ranging from 2–515 ppb. These G abundances are approximately 1–2 orders of magnitude lower than the glycine measured in the same meteorites. The range of G abundances in CM meteorites is closer to the intermediate and less abundant amino acids in carbonaceous chondrites: valine and aspartic acid. G is approximately 1 order of magnitude lower to 1 order of magnitude higher than both the valine and aspartic acid measured in the same meteorites. G and aspartic acid remain in relatively close abundance with each other. A and U are generally less abundant than G by a factor of 2–10.

The G abundance curve in Figure 1 has a localized peak in the middle, but still trends downwards overall, generally following the glycine curve. The A abundance curve in Figure 1 trends downward as well, and appears to have a local maximum in the same location as the G curve did. There is not enough U data to say anything about its curve. The correspondence between the amino acid and nucleobase curves suggests that conditions that favor the synthesis of glycine are related to those that optimize the production of nucleobases. The 1–2 orders of magnitude differences in abundance between nucleobases and glycine could have several causes: different decay rates, differences in synthesis, or competing chemical reactions for the same basic materials. These factors will be the future considerations of our theoretical work. The similarity in the bumps created by the G and A curves in Figure 1 could suggest that a similar mechanism is used to synthesize G and A within the meteorite parent bodies.

The nucleobase abundances in CI and CR meteorites are displayed in Figure 2, again, along with the abundances of glycine, valine, and aspartic acid from Cobb & Pudritz (2014) as a guide. These abundances are much more reduced than in the CM meteorites, most lying within the 1–20 ppb range. The Orgueil meteorite obtained from the Muséum National d’Histoire Naturelle (MNHN) is the only exception, with slightly higher abundances of nucleobases than the other samples (~100 ppb). Abundances of nucleobases in CI and CR meteorites range from 1–4 orders of magnitude lower than glycine abundances in the same meteorites. Nucleobases range up to 4 orders of magnitude lower than valine, and up to 3 orders of magnitude lower than aspartic acid in CI and CR meteorites.

Due to the relatively low abundances of nucleobases in CM1, CR1, CR3, and CI1 meteorites in comparison to CM2 meteorites, and from the relatively low abundances of amino acids in the same meteorite types in Cobb & Pudritz (2014), it is likely that the parent bodies of CM1, CR1, CR3, and CI1 meteorites have a less suitable environment for organic synthesis than the parent bodies of CM2 meteorites.

Other purines were also measured in CM, CI, and CR meteorites. Xanthine, a catabolic intermediate of G, was found in abundances of 4–2300 ppb and hypoxanthine, a catabolic intermediate of A, was found in abundances of 3–243 ppb. Nucleobase analogs, purine, 2, 6-diaminopurine, and 6,
8-diaminopurine were also measured in lesser abundances (0.2–9 ppb).

In Figure 3, we sum up G, A, and U in all the meteorite sources and plot the total nucleobase abundances by meteorite type. The total amino acid abundances measured in the same meteorites in this study are added to this plot for comparison. The total amino acid abundances include glycine, alanine, serine, aspartic acid, glutamic acid, and valine, and are taken from Cobb & Pudritz (2014) and Shimoyama et al. (1979). The total amino acid abundances from Cobb & Pudritz (2014) are verified from the original sources and in some cases refinements are made.

The ordering of meteorites is in accordance with the total amino acid abundance plot in Cobb & Pudritz (2014). It is clear from this plot that CM2 meteorites dominate in total nucleobase abundance, averaging $330 \pm 250$ ppb. This is interesting because CM2 meteorites also appear to be one of the most abundant in amino acids, with total abundances averaging $\sim 10^4$ ppb. This could suggest a similarity in the synthesis mechanisms of amino acids and nucleobases in the parent bodies of CM2 meteorites, e.g., both sharing HCN as a reactant. Conversely, CR2 meteorites, which appear to be the most abundant in total amino acids (averaging $\sim 10^5$ ppb), are one of the least abundant in nucleobases, with a total average abundance of $16 \pm 13$ ppb. These differences could arise from different reaction rates, decay rates, or chemical composition within the CR2 parent bodies.

The total abundances of nucleobases in Figure 3 range from $\sim 1$ to 4 orders of magnitude smaller than the total abundances of amino acids in the same meteorites. A general conformity is seen between the pattern given by the total nucleobase abundances and the pattern given by the total amino acid abundances when solely considering the CM meteorites. The total abundances of nucleobases in the CM2 meteorites generally maintain both an increasing order and a separation of approximately 2 orders of magnitude from the amino acids (with the main exception being the Murchison Smith meteorite). The total abundances of nucleobases in the CM1 meteorites maintain a decreasing order and a separation of approximately 1–2 orders of magnitude from the amino acids. The patterns given by the total nucleobase and total amino acid abundances disagree in the sections containing the CI and CR meteorites. Nevertheless, more meteoritic nucleobase assays need to be performed on these meteorite subclasses to verify that the disagreement in patterns is not the result of a poor sample size. This general conformity between total nucleobases and total amino acid abundances in the CM meteorites agrees with the above suggestion: there may be similar reaction mechanisms for nucleobase and amino acid synthesis within the CM meteorite parent bodies, but perhaps there are different reaction and decay rates (e.g., due to different temperatures, hydration) or chemical compositions within the CR and CI meteorite parent bodies.

### Figure 1
Abundances of three nucleobases (G: blue, A: green, U: yellow) and three amino acids (glycine: red, valine: magenta, aspartic acid: cyan) in CM meteorites. The meteorite order is monotonically decreasing with respect to glycine. Amino acid data is obtained from Cobb & Pudritz (2014) and Shimoyama et al. (1979).

### Figure 2
Abundances of three nucleobases (G: blue, A: green, U: yellow) and three amino acids (glycine: red, valine: magenta, aspartic acid: cyan) in CR and CI meteorites. The meteorite order is monotonically decreasing with respect to glycine. Amino acid data is obtained from Cobb & Pudritz (2014).

### Figure 3
Abundances of three nucleobases (G: blue, A: green, U: yellow) in CM meteorites. The meteorite order is monotonically decreasing with respect to glycine. Amino acid data is obtained from Cobb & Pudritz (2014).
the relative abundances of A and U with respect to G from CM2 meteorites in Figure 4. Here we can see that G is the most common nucleobase in carbonaceous chondrites, followed by A at 0.36 ± 0.48, and then U at 0.23 ± 0.19.

4. ABIOTIC NUCLEOBASE SYNTHESIS

We now turn to the question of which chemical reactions might be responsible for nucleobase formation in planetesimals. To pursue this we first consider each well known abiotic nucleobase-synthesizing mechanism, and we filter out the mechanisms that require environments dissimilar to the interior of a planetesimal. We then consider the most frequently discussed reaction pathways for each remaining mechanism and filter these reactions down to a candidate list based on assumed reactant and catalyst availability within planetesimals.

4.1. Reaction Mechanisms

Here we categorize the known types of reactions that synthesize nucleobases abiotically into seven groups. The following list of reaction types is in rough order of decreasing likelihood of occurrence within planetesimals.

Fischer–Tropsch (FT) synthesis uses carbon monoxide, hydrogen, and ammonia gases as reactants in the presence of a catalyst (such as nickel–iron alloy or aluminum oxide) to create all five nucleobases (Hayatsu et al. 1968, 1972; Yang & Oró 1971; Anders et al. 1974). FT synthesis is already thought by some to be the mechanism for producing meteoritic organics such as purines, pyrimidines, amino acids, and aromatic hydrocarbons (Hayatsu et al. 1972; Anders et al. 1974).

Several non-catalytic (NC) chemical reactions have been theorized or proven to synthesize all five nucleobases, and only involve a solution being heated, cooled, or maintained at room temperature. The reactants in these reactions vary, although HCN is found to be the most common (Oró & Kimball 1961, 1962; Wakamatsu et al. 1966; Yamada et al. 1969, 1968; Ferris et al. 1978; Voet & Schwartz 1982; Schwartz & Bakker 1989; Hill & Orgel 2002; LaRowe & Regnier 2008). HCN is also one of the main reactants in Strecker synthesis, which is proposed to be the reaction that produces amino acids within meteorite parent bodies (Peltzer et al. 1984; Cobb & Pudritz 2014).

Various other catalytic (CA) reactions have synthesized A, T, C, and U (Bendich et al. 1948; Oró 1961b; Subbaraman et al. 1980; Saladino et al. 2001; Kumar et al. 2014). The most common of these reactions uses neat formamide as the sole reactant, which successfully forms nucleobases in the presence of several different catalysts.

Spark discharge experiments first introduced by Stanley L. Miller have produced G and A (Yuasa et al. 1984; Miyakawa et al. 2000, 1999). These experiments send a high voltage electrical discharge through gaseous mixtures of reactants, e.g., methane, ethane, and ammonia, or water, carbon monoxide, and nitrogen, to produce organics.

Ultraviolet irradiation in various solutions, e.g., water, ice, and urea, or water, ammonia, and pyrimidine, has produced G, C, and U (Lemmon 1970; Nuevo et al. 2012; Menor-Salván & Marín-Yaseli 2013). Photo-dehydrogenation, i.e., using
ultraviolet light to remove hydrogen from molecules, of 5, 6-dihydrouracil and 5, 6-dihydrothymine has yielded U and T (Chittenden & Schwartz 1976; Schwartz & Chittenden 1977). Finally, electron irradiation in a gaseous mixture of methane, ammonia, and water has successfully synthesized A (Ponnamperuma et al. 1963).

This research is on the potential synthesis of nucleobases within planetesimals, thus only the mechanisms listed above that could possibly occur in such environments are of interest. Since the rocky, solid, and liquid water-filled interior of a planetesimal (Travis & Schubert 2005) is likely not an environment where electron beams, ultraviolet light, or electric discharges would occur, we only consider FT, NC, and CA reactions as likely producers of the nucleobases measured in carbonaceous chondrites.

4.2. Reaction Pathways

To compile a thorough list of FT, NC, and CA reactions that have been employed or suggested to produce nucleobases, we use a combination of browsing the Internet with search criteria relevant to nucleobase synthesis (e.g., “abiotic adenine synthesis,” “FT synthesis of nucleobases,” etc.), and reading through citations from nucleobase synthesis studies.

The 60 most discussed FT, NC, and CA nucleobase-synthesizing reactions in the scientific literature are formulated in Table 3, along with their experimental nucleobase yields. All of the reactions in Table 3 have successfully synthesized a nucleobase in the laboratory, with the exception of the five reaction pathways from LaRowe & Regnier (2008). These reaction pathways have been studied for their thermodynamic potential in hydrothermal environments and have been proven to be favorable from a theoretical standpoint. If a nucleobase synthesis study suggests a chemical equation for the synthesis of their nucleobase(s), the chemical equation from the study is copied into the reaction column of Table 3. For studies that do not suggest a chemical equation, a simple

reactants → nucleobase

(1)
scheme is used. In the case of FT reactions, liquid water is also added as a potential product due to the fact that it generally forms along with nucleobases in laboratory experiments (Hayatsu & Anders 1981). For the deamination of C into U (reaction 32), ammonia is added as a potential product in order to perfectly balance the reaction.

For catalytic reactions, the chemical equation includes one or more catalyst(s) written above the reaction arrow. In the case of multiple catalysts, a “+” is used to signify “and,” a “||” is used to signify “or,” and a “|||” is used to signify “and/or.”

The reactions in Table 3 are first grouped by product nucleobase in order of decreasing number of reactions. Then each nucleobase group is sub-grouped by reaction type (starting with FT synthesis). Finally, the reaction type subgroups are ordered by increasing total molecular mass of the reactants (ignoring coefficients).

5. RESULTS: CANDIDATE REACTION PATHWAYS WITHIN PLANETESIMALS

In order for a reaction pathway from Table 3 to be considered a candidate reaction within planetesimals, the reactants and (if applicable) catalyst(s) must be present within the planetesimal environment. Since comets are thought to contain material that would have also been incorporated into planetesimals during the latter’s formation (Schulte & Shock 2004; Alexander 2011), we consider all reaction schemes with no reactant cometary abundances unlikely to occur in planetesimals. In the case of catalytic reactions, the catalyst(s) must also be found in meteorites in order for the reaction scheme to be considered a candidate.

Many spectroscopic molecular surveys and one in situ molecular analysis (done with MS) have been carried out on various comets (Bockelee-Morvan et al. 2000; Ehrenfreund & Charnley 2000; Bockelee-Morvan et al. 2004; Crovisier et al. 2004; Liu et al. 2007; Mumma & Charnley 2011). From these surveys only eight of the reactants in Table 3 have been measured: H₂, H₂O, CH₂O, NH₃, CO, HCN, Cyanoacetylene, and Formamide. All reaction pathways with reactants not from the list of eight above are disregarded. Deuterated hydrogen has only been found in comets in the form of HDO, DCN, HDCO, NH₂D, HDS, CH₃OD, and CH₂DOH (Crovisier et al. 2004), though because D₂ and ND₃ are not substantially different from H₂ and NH₃, we do not immediately disregard the deuterated FT reactions from Hayatsu et al. (1972) as candidates.

The temperature limit for the interior of carbonaceous chondrite parent bodies based on the theoretical temperature for which amino acid synthesis in planetesimals generally shuts off is ~300°C (Cobb et al. 2014). In thermal evolution simulations of the interiors of carbonaceous chondrite parent bodies, Travis & Schubert (2005) found that temperatures reached a maximum of 180°C. McSween et al. (2002) had similar results, with their smallest-radius carbonaceous chondrite parent bodies reaching a maximum interior temperature of 227°C. From a study that classifies temperature ranges within the parent bodies of the various carbonaceous chondrite subclasses and petrologic types, Sephton (2002) assigns a temperature limit of 400°C for the parent bodies of the carbonaceous chondrites in which nucleobases have been found. Furthermore, based on nucleobase decomposition experiments from Levy & Miller (1998), all five nucleobases decompose in seconds, at temperatures above 400°C in an aqueous environment.

Since the FT synthesis of A, G, U, and T in Hayatsu et al. (1972) was only successful when temperatures reached as high as 700°C, we disregard these reactions as candidates. This temperature is much higher than those within CM, CR, and CI carbonaceous chondrite parent bodies, and much too high to sustain nucleobases in aqueous environments (Travis & Schubert 2005).

Jarosewich (1990) and Wiik (1956) have conducted complete chemical analyses of several carbonaceous chondrites. From these two surveys, only Al₂O₃, SiO₂, Ni, and Fe (satisfying NiFe) of the above catalysts has been found. This allows us to disregard schemes 23, 25, 50, and 60, as the catalysts for these reactions were unlikely to have been available within carbonaceous chondrite parent bodies.

The remaining reaction schemes complete our list of candidate reaction pathways for the synthesis of nucleobases within planetesimals. This list is presented in Table 2 and the corresponding reactions are marked in Table 3. In total, there are seven candidate reactions for A, 2 for U, 3 for C, 2 for G, and 1 for T.

Although some of the reactions in Table 3 that did not make the candidate list have experimental yields that are indeed high, these pathways require reactants that may not be present in
planetesimals. For this study, we limit our candidates to the reactions for which there is some evidence of the reactants being present within meteorite parent bodies.

### 6. DISCUSSION

Because nucleobases, nucleobase catabolic intermediates, and nucleobase analogs are present in carbonaceous chondrites, these molecules would have likely also been present on the pregenetic, meteorite-accreting Earth. C and T have yet to be found in meteorites. A plausible astrophysical source of C and T could arise from ultraviolet radiation-driven chemical reactions on icy particles in space (Nunez et al. 2014). This would supply the C needed for the onset of the RNA world that likely preceded DNA-based life (Neveu et al. 2013), as well as the T needed for the later appearance of the DNA, RNA, and protein world.

It is currently not known why C or T have not been measured in carbonaceous chondrites. Photodissociation is unlikely to be the main cause as Pilling et al. (2008) have found that G, A, C, T, and U have similar survival rates when exposed to vacuum UV photons at energies ranging from ~4 to 30 eV. Deamination could explain the lack of C in meteorites, since C deaminates to U in aqueous solutions (Ferris et al. 1968; Garrett & Tsau 1972; Robertson & Miller 1995), and meteorite parent bodies are thought to remain aqueous on the order of millions of years (Travis & Schubert 2005).

Perhaps the most likely explanation of the deficit in C and T is a purely chemical one. C and T are known to readily oxidize into 5-hydroxyhydantoin and 5-methyl-5-hydroxyhydantoin, respectively (Redejo-Rodriguez et al. 2011), which could explain the lack of both C and T in meteorites. Although 5-hydroxyhydantoin and 5-methyl-5-hydroxyhydantoin have not been measured in carbonaceous chondrites, a few amino acid hydantoins have, e.g., 5-(2-carboxyethyl)hydantoin (Cooper & Cronin 1995).

A final possibility for the lack of C and T in meteorites could be that the reactions synthesizing A, G, and U in meteorite parent bodies are more thermodynamically favorable than those synthesizing C and T. This would result in a reduced production of C and T with respect to the other nucleobases within planetesimals, which could then be further diminished to negligible amounts from photodissociation, deamination, or oxidation. An important goal for our future investigations is to address this question, i.e., how much C or T could be synthesized within meteorite parent bodies?

Since the abundances of xanthine and hypoxanthine measured in carbonaceous chondrites are comparable to those of G and A, the former would have been just as available as the latter during the evolution of the genome and the genetic code. Xanthine and hypoxanthine were therefore not selected to have a place in the genome for a reason other than availability.

What is particularly interesting is the low abundance of nucleobase analogs that have been measured in carbonaceous chondrites. Nucleobase analogs are structurally similar to nucleobases, and 2,6-diaminopurine, like A, can actually base pair with T or U (Kirnos et al. 1977). If nucleobase analogs can replace some of the genome nucleobases, but were perhaps only available in very small (<10 ppb) abundances on the pregenetic Earth, then it is possible to consider meteorite abundance as a driving factor in A’s incorporation into the genome over these nucleobase analogs.

Total nucleobase abundances in carbonaceous chondrites are consistently lower than amino acids by ~1–4 orders of magnitude. The decay rates of molecules due to hydrolysis have been measured and a useful tool for describing them is Arrhenius plots. These results show that nucleobases decay more rapidly than glycine, alanine, serine, glutamic acid, aspartic acid, and phenylalanine at temperatures above 200°C (Qian et al. 1993; Levy & Miller 1998; Sato et al. 2004). Though the amino acid studies were not performed at temperatures lower than 200°C, by extrapolating the Arrhenius curves from Sato et al. (2004) and Qian et al. (1993), it can be seen that amino acids should be more stable than nucleobases at all aqueous temperatures. Since carbonaceous chondrite parent bodies are thought to have had aqueous interiors for millions of years (Travis & Schubert 2005), the ~1–4 orders of magnitude differences in abundance between amino acids and nucleobases within carbonaceous chondrites could simply be a result of the more rapid hydrolysis decay rate of nucleobases.

It is clear from the number of individual nucleobase reactions in Table 3 that A is the most commonly produced nucleobase in the lab. Five out of the seven candidate reaction producing A are NC reactions (all involving HCN), producing a maximum 15% yield. G, on the other hand, has only one theoretical NC reaction candidate, with no laboratory yield. Since G happens to be the most abundant nucleobase within carbonaceous chondrites (Figure 4) and A is the second most abundant, NC reactions are perhaps less likely to be the main reaction mechanism for producing nucleobases within meteorite parent bodies. CA reactions are also not an obvious choice for the main reaction mechanism since they are missing a reaction pathway for the G and U found in meteorites.

The last candidate reaction mechanism to consider is FT synthesis, which produces G, A, and C. In experiments by Hayatsu et al. (1968), A had the highest yield (0.16%), followed by G (0.09%) and C (0.05%). This mechanism may at first seem to be an unlikely candidate since C and T are not

| Nucleobase | Reaction Number | Type |
|------------|----------------|------|
| Adenine    | 1              | FT   |
|            | 3              | NC   |
|            | 4              | NC   |
|            | 6              | NC   |
|            | 7              | NC   |
|            | 8              | NC   |
|            | 24             | CA   |
| Uracil     | 29             | NC   |
|            | 32             | NC   |
| Cytosine   | 43             | FT   |
|            | 44             | NC   |
|            | 49             | CA   |
| Guanine    | 51             | FT   |
|            | 54             | NC   |
| Thymine    | 58             | NC   |

**Table 2**

Candidate Reaction Pathways for the Production of Nucleobases within Meteorite Parent Bodies

**Note.** The reaction numbers pertain to those in Table 3. NC: non-catalytic; CA: catalytic; FT: Fischer–Tropsch.
### Table 3
Reaction Schemes and Experimental Yields for FT, NC, and CA Nucleobase Synthesis

| No. | Type  | Reaction                                                                 | Max Yield (%) | Source(s) |
|-----|-------|--------------------------------------------------------------------------|----------------|-----------|
|     |       |                                                                          |                |           |
| **Adenine** |       |                                                                          |                |           |
| 1<sup>a</sup> | FT    | CO + H₂ + NH₃<sub>3</sub> → A + H₂O                                    | detected       | York & Oró (1971). | 0.16 | Hayatsu et al. (1968) |
| 2   | FT    | CO + D₂ + ND₃<sub>3</sub> → A + H₂O                                    | + +            | Hayatsu et al. (1972) |
| 3<sup>a</sup> | NC    | 5HCN<sub>(aq)</sub> → A<sub>(aq)</sub>                                 | theoretical    | LaRowe & Regnier (2008) |
| 4<sup>a</sup> | NC    | HCN + NH₃ → A                                                          | detected       | Yamada et al. (1969), | 0.029 | Miyakawa et al. (2002), |
| 5   | NC    | Ammonium cyanide → A                                                   | detected       | Oró (1960) | 0.05  | Levy et al. (1999) |
| 6<sup>a</sup> | NC    | 5CO + 5NH₃ → A + 5 H₂O                                                 | detected       | Hayatsu et al. (1968) |
| 7   | NC    | HCN + H₂O → A                                                          | 0.04           | Ferris et al. (1978) |
| 8<sup>a</sup> | NC    | HCN + NH₃ + H₂O → A                                                   | 0.00           | Oró & Kimball (1961) |
| 9   | NC    | Ammonium cyanide + H₂O → A                                              | detected       | Oró (1960) |
| 10  | NC    | HCN + Glycolonitrile → A                                               | 0.06           | Schwartz & Bakker (1989) |
| 11  | NC    | HCN + Ammonium formate → A                                             | 18             | Hill & Orgel (2002) |
| 12  | NC    | 4-aminomidazole-5-carbonitrile + HCN → A                              | 24             | Sanchez et al. (1968) |
| 13  | NC    | 4-aminomidoazole-5-carbonitrile + Ammonium cyanide → A                 | 11             | Sanchez et al. (1968) |
| 14  | NC    | 4-aminomidoazole-5-carbonitrile + Sodium cyanide → A                   | 7              | Sanchez et al. (1968) |
| 15  | NC    | KNC + Ammonium formate + Formamidine → A                               | 4.7            | Hudson et al. (2012) |
| 16  | NC    | NaCN + HCN + Acetamidine hydrochloride + NH₃ → A                       | detected       | Yamada et al. (1968) |
| 17  | NC    | NaCN + Ammonium chloride + Formamidine acetate + NH₃ → A               | 25             | Yamada et al. (1968) |
| 18  | NC    | Diaminomalonitrile + Formamidine acetate + NH₃ → A                     | 1              | Sanchez et al. (1967) |
| 19  | NC    | 4-aminocyanomidoazole + Formamidine acetate + H₂O → A                 | 3              | Ferris & Orgel (1966) |
| 20  | NC    | 4-Formamidopyrimidine-5-imidazolcarboxamide + Potassium bicarbonate → A| 80             | Shaw (1950) |
| 21  | NC    | 6-chloropurine + Ammoniacal butanol → A                               | detected       | Bendich et al. (1954) |
| 22  | NC    | Aminomalonitrile p-toluenesulfonate + NaCN + Formamidine acetate + NH₃→ A | 21             | Yamada et al. (1968) |
| 23  | CA    | 5HCN + 4NH₃<sub>3</sub> → A + 4NH₃                                      | detected       | Oró & Kimball (1962), | 0.09 | Oró (1961b) |
| 24<sup>a</sup> | CA    | Formamide<sub>2Fe(O)₃[S2O₅]K[Ni][ZnO]₂</sub> → A                      | detected       | Saladin et al. (2001) |
| 25  | CA    | Formamide<sub>2Fe(O)₃[S2O₅]K[Ni][ZnO]₂</sub> → A                      | 0.62           | Kumar et al. (2014) |
| 26  | CA    | Thioureasguanine sulfate → A                                           | 21.25          | Bendich et al. (1948) |
|     |       |                                                                          |                |           |
| **Uracil** |       |                                                                          |                |           |
| 27  | FT    | CO + D₂ + ND₃<sub>3</sub> → U + H₂O                                    | +              | Hayatsu et al. (1972) |
| 28  | NC    | Ammonium cyanide → U                                                   | 0.0017         | Miyakawa et al. (2002) |
| 29<sup>a</sup> | NC    | 2HCN<sub>(aq)</sub> + 2CH₂O<sub>(aq)</sub> → U<sub>(aq)</sub> + H₂<sub>(aq)</sub> | theoretical   | LaRowe & Regnier (2008) |
| 30  | NC    | HCN + Ammonium hydroxide + H₂O → U                                    | 0.005          | Voet & Schwartz (1982) |
| 31  | NC    | 2,4-Diaminopyrimidine + H₂O → U                                      | 36             | Ferris et al. (1974) |
| 32<sup>a</sup> | NC    | C + H₂O → U + NH₃                                                     | detected       | Garrett & Miller (1995), | 95 | Garrett & Tsau (1972), |
|     |       |                                                                          | detected       | Ferris et al. (1968) |
| 33  | NC    | Cyanocacetaldehyde + Urea → U                                        | 0.08           | Nelson et al. (2001) |
| 34  | NC    | Acrylonitrile + Urea + H₂O → U                                      | <1             | Grossenbacher et al. (1965) |
| 35  | NC    | Acrylonitrile + Urea + Ammonium chloride → U                           | <1             | Oró (1963) |
| 36  | NC    | Propionic acid + Urea + Sulfuric acid + H₂O → U                       | 59             | Harada & Suzuki (1976) |
| 37  | NC    | Propionic acid + Urea + Polyphosphoric acid + H₂O → U                | 75             | Harada & Suzuki (1976) |
| 38  | NC    | Fumaric acid + Urea + Polyphosphoric acid → U                        | 5              | Takamoto & Yamamoto (1971) |
| 39  | NC    | Maleic acid + Urea + Polyphosphoric acid → U                         | 20             | Takamoto & Yamamoto (1971) |
| 40  | NC    | Malic acid + Urea + Sulfuric acid → U                                 | 55             | Davidson & Baudisch (1926) |
| 41  | NC    | Malic acid + Urea + Polyphosphoric acid → U                          | 9.3            | Fox & Harada (1961) |
| 42  | CA    | Acetylene dicarboxylic acid + Urea → U                               | 6.3            | Subbaranan et al. (1980) |
|     |       |                                                                          |                |           |
| **Cytosine** |       |                                                                          |                |           |
| 43<sup>a</sup> | FT    | CO + H₂ + NH₃<sub>3</sub> → C + H₂O                                    | detected       | York & Oró (1971), | 0.05 | Hayatsu et al. (1968) |
| 44<sup>a</sup> | NC    | 3HCN<sub>(aq)</sub> + CH₂O<sub>(aq)</sub> → C<sub>(aq)</sub>          | theoretical   | LaRowe & Regnier (2008) |
| 45  | NC    | Cyanocacetaldehyde + Urea → C                                        | 0.23           | Nelson et al. (2001), | 53 | Robertson & Miller (1995) |
| 46  | NC    | 2,4-Diaminopyrimidine + H₂O → C                                      | trace          | Ferris et al. (1974) |
| 47  | NC    | Cyanocaceticine + Urea + H₂O → C                                     | 5              | Ferris et al. (1968) |
| 48  | NC    | Cyanocacetylene + Potassium cyanate + H₂O → C                       | 19             | Ferris et al. (1968), |
|     |       |                                                                          | 5              | Sanchez et al. (1966) |
found in carbonaceous chondrites. However, it is possible that reaction 32 accounts for the missing C in carbonaceous chondrites, as in this reaction C deaminates into U. Though G is on average the most abundant nucleobase in CM2 meteorites, there are also a few instances where A is more abundant than G in CR2, CR3, CM1, and CM2 meteorites. This increases the plausibility of the FT reaction pathways in Hayatsu et al. (1968) occurring within meteorite parent bodies.

7. CONCLUSIONS

Unlike amino acids, hydroxy acids, carboxylic acids, hydrocarbons, and many other organic molecules, nucleobases have not been found in great (ppm-range) abundances in meteorites. G, A, and U have been found in carbonaceous chondrites in the 1–500 ppb range. No C or T has been measured in any meteorites to date. Nucleobase catabolic intermediates xanthine and hypoxanthine have been measured in similar abundances as nucleobases (3–2300 ppb). Nucleobase analogs purine, 2,6-diaminopurine, and 6,8-diaminopurine, have been measured in low abundances around 0.2–9 ppb.

CM2 meteorites appear to be the preferred type for nucleobases, with an average total nucleobase abundance of 330 ± 250 ppb. Conversely, CR2 meteorites are the least abundant in nucleobases, with an average total abundance of 16 ± 13 ppb. These results are dissimilar to amino acid abundances in carbonaceous chondrites, where CR2 and CM2 meteorites both contain the greatest abundances. This may suggest that amino acids and nucleobases could share a reaction mechanism within the parent bodies of CM2 meteorites, but may have differing reaction mechanisms within the parent bodies of CR2 meteorites.

Nucleobases are typically 1–3 orders of magnitude less abundant in carbonaceous chondrites than glycine (which is the most abundant amino acid in carbonaceous chondrites). Nucleobases can be 2 orders of magnitude less abundant or even 1 order of magnitude more abundant in carbonaceous chondrites than aspartic acid (one of the less abundant amino acids in carbonaceous chondrites). The most abundant nucleobase in carbonaceous chondrites is guanine, ranging from 2–515 ppb. Adenine is the second most abundant nucleobase, with an average relative abundance to G of 0.36 ± 0.48 within CM2 meteorites. Uracil is the least abundant nucleobase, with an average relative abundance to G of 0.23 ± 0.19 within CM2 meteorites. The total abundance of nucleobases in carbonaceous chondrites is 1–4 orders of magnitude less than the total abundance of amino acids.

Of the 60 most discussed FT, NC, and CA nucleobase-synthesizing reactions in the literature, 3 FT, 10 NC, and 2 CA reactions are proposed as the candidate reactions for producing nucleobases within meteorite parent bodies. It appears as if the FT synthesis reaction mechanism best complies with the nucleobases found in carbonaceous chondrites thus far.

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