Published in final edited form as:

Meteorit Planet Sci. 2017 December ; 52(12): 2632–2646. doi:10.1111/maps.12959.

Distribution of Aliphatic Amines in CO, CV and CK Carbonaceous Chondrites and Relation to Mineralogy and Processing History

José C. Aponte^{1,2,*}, Neyda M. Abreu³, Daniel P. Glavin¹, Jason P. Dworkin¹, Jamie E. Elsila¹

¹Solar System Exploration Division, Code 691, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, USA.

²Department of Chemistry, Catholic University of America, Washington, DC 20064, USA.

³Earth Science Program, Pennsylvania State University – Du Bois Campus, Du Bois, Pennsylvania 15801, USA.

Abstract

The analysis of water-soluble organic compounds in meteorites provides valuable insights into the prebiotic synthesis of organic matter and the processes that occurred during the formation of the solar system. We investigated the concentration of aliphatic monoamines present in the hot acid-water extracts of the unaltered Antarctic carbonaceous chondrites DOM 08006 (CO3) and MIL 05013 (CO3), and the thermally altered meteorites Allende (CV3), LAP 02206 (CV3), GRA 06101 (CV3), ALH 85002 (CK4), and EET 92002 (CK5). We have also reviewed and assessed the petrologic characteristics of the meteorites studied here, to evaluate the effects of asteroidal processing on the abundance and molecular distributions of monoamines. The CO3, CV3, CK4, and CK5 meteorites studied here contain total concentrations of amines ranging from 1.2 to 4.0 nmol/g of meteorite; these amounts are one to three orders of magnitude below those observed in carbonaceous chondrites from the CI, CM and CR groups. The low amine abundances for CV and CK chondrites may be related to their extensive degree of thermal metamorphism and/or to their low original amine content. Although the CO3 meteorites DOM 08006 and MIL 05013 do not show signs of thermal and aqueous alteration, their monoamine contents are comparable to those observed in moderately/extensively thermally altered CV3, CK4, and CK5 carbonaceous chondrites. The low content of monoamines in pristine CO carbonaceous chondrites suggests that the initial amounts, and not asteroidal processes, play a dominant role in the content of monoamines in carbonaceous chondrites. The primary monoamines, methylamine, ethylamine and *n*-propylamine constitute the most abundant amines in the CO3, CV3, CK4, and CK5 meteorites studied here. Contrary to the predominance of *n*- ω -amino acid isomers in CO3 and thermally altered meteorites, there appears to be no preference for the larger *n*- α -amines.

*Corresponding author: jose.c.aponte@nasa.gov; tel.: +1.301.614.6916; fax: +1.301.286.1683.

INTRODUCTION

Comparing the analysis of organic compounds in meteorites with the mineralogical and processing histories of their parent bodies can provide insights into the early history of the solar system. Carbonaceous chondrites are of particular interest, as they have higher carbon content (up to 5 wt.%; Wetherill and Chapman 1988) and volatile element enrichments than other classes of meteorites. Based on their mineralogical composition and oxygen isotope ratios, carbonaceous chondrites are subdivided into eight groups (CI, CM, CR, CO, CV, CK, CB, and CH; Sears and Dodd 1988). We have previously investigated the molecular abundance and distributions of aliphatic monoamines (hereafter called “amines”) in the CI, CM, and CR meteorites and have evaluated their potential synthetic relationships with their structurally analogous amino acids (Aponte et al. 2014, 2015, 2016). CV, CK, and CO meteorites contain much less carbon than CI and CM meteorites (e.g., Pearson et al. 2006). Only a small fraction of the carbon in carbonaceous chondrites is soluble in solvents such as water, methanol, and dichloromethane (DCM; see reviews and references therein: Cronin and Chang 1993; Botta and Bada 2002; Sephton 2002; Pizzarello et al. 2006). A diverse suite of soluble organic compounds isolated from carbonaceous chondrites reflects their relevance towards understanding the synthetic pathways that occurred in the presolar nebula, the protoplanetary disk, and later during parent body processing. In this report, we focus our attention on the abundance and distribution of amines in CV, CK, and CO meteorites, and evaluate the occurrence of these organic compounds in relation to the petrologic characteristics of their parent bodies and other water-soluble organics (e.g., Burton et al., 2012, 2015).

McSween (1977a) divided the CV chondrites into the reduced and oxidized sub-groups. According to Krot et al. (1998), the oxidized subgroup can be further sub-divided into the Allende-like CV3 chondrites (CV3_{oxA}) and the Bali-like CV chondrites (CV3_{oxB}). Oxidized CVs contain magnetite, taenite, and pentlandite. The Bali-like sub-group shows evidence of significant fluid-rock interaction, whereas the members of the Allende-like sub-group are essentially anhydrous. CV3_{oxA} Allende records a complex history of alteration, involving aqueous alteration followed by thermal metamorphism (e.g., Brearley 1997, Kojima et al. 1993, Kojima and Tomeoka 1996, Krot et al. 1995, 1997a, 1997b, 1998). However, there is no consensus on its metamorphic grade; Guimon et al. (1995) classified Allende as petrologic type 3.2, whereas Bonal et al. (2006) classified it as a 3.6. Consistent with the higher, 3.6 petrologic type, ferroan, micron-sized matrix olivine in Allende show a narrow, more equilibrated compositional range (Fa₄₅₋₅₅ – Abreu and Brearley 2003) compared to other CVs.

Members of the CK group have experienced significantly more thermal metamorphism than the CV3 chondrites, as evidenced by extensive recrystallization of fine-grained matrix materials and the highly equilibrated composition of matrix olivines (e.g., Kallemeyn et al. 1991). Some authors have argued that the CV and CK chondrites originated on the same parent body, with CK chondrites resulting from water-assisted oxidation, loss of volatiles, and metamorphic recrystallization of CV precursors (Greenwood et al. 2010; Wasson et al. 2013). However, recent minor element analyses of magnetite in unequilibrated CK and CV chondrites indicate that these meteorites may not be members of the same metamorphic

sequence and hence may not have come from the same parent body (Dunn et al. 2016). CO chondrites present a range of thermal metamorphism (McSween 1977b). Low petrologic type (>3.1) CO chondrite matrices contain abundant amorphous silicates (e.g. Brearley 1993). Metasomatism in the CO chondrites has been determined to be less intense and more heterogeneous than in the CV chondrites (e.g., Brearley and Krot 2013). Davidson et al. (2014) assigned metamorphic grade 3.0 to DOM 08006 and 3.1 to MIL 05024 based on the plot of standard deviation versus the mean of Cr₂O₃ content of ferroan olivine phenocrysts. A variety of other observations, including Raman spectroscopy of the organic component of these two CO meteorites have recently confirmed that they are indeed very primitive (Bonal et al. 2016; Alexander et al. 2017). However, DOM 08006 does show some evidence of aqueous alteration (Krot et al. 2017).

Here, we also compare the amine abundance in four of the least altered meteorites (i.e., CO 3.0 versus CR 2.5–2.8; Alexander et al. 2013; Davidson et al. 2014; Harju et al. 2014; Howard et al. 2015; Abreu 2016), and that in more aqueously (i.e., CI1, CM1.1–1.8; Alexander et al. 2013). and thermally (i.e., CV3, CK4, and CK5; McSween et al. 1977; Kallemeyn et al. 1991; Keller et al. 1992; Krot et al. 1995) altered carbonaceous chondrites. This is one of the few investigations that directly tests the hypothesis that soluble organic compounds inherited by chondritic groups have common origins. This work has only become possible recently, as more primitive carbonaceous chondrites have become available and we have been able to identify commonalities and differences in the matrix mineralogy across carbonaceous chondrite groups. Some researchers have argued for a common origin for insoluble organic matter (IOM) in meteorites, IDPs, and comets, based on bulk elemental and isotopic compositions (Busemann et al. 2006; Alexander et al. 2007; Kebukawa et al. 2011). The origin of soluble organic compounds is a separate question that has bearing on the origins of the IOM, as some soluble compounds may have originated from breaking branches of more complex and larger macromolecules, including IOM. Aqueous processes inside the meteorite parent body and hydrolysis during meteorite extraction may have resulted in the production of amines from the breakdown of complex macromolecules, or from synthetic processes out of small precursor molecules such as hydrogen cyanide, amides, formaldehyde, and others meteoritic species (Aponte et al. 2017). The synthesis and decomposition of soluble amines through parent body processes however, remains to be tested under parent body-like conditions and goes beyond the scope of this report. In this study, we compared meteoritic amine content with parent-body processing histories to try to interpret their potential connection.

MATERIALS AND METHODS

Materials and reagents.

All glassware and sample handling tools used for processing the meteorite samples and procedural blanks were rinsed with Millipore Direct Q3 UV ultrapure water (18.2MΩ, 3 ppb total organic carbon; hereafter referred to as “water”), wrapped in aluminum foil, and then pyrolyzed in air at 500 °C overnight. Amine standards and reagents were obtained from Sigma Aldrich, Acros Organics, and Alfa Aesar and were used without further purification. Concentrated hydrochloric acid (37% HCl) was purchased from Sigma Aldrich, diluted to

6N using water, and then doubly distilled prior to use. Amines were extracted using a 1 M solution of semi-conductor grade sodium hydroxide (NaOH; Sigma Aldrich), and dried over pyrolyzed anhydrous sodium sulfate (Na_2SO_4). (*S*)-(-)-*N*-(trifluoroacetyl)pyrrolidine-2-carbonyl chloride (*S*TPC, 97% *ee*), was purchased from Sigma Aldrich. Guanidine and aminopropyl silica gels (Si-Gua and Si-NH₂ respectively) were bought from SiliCycle (SiliaBond®, 40–63 µm particle size) and cleaned using LCMS grade methanol and HPLC grade dichloromethane (DCM) followed by drying under vacuum.

Meteorite extraction procedures and derivatization.

We studied six meteorites provided by the Antarctic meteorite curator at the NASA Johnson Space Center: Dominion Range (DOM) 08006 (CO3, specific 52, parent 31; 6.6025 g); Miller Range (MIL) 05013 (CO3, specific 20, parent 3; 12.0086 g); La Paz Icefield (LAP) 02206 (CV3, specific 52, parent 50; 9.2376 g); Graves Nunataks (GRA) 06101 (CV3, specific 56, parent 3; 8.3217 g); Allan Hills (ALH) 85002 (CK4, specific 98, parent 0; 7.7923 g); Elephant Moraine (EET) 92002 (CK5, specific 52, parent 6; 11.0227 g). We also studied a single chip of the Allende carbonaceous chondrite (CV3, USNM 352921; 10.0512 g) provided by the Smithsonian National Museum of Natural History, Washington, DC. All seven meteorite samples were obtained from interior chips that did not contain any visual evidence of fusion crust. Analyses of amines were performed according to previously published methods (Aponte et al., 2014, 2015, 2016). The meteorite samples were powdered and homogenized by mixing using a mortar and pestle in a positive pressure ISO 5 HEPA-filtered laminar flow hood, and separated into ~500 mg portions. Each portion was extracted at 100 °C for 24 h inside a flame-sealed glass ampoule containing 1 mL of 0.1 M HCl. Extracts were separated from residues by centrifugation and transferred to a test tube containing 1 mL of 6 M HCl; sample residues were rinsed with water (3 × 0.5 mL) and the rinses combined with the aqueous acid portion. Extracts were dried under reduced pressure and subjected to acid-vapor hydrolysis using 1 mL of 6 M HCl at 150 °C for 3 h. After hydrolysis, iron hydroxides were precipitated by the addition of 4 mL of 1 M NaOH; the aqueous layer was then separated by centrifugation and the solid residue rinsed with water (2 × 4 mL). The aqueous portions were combined, re-acidified using 1 mL of 6 M HCl, and dried under reduced pressure. The residues were re-dissolved in 2 mL of 1 M NaOH and extracted using DCM (3 × 1 mL). The combined DCM extracts were passed through a plug of anhydrous Na_2SO_4 , rinsed once with 0.5 mL of DCM, and derivatized by stirring with 50 mg of Si-Gua and 50 µL of 0.1 M *S*-TPC for 1 hour at room temperature. Next, 50 mg Si-NH₂ were added to the mixture, which was stirred for 30 min at room temperature. Finally, the slurry was filtered, rinsed with ~3 mL of DCM, dried under flowing nitrogen gas then dissolved in 50 µL of ethyl acetate prior to analysis. A procedural blank (used to quantify the background levels of amines present in the solvents and derivatization reagents) was carried through the same procedures.

Compositional and isotopic analyses.

Derivatized amines were analyzed using a Thermo Trace Gas Chromatograph (GC) equipped with a 5 m base-deactivated fused silica guard column (Restek, 0.25 mm ID) and four 25 m length × 0.25 mm I.D. × 0.25 µm film thickness Chirasil L Val capillary columns (Agilent) using an oven program set as follows: initial temperature was 40°C, ramped at 10

°C/min to 162 °C, ramped at 2 °C/min to 176 °C, and ramped at 20 °C/min to 200 °C with a final hold of 20 min (UHP helium was used as carrier gas at 0.6 mL/min flow rate). The GC was interfaced with a Thermo DSQII electron-impact quadrupole mass spectrometer (MS) and a Thermo MAT 253 isotope-ratio mass spectrometer (IRMS) coupled to a Thermo GC-C III oxidation interface to attempt to make isotopic measurements; however, given the low abundances of amines in the analyzed meteorite extracts, we were not able to obtain $\delta^{13}\text{C}$ values for any of the amines examined. Triplicate injections of derivatized amines were made in splitless mode in aliquots of 1 μL . The mass spectrum was used to identify and quantify compounds through comparison to reference standards and the application of a 5-point calibration curve. Single ion mass-to-charge ratio (m/z) was used to identify and quantify compounds; $m/z = 165\text{--}168$ was used for compounds 1, 2, 4–8, 10, 11, 13–14, 18 and 20–25; while compound 3 was extracted at $m/z = 223\text{--}225$; $m/z = 236\text{--}238$ for compounds 12, 15–16 and 19; $m/z = 99\text{--}101$ for compound 9; and $m/z = 113\text{--}115$ for compound 17 (Table 1).

Petrographic Observations.

The Astromaterials Acquisition and Curation Office at the Johnson Space Center prepared and provided doubly-polished, demountable, petrographic thin sections from CV3 LAP 02206, CV3 GRA 06101, and CK4 ALH 85002, CK5 EET 92002. We analyzed a single petrologic thin section for each meteorite. Thin sections were studied on a FEI Quanta 200 SEM operating at 20kV in the low-vacuum mode using back-scattered electron (BSE) imaging. An energy dispersive (EDS) detector was used on the SEM for qualitative X-ray analyses for initial identification of different mineral phases. SEM measurements were not carried out using the same chips that were powdered to analyze their amine contents. However, provided that thermal metamorphism occurred after final assembly, petrologic characteristics are expected to be similar in the powdered chips as the samples here have undergone significant heat-driven homogenization. The possibility of post-heating mixing of volatile-rich and anhydrous, thermally modified materials is discussed below. Regions of matrix showing signs of terrestrial weathering were systematically excluded from further petrologic analysis.

The chemical composition of representative areas was obtained *via* point analyses and X-ray quantitative maps using a Cameca SX-50, operating at an accelerating voltage of 15 kV and beam current of 20 nA. This instrument is equipped with five wavelength-dispersive X-ray spectrometers (WDS). Electron probe microanalyses (EPMA) point analyses were collected for 13 elements (Na, Mg, Al, Si, P, S, K, Ca, Cr, Ti, Fe, Co and Ni) using a 10 μm -beam for fine-grained materials (<5 μm diameters in average) and 1 μm -beam for coarser materials (Table 2). Electron probe point analyses were collected for 13 elements. Analytical details are shown in Table S1 (electronic annex). Petrologic thin sections were carbon-coated for EPMA analysis.

RESULTS

Amines in the CV, CK, and CO carbonaceous chondrites.

We evaluated the abundance and molecular distribution of amines in five thermally metamorphosed meteorites belonging to the CV3 (Allende, LAP 02206, and GRA 06101), CK4 (ALH 85002), and CK5 (EET 92002) groups and two unheated CO3 meteorites (DOM 08006 and MIL 05013; Table 1). Amines have not been previously investigated from these carbonaceous chondrites. The overall low abundance of amines prevented measurement of the $\delta^{13}\text{C}$ isotopic composition of the amines, limiting our analyses to GC-MS as shown in Figure 1. Given the lack of isotopic analyses, the enantiomeric composition of *R*- and *S*-*sec*-butylamine may provide clues about the indigeneity of the detected amines, indeed, the *R/S* of *sec*-butylamine found in MIL 05013 (CO3), LAP 02206 (CV3), GRA 06101 (CV3), Allende (CV3), and EET 92002 (CK5) are 1.00, 1.09, 1.09, 0.98, and 0.96 respectively suggesting the composition of these chiral compounds are racemic and nearly racemic. However, without knowing the synthetic mechanism resulting in these compounds and without knowing the preferential use or synthesis of biological *R*- and *S*-*sec*-butylamine, it results challenging to argue that the racemic nature of *R*- and *S*-*sec*-butylamine would suggest the meteoritic indigeneity of these meteoritic species. Although the CO3 meteorites studied here do not show signs of thermal metamorphism (Davidson et al. 2014), their amine content was low and comparable to that of more extensively thermally altered CV3, CK4 and CK5 meteorites. The total abundance of amines ranged from 1.2 to 4.0 nmol/g of meteorite (abundance data for specific amines are presented in Table 1).

The total abundance of amines from the seven meteorites analyzed here and from those previously reported in the CI1 Orgueil, the CM1/2 ALH 83100, the CM2s LEW 90500, LON 94101, and Murchison, and the CR2s GRA 95229 and LAP 02342 (Aponte et al. 2014, 2015, 2016) are shown in Figure 2. We included the amine content in those meteorites for comparison of the effects of aqueous and thermal processing on the abundance of amines. The total amine abundances measured in this study are within one to three orders of magnitude lower than those previously found in aqueously altered CI, CM, and CR carbonaceous chondrites.

Level of processing of carbonaceous chondrites based on mineralogical and petrologic characteristics.

To evaluate the effects of asteroidal processing on the abundance and molecular distributions of amines, we have reviewed the petrologic characteristics of the meteorites studied here in Table 2. It is generally accepted that organic materials are located in the matrices of carbonaceous chondrites (Michel-Levy and Lautie 1981; Makjanic et al. 1993; Brearley 1999; Pearson et al. 2002; Abreu and Brearley 2010; Le Guillou et al. 2014). Owing to their fine-grained nature (sub-micron) and high abundance of non-crystalline materials (e.g. Brearley 1993), matrices are thought to be some of the earliest materials to be affected by thermal metamorphism and hence are disproportionately affected by mineral replacement (e.g., Huss et al. 2006). In the case of the CV3 meteorites LAP 02206 and GRA 06101, CK4 ALH 85002, and CK5 EET 92002, additional petrologic observations of their matrices were collected (Table 2; Figures 3–5). Several regions of matrix from the CV3s LAP 02206 and

GRA 06101 were examined. Our SEM observations (Figure 4) are consistent with previous descriptions of other CV_{oxA} meteorites. There is some evidence of mobilization of Fe from the matrix to chondrules, in particular for type II chondrules (Figure 4c). The matrices of both meteorites are relatively homogeneous in texture and there are no major textural or mineralogical differences between the matrix and the rims in BSE images (Figures 4b and 4d). Electron microprobe analysis showed that olivines in LAP 02206 and GRA 06101 have compositions in the range Fa_{41–47} and Fa_{42–46} and average compositions of Fa₄₄ and Fa₄₅ respectively as shown in Figure 3. Compositional data from these matrix olivines is consistent with the lack of Z-contrast observed among olivine grains in Figures 4d and 4f. Because LAP 02206 and GRA 06101 show narrower Fa-content ranges than Allende (Fa_{45–55} – Abreu and Brearley 2003), we suggest that these meteorites belong to a higher petrologic type. For the purpose of this paper, we adopt the Bonal et al. (2006) classification of Allende (petrologic type 3.6) and argue that LAP 02206 and GRA 06101 can be assigned to petrologic type 3.7.

Our observations of CK4 ALH 85002 and CK5 EET 92002 show extensive compositional and textural integration between matrix and chondrules (Figure 5). In the case of CK5 EET 92002, only the outline of the largest chondrules is observable. Matrix in both meteorite is either very coarse-grained or no grain outlines are preserved. These results agree with the et al. (1991) study, ALH 85002 matrix olivines range in composition from Fa_{30–32} with mean fayalite content of 30.9 mol%. In the case of EET 92002, we observed that the matrix olivines have an equally narrow range of compositions (Fa_{31–33}) and a slightly higher mean fayalite content than ALH 85002 (32.2 mol%) than ALH 85002 matrix olivines. It is unclear why matrix olivines in EET 92002 are more FeO-rich than those in ALH 85002. ALH 85002 has well-defined chondrules and matrix with grain sizes ranging from 10–50 µm. In contrast, chondrules and matrix in EET 92002 are thoroughly integrated and have grain sizes ranging from ~100–300 µm. Extensive integration between matrix and chondrules is characteristic of carbonaceous chondrites belonging to petrologic type 5.

DISCUSSION

Amines in thermally metamorphosed CV carbonaceous chondrites.

We report low total amine abundances in the three CV3 meteorites analyzed here (abundances ranged from 1.2 to 3.3 nmol/g of meteorite). Compared with aqueously altered carbonaceous chondrites, CV3 meteorites have 2 to 3 orders of magnitude lower amine contents than CI1, CM2 and CR2 meteorites (Figure 2). Among CV3 meteorites, Allende contains both a higher abundance and a more diverse compositional range of amines than LAP 02206 and GRA 06101. Multiple studies have demonstrated that organic materials in CV meteorites progressively mature as a result of thermal metamorphism and that there is a correlation between carbonization of organics and the mineralogical characteristics of matrices (e.g., Brearley 1999; Le Guillou et al. 2012; Abreu and Brearley 2003; Bonal et al. 2006, 2016). The narrow compositional range of chondrule olivines we observed in LAP 02206 and GRA 06101 suggest these CV_{oxA} meteorites have undergone a higher degree of carbonization and probably more extensive losses of amines than in Allende (Table 2). Figure 2 and Table 1 agree with this suggestion, as the total amine contents of Allende are at

least a factor of two larger than those in LAP 02206 and GRA 06101. Lower amine contents in more metamorphosed CVs are consistent with the argument that bulk carbon losses, which could be reflected by losses of particular compounds, may occur as a consequence of thermal metamorphism (e.g., Pearson et al. 2006). However, such an argument rests on the assumption that all CV meteorites (and carbonaceous chondrites in general) had the same initial carbon content, which has not been demonstrated. It is also important to note that the amine contents have only been measured in three CV meteorites and that the trend observed in the CV group is not mirrored in the other carbonaceous chondrite groups (see later sections). Therefore, it is premature to use the amine content of CV meteorites as an indicator of thermal metamorphism in CV meteorites.

Amines in CK and CV carbonaceous chondrites.

The amine abundances in ALH 85002 (CK4) and EET 92002 (CK5) are also low and similar within the range of CV3 meteorites. The higher abundance and more diverse suite of amines in the more thermally metamorphosed EET 92002 (CK5) relative to that found in ALH 85002 (CK4; Table 2) may suggest that, contrary to what was observed in the CV3 meteorites, increasing thermal processing may have not had an extensive effect on the abundance of amines in CK4 and CK5 meteorites. However, we have only analyzed one specimen of each CK4 and CK5 subgroups, and these molecular observations may need to be further evaluated in a larger suite of samples. Although some molecular analyses of soluble organics in CK meteorites have been reported (e.g., Elsila et al. 2005; Burton et al., 2015), no studies of the characteristics of the meteorite matrix and the distribution of soluble organic compounds in CK meteorites have been undertaken. Consequently, it is unclear if there are any relationships between organic materials and matrix minerals that could hint to the processes that amines might have undergone during thermal metamorphism. On the other hand, if CK meteorites indeed originate from the same parent body as the CV meteorites, as some studies suggest (e.g., Greenwood et al. 2010; Wasson et al. 2013), it could be suggested that the initial amine content was variable within the putative CV-CK parent body. Further studies, including a larger number of samples are needed to explore this suggestion.

Amine content in the non-altered CO3 carbonaceous chondrites.

The amine content of the CO meteorites DOM 08006 and MIL 05013 is very low (1.3 to 4.0 nmol/g of meteorite), consistent with the values observed for the CV and CK meteorites, and 2 to 3 orders of magnitude lower than those observed in CM, CI, and CR meteorites (Aponte et al. 2014, 2015, 2016; Figure 2). Here, we argue that asteroidal processes are unlikely to have driven losses of amines in these specific CO3 meteorites. Although some CO meteorites record extensive signs of thermal metamorphism (e.g., McSween 1977b; Scott and Jones 1990; Chizmadia et al. 2002; Bonal et al. 2007, 2016), DOM 08006 and MIL 05013 (Davidson et al. 2014). The mineralogy of pristine and weakly altered CO meteorites is fundamentally different from CV and CK matrices (e.g., Keller and Buseck 1990; Brearley 1997; Davidson et al. 1994), but similar to primitive CR (e.g., Abreu and Brearley 2010; Abreu 2016) and CM (e.g., Chizmadia and Brearley 2008; Leroux et al. 2015) meteorites. Although bulk water contents do not necessarily translate into replacement of primary mineralogy, measurements of H in water or OH measured by Alexander et al. (2013, 2017) are consistent with the petrologic similarities between primitive CR and CO

chondrites. Alexander et al. (2013) measured that CR GRA 95229 contains 0.36 wt.% and CR LAP 02342 contains 0.33 wt.% water/OH (contents were estimated by subtracting H from a bulk carbonaceous material). For comparison Alexander et al. (2017) measured that DOM 08006 contains 0.43 wt.%, clearly higher than values measured for the CR chondrites in this study. In fact, if DOM 08006 were to be classified using the scheme proposed by Alexander et al. (2013), it would be approximately assigned to petrologic type 2.4. MIL 05013 (paired with MIL 05024) contains 0.30 wt.% water/OH, which would correspond to approximately petrologic type 2.6 in the Alexander et al. (2013) scheme. Recent petrologic observations also suggest that DOM 08006 has undergone comparable or perhaps higher degrees of aqueous alteration than the least altered CR chondrites (Krot et al. 2017). For example, Krot et al. (2017) observed that most Fe-Ni-metal nodules in chondrules are pseudomorphically replaced by Cr-bearing magnetite and Ni-rich metal. Fe-Ni metal nodules in GRA 95229 and LAP 02432 are either intact or have been partly replaced by terrestrial weathering (Abreu 2016). In addition, magnetite was also identified in DOM 08006 Krot et al. (2017), supporting the assertion that alteration in this CO chondrite is similar in style and scope as alteration in CRs GRA 95229 and LAP 02432.

As in the case of thermal metamorphism, aqueous alteration does not explain the differences in the amine content observed between the hydrated carbonaceous chondrites (CI, CM, and CRs) and unaltered CO carbonaceous chondrites. If the CR meteorites GRA 95229 and LAP 02342 (Harju et al. 2014; Abreu 2016) are compared with the CO meteorites DOM 08006 and MIL 05013 (Davidson et al. 2014; Alexander et al. 2017; Schrader and Davidson 2017), they have experienced the same, very minimal degrees of aqueous alteration. Yet Figure 2 shows that CR meteorites contain over three orders of magnitude more amines than CO meteorites, a relationship that mirrors the contrast between CR high amino acid abundances (Martins et al. 2007; Pizzarello and Holmes 2009; Glavin et al. 2011) with low CO abundances (Burton et al. 2012; Chan et al. 2012). Because DOM 08006 and MIL 05013 do not record any significant signs of asteroidal processing, their low amine (and amino acids) contents appear to be pre-accretional in origin and not caused by processes occurring in a parent body. Low amine contents cannot be explained by differences in bulk C content either. Weakly altered CO and CR meteorites contain approximately the same amount of bulk C (Wiik 1956; Mason 1963; Pearson 2006; Alexander et al. 2012, 2017). Instead, low amine contents in CO would suggest that there were heterogeneities in the abundance of specific organic compounds across chondritic groups (Remusat et al. 2010; 2016).

Comparison of amine content in CV, CK, and CO carbonaceous chondrites with other groups.

We have analyzed the amine content in a limited set of samples belonging to various carbonaceous chondrite subtypes (Aponte et al. 2014, 2015, 2016) and can now add examples from CO, CV, and CK meteorites to this data set. Although the number of analyzed samples remains small, we observe some variations within each group of meteorites (Figure 2). Distinctive total amine concentrations are shown within varying meteorite groups, with the concentrations in the order of CR2 > CI1 $\approx$ CM2 > CM1/2 >> CO3 $\approx$ CV3_{oxA} $\approx$ CK4–5. This essentially the same sequence as for the abundances of amino acids (Glavin et al. 2011; Burton et al. 2012; Elsila et al. 2016). Nevertheless, further

evaluation of the total amine content (and that of other soluble meteoritic organics) in a larger set of samples belonging to these carbonaceous chondrite groups are needed to establish firmer correlations between meteorite types and amine abundances.

With the limited number of analyzed samples, and under the assumption that the amine content was homogeneous within the different asteroid parent bodies, the molecular distributions of amines extracted from carbonaceous chondrites belonging to different petrologic types might suggest a potential link between the abundance of specific amine species and the different levels of processing experienced by each parent body. To simplify the analysis of abundance and parent body processing, we plotted the relative abundance of methylamine (C_1), ethylamine (C_2), and the combined abundances of all structural isomers of propylamine (C_3), butylamine (C_4), and pentylamine (C_5) in Figure 6. Methylamine is the predominant amine species in Orgueil (CI1) and ALH 83100 (CM1/2) which have experienced extensive aqueous alteration and in meteorites that faced extensive thermal metamorphism such as CV3 (LAP 02206, GRA 06101, Allende), CK4 (ALH 85002) and CK5 (EET 92002); conversely C_3 - C_5 amines are the most abundant species in less altered CR2 meteorites. CO3 meteorites DOM 08006 and MIL 05013 however, seemed to go against this trend of molecular distribution and parent body alteration, as these specimens show no signs of thermal and very incipient signs of aqueous alteration (Krot et al. 2017), yet methylamine appeared as the most abundant amine in these meteorites. There was no consistent correlation observed between the relative abundance of methylamine and increasing parent body processing within the CM carbonaceous chondrite group (Figure 6). Previous studies have shown that the abundance of water-soluble meteoritic organics such as amino acids is highest in the least altered meteorites such as CR meteorites, and that the total amino acid abundances decrease and the relative distributions change with increasing levels of both aqueous and thermal processing (Ehrenfreund et al. 2001; Aponte et al. 2011; Glavin et al. 2011; Burton et al. 2014). The current amine results may be aligned with those previous analyses and also suggest that the higher concentrations of methylamine in more aqueously and thermally altered carbonaceous chondrites may have resulted from the preferential decomposition of larger and more parent body processing-resistant macromolecular species during our extraction and hydrolysis steps, as opposed to being formed from smaller precursor molecules such as carbon monoxide, ammonia, and hydrogen cyanide inside the parent body. These observed molecular differences may also be inherited signatures of the original formation localities and the pre-accretionary processes for different parent bodies, rather than the result of parent body processing (Remusat et al. 2010; 2016); future synthetic experiments and computational modeling of parent body processing may provide valuable insights about the abiotic origins of amines and other meteoritic organic compounds.

Molecular relationship between amines and amino acids.

Amines may be produced from the decarboxylation of amino acids at high temperatures inside the CV and CK parent body (Li and Brill 2003; Cox and Seward 2007); this synthetic mechanism for amines, however, may not be possible in non-altered CO3 meteorites DOM 08006 and MIL 05013. Burton et al. (2012, 2015) reported a predominance of n - ω -amino acids over other structural isomers in CO3 meteorites DOM 08006 and MIL 05013, CV3

meteorites Allende, MIL 05013, LAP 02206, and GRA 06101, and CK4 ALH 85002 and CK5 EET 92002 meteorites. Of the amines detected, the isomeric distribution only of propylamine, butylamine, and pentylamine can be examined to test to see if *n*- α -amines are also dominant. The complete isomeric suite of neither butylamine nor pentylamine of these amines was detected (Table 2). Neither *n*-butylamine nor *n*-pentylamine was detected in any sample, but the *tert*- and *sec*-butylamines were detected in most samples and *tert*-pentylamine in Allende. At the same time, only Allende exhibited *iso*-propylamine and no *n*-propylamine while all the other samples showed *n*-propylamine but no detectable *iso*-propylamine. This shows that there is no clear predominance of the straight-chain terminal amine as seen in amino acids.

The primary amines, methylamine, ethylamine and propylamine which may derive from glycine, α - and β -alanine and α -, β - and γ -aminobutyric acid respectively, are the most abundant amines in CO3, CK4, and CK5 meteorites. All these amino acids have been found in similar samples of these carbonaceous meteorites, and constitute some of the most abundant amino acid species in them. Without isotopic data, it remains challenging to trace parent-daughter relationships for amine and amino acids in these meteorites, as amines may be indigenous in the meteorite samples, or they may have formed from the decarboxylation of amino acids (any isomer where possible) during sample work-up, and at least a portion of these amino acids (especially α - amino acids) may potentially derive from terrestrial contamination.

CONCLUSIONS

Conscious that the processes occurred during and after the formation of the asteroid parent body may play an important role in the preservation, synthesis and destruction of soluble organic compounds, we investigated the amine abundance in the hot acid-water extracts of the unaltered CO3 carbonaceous chondrites and the thermally altered CV3, CK4, and CK5 meteorites. The amine content in these meteorites was lower than that observed in other carbonaceous chondrites from the CI, CM and CR subgroups. The low concentration of amines may be the result of extensive heating that occurred for CV3, CK4, and CK5 carbonaceous chondrites. Conversely, the low amine concentration in the unaltered CO3 meteorites DOM 08006 and MIL 05013 may be representative of the chemical composition of the environment where this parent body (or group of parent bodies) was originally accreted and may not result from asteroidal aqueous and/or thermal processing. Future analyses of the abundance and molecular distributions, as well as the isotopic and enantiomeric analysis of meteoritic amines and their structural analogs in carbonaceous chondrites will advance our understanding of the prebiotic formation of extraterrestrial organic compounds.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGEMENTS

US Antarctic meteorite samples are recovered by the Antarctic Search for Meteorites (ANSMET) program which has been funded by NSF and NASA, and characterized and curated by the Department of Mineral Sciences of the Smithsonian Institution and Astromaterials Curation Office at NASA Johnson Space Center. The authors would like to thank T. McCoy, J. Hoskin, and the Smithsonian National Museum of Natural History - Division of Meteorites for providing the meteorite sample used in this study. Thanks for technical assistance to Dr. K. Crispin at Penn State, and Queenie H. S. Chan and an anonymous reviewer for insightful criticism and suggestions to improve the manuscript. This research was supported by the NASA Astrobiology Institute and the Goddard Center for Astrobiology and a grant from the Simons Foundation (SCOL award 302497 to J.P.D.).

REFERENCES

- Abreu NM 2016 Why is it so difficult to classify Renazzo-type (CR) carbonaceous chondrites? – Implications from TEM observations of matrices for the sequences of aqueous alteration. *Geochimica et Cosmochimica Acta* 194:91–122.
- Abreu NM and Brearley AJ 2003 HRTEM and EFTEM observations of matrix in the oxidized CV3 chondrite ALH 84028: Implications for the origins of matrix olivines 34th Annual Lunar and Planetary Science Conference, 3 17-21, 2003, League City, Texas, abstract no.1397.
- Abreu NM and Brearley AJ 2010 Early solar system processes recorded in the matrices of two highly pristine CR3 carbonaceous chondrites, MET 00426 and QUE 99177. *Geochimica et Cosmochimica Acta* 74:1146–1171.
- Abreu NM and Brearley AJ 2011 Deciphering the nebular and asteroidal record of silicates and organic material in the matrix of the reduced CV3 chondrite Vigarano. *Meteoritics & Planetary Science* 46: 252–274.
- Alexander CMO'D, Fogel M, Yabuta H, and Cody GD 2007 The origin and evolution of chondrites recorded in the elemental and isotopic compositions of their macromolecular organic matter. *Geochimica et Cosmochimica Acta* 71: 4380–4403.
- Alexander CMO'D, Bowden R, Fogel ML, Howard KT, Herd CDK, and Nittler LR 2012 The Provenances of Asteroids, and Their Contributions to the Volatile Inventories of the Terrestrial Planets. *Science* 337: 721–723. [PubMed: 22798405]
- Alexander CMO'D, Howard KT, Bowden R and Fogel ML 2013 The classification of CM and CR chondrites using bulk H, C and N abundances and isotopic compositions. *Geochimica et Cosmochimica Acta* 123: 244–260.
- Alexander CMO'D, Greenwood RC, Bowden R, Gibson JM and Howard KT 2017 A mutli-technique search for the most primitive CO chondrites. *Geochimica et Cosmochimica Acta*. In press.
- Aponte JC, Alexandre MR, Wang Y, Brearley AJ, Alexander CMO'D, Huang Y 2011 Effects of secondary alteration on the composition of free and IOM-derived monocarboxylic acids in carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 75, 2309–2323.
- Aponte JC, Dworkin JP, and Elsila JE 2014 Assessing the origins of aliphatic amines in the Murchison meteorite from their compound-specific carbon isotopic ratios and enantiomeric composition. *Geochimica et Cosmochimica Acta* 141:331–345.
- Aponte JC, Dworkin JP, and Elsila JE 2015 Indigenous aliphatic amines in the aqueously altered Orgueil meteorite. *Meteoritics & Planetary Science* 50:1733–1749.
- Aponte JC, McLain HL, Dworkin JP, and Elsila JE 2016 Aliphatic amines in Antarctic CR2, CM2 and CM1/2 carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 189:296–311.
- Aponte JC, Elsila JE, Glavin DP, Milam SN, Charnley SB, Dworkin JP 2017 Pathways to meteoritic glycine and methylamine. *ACS Earth & Space Chemistry* 1:3–13.
- Bonal L, Quirico E, Bourot-Denise M, and Montagnac G 2006 Determination of the petrologic type of CV3 chondrites by Raman spectroscopy of included organic matter. *Geochimica et Cosmochimica Acta* 70:1849–1863.
- Bonal L, Bourot-Denise M, Quirico E, Montagnac G, and Lewin E 2007 Organic matter and metamorphic history of CO chondrites. *Geochimica et Cosmochimica Acta* 71:1605–1623.

- Bonal L, Quirico E, Flandinet L, and Montagnac G 2016 Thermal history of type 3 chondrites from the Antarctic meteorite collection determined by Raman spectroscopy of their polyaromatic carbonaceous matter. *Geochimica et Cosmochimica Acta* 189:312–337.
- Botta O and Bada JL 2002 Extraterrestrial organic compounds in meteorites. *Surveys in Geophysics* 23:411–467.
- Brearley AJ 1993 Matrix and fine-grained rims in the unequilibrated CO3 chondrite, ALHA77307 - Origins and evidence for diverse, primitive nebular dust components. *Geochimica et Cosmochimica Acta* 57:1521–1550.
- Brearley AJ 1997 Disordered biopyriboles, amphibole, and talc in the Allende meteorite: Products of nebular or parent body alteration? *Science* 276:1103–1105. [PubMed: 9148802]
- Brearley AJ and Jones RH 1998 Chondritic Meteorites In: *Planetary Materials*. Ed.: Papike JJ, Mineralogical Society of America, chapter 3, 1–398.
- Brearley AJ 1999 Origin of graphitic carbon and pentlandite in matrix olivines in the Allende meteorite. *Science* 285:1380–1382. [PubMed: 10464092]
- Brearley AJ and Krot A 2013 Metasomatism in the Early Solar System: The Record from Chondritic Meteorites In: *Metasomatism and the Chemical Transformation of Rock: The Role of Fluids in Terrestrial and Extraterrestrial Processes*. Eds.: Harlov DE, Austrheim H, Springer, chapter 15, 659–789.
- Burton AS, Elsila JE, Callahan MP, Martin MG, Glavin DP, Johnson NM, and Dworkin JP 2012 A propensity for *n*- ω -amino acids in thermally altered Antarctic meteorites. *Meteoritics & Planetary Science* 47:374–386.
- Burton AS, Grunsfeld S, Elsila JE, Glavin PD, and Dworkin JP 2014 The effects of parent-body hydrothermal heating on amino acid abundances in CI-like chondrites. *Polar Science* 8:255–263.
- Burton AS, McLain H, Glavin DP, Elsila JE, Davidson J, Miller KE, Andronikov AV, Lauretta D, and Dworkin JP 2015 Amino acid analyses of R and CK chondrites. *Meteoritics & Planetary Science* 50:470–482.
- Busemann H, Young AF, Alexander CMO'D, Hoppe P, Mukhopadhyay S, Nittler LR 2006 Interstellar chemistry recorded in organic matter from primitive meteorites. *Science* 312: 727–730. [PubMed: 16675696]
- Chan H-S, Martins Z, and Sephton MA 2012 Amino acid analyses of type 3 chondrites Colony, Ornans, Chainpur, and Bishunpur. *Meteoritics & Planetary Science* 47:1502–1516.
- Chizmadia LJ, Rubin AE, and Wasson JT 2002 Mineralogy and petrology of amoeboid olivine inclusions in CO3 chondrites: Relationship to parent-body aqueous alteration. *Meteoritics & Planetary Science* 37:1781–1796.
- Cronin JR and Chang S 1993 Organic matter in meteorites: Molecular and isotopic analysis of the Murchison meteorite In *The chemistry of life's origins*, edited by Greenberg JM, Mendoza CX, and Pirronelle V Dordrecht: Kluwer Academic Publishers pp. 209–258.
- Davidson J, Nittler LR, Alexander CMO'D, and Stroud RM 2014 Petrography of very primitive CO3 chondrites: Dominion Range 08006, Miller Range 07687, and four others 45th Lunar and Planetary Science Conference, held 17-21 3, 2014 at The Woodlands, Texas LPI Contribution No. 1777, p.1384.
- Dunn TL, Gross J, Ivanova MA, Runyon SE, and Bruck AM 2016 Magnetite in the unequilibrated CK chondrites: Implications for metamorphism and new insights into the relationship between the CV and CK chondrites. *Meteoritics & Planetary Science* 51: 1701–1720.
- Ehrenfreund P, Glavin DP, Botta O, Cooper G, and Bada JL 2001 Extraterrestrial amino acids in Orgueil and Ivuna: Tracing the parent body of CI type carbonaceous chondrites. *Proceedings of the National Academy of Sciences of the United States of America* 98:2138–2141. [PubMed: 11226205]
- Elsila JE, de Leon NP, Buseck PR, and Zare RN 2005 Alkylation of polycyclic aromatic hydrocarbons in carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 69:1349–1357.
- Elsila JE, Aponte JC, Blackmond DG, Burton AS, Dworkin JP, and Glavin DP 2016 Meteoritic amino acids: Diversity in compositions reflects parent body histories. *ACS Cent. Sci* 2:370–379. [PubMed: 27413780]

- Glavin DP, Callahan MP, Dworkin JP, and Elsila JE 2011 The effects of parent body processes on amino acids in carbonaceous chondrites. *Meteoritics & Planetary Science* 45:1948–1972.
- Greenwood RC, Franchi IA, Kearsley AT, and Alard O 2010 The relationship between CK and CV chondrites. *Geochimica et Cosmochimica Acta* 74:1684–1705.
- Grossman JN and Brearley AJ 2005 The onset of metamorphism in ordinary and carbonaceous chondrites. *Meteoritics & Planetary Science* 40:87–122.
- Guimon RK, Symes SJK, Sears DWG, and Benoit PH 1995 Chemical and physical studies of type 3 chondrites XII: The metamorphic history of CV chondrites and their components. *Meteoritics & Planetary Science* 30: 704–714.
- Harju ER, Rubin AE, Ahn I, Choi B-G, Ziegler K and Wasson JT 2014 Progressive aqueous alteration of CR carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 139: 267–292.
- Howard KT, Alexander CMOD, Schrader DL and Dyl KA 2015 Classification of hydrous meteorites (CR, CM and C2 ungrouped) by phyllosilicate fraction: PSD-XRD modal mineralogy and planetesimal environments. *Geochimica et Cosmochimica Acta* 149: 206–222.
- Huss GR, Rubin AE and Grossman JN 2006 Thermal metamorphism in chondrites Meteorites and the Early Solar System II, Lauretta DS and McSween HY Jr. (eds.), University of Arizona Press, Tucson, 943 pp., p.567–586.
- Ito M and Messenger S 2010 Thermal metamorphic history of a Ca, Al-rich inclusion constrained by high spatial resolution Mg isotopic measurements with NanoSIMS 50L. *Meteoritics & Planetary Science* 45: 583–595.
- Kallemeyn GW, Rubin AE, and Wasson JT 1991 The compositional classification of chondrites: VI. The CR carbonaceous chondrite group. *Geochimica et Cosmochimica Acta* 55:881–892.
- Kebukawa Y, Alexander CMO'D and Cody GD 2011 Compositional diversity in insoluble organic matter in type 1, 2 and 3 chondrites as detected by infrared spectroscopy. *Geochimica et Cosmochimica Acta* 75: 3530–3541.
- Keller LP, Clark JC, Lewis CF, and Moore CB 1992 Maralinga, a metamorphosed carbonaceous chondrite found in Australia. *Meteoritics* 27: 87–91.
- Kojima T, Tomeoka K, and Takeda H 1993 Unusual dark clasts in the Vigarano CV3 chondrite: Record of parent body processes. *Meteoritics & Planetary Science* 28:649–58.
- Kojima T and Tomeoka K (1996). Indicators of aqueous alteration and thermal metamorphism on the CV parent body: Microtextures of a dark inclusion from Allende. *Geochimica et Cosmochimica Acta* 60:2651–66.
- Krot AN, Scott ERD, and Zolensky ME 1995 Mineralogical and chemical modification of Components in CV3 Chondrites: Nebular or asteroidal processing? *Meteoritics & Planetary Science* 30:748–776.
- Krot AN, Zolensky M, Wasson JT, Scott ERD, Keil K, and Ohsumi K 1997a Carbide magnetite assemblages in type-3 ordinary chondrites. *Geochimica et Cosmochimica Acta* 61:219–237.
- Krot AN, Scott ERD, and Zolensky ME 1997b Origin of fayalitic olivine rims and lath- shaped matrix olivine in the CV3 chondrite Allende and its dark inclusions. *Meteoritics & Planetary Science* 32:31–49.
- Krot AN, Petaev MI, Scott ERD, Choi B-G, Zolensky ME, and Keil K 1998 Progressive alteration in CV3 chondrites: More evidence for asteroidal alteration. *Meteoritics & Planetary Science* 33:1065–85.
- Krot AN, Nagashima K and Simon SB 2017 Diverse alteration of DOM 08006 (CO3.0) and DOM 08004 (CO3.1) and its effect on oxygen isotopic compositions of grossite-bearing refractory inclusions 48th Lunar and Planetary Science Conference, held 20-24 3 2017, at The Woodlands, Texas LPI Contribution No. 1964, id.1084.
- Le Guillou C, Rouzaud J-N, Bonal L, Quirico E, Derenne S and Remusat L (2012) High resolution TEM of chondritic carbonaceous matter: Metamorphic evolution and heterogeneity. *Meteoritics & Planetary Science* 47:345–362.
- Guillou Le, Bernard S, Brearley AJ, and Remusat L (2014). Evolution of organic matter in Orgueil, Murchison and Renazzo during parent body aqueous alteration: In situ investigations. *Geochimica et Cosmochimica Acta* 131:368–392.

- Leroux H, Cuvillier P, Zanda B, Hewins, and R. H 2015 GEMS-like material in the matrix of the Paris meteorite and the early stages of alteration of CM chondrites. *Geochimica et Cosmochimica Acta* 170:247–265.
- Makjanic J, Vis RD, Hovenier JW, and Heymann D 1993 Carbon in the matrices of ordinary chondrites. *Meteoritics* 28:63–70.
- Mason B 1963 The carbonaceous chondrites. *Space Science Reviews* 1:621–646.
- Martins Z, Alexander CMOD, Orzechowska GE, Fogel ML, and Ehrenfreund P 2007 Indigenous amino acids in primitive CR meteorites. *Meteoritics & Planetary Science* 42:2125–2136.
- McSween HY Jr. 1977a Petrographic Variations among Carbonaceous Chondrites of the Vigarano Type. *Geochimica et Cosmochimica Acta* 41:1777–1790.
- McSween HY Jr. 1977b Carbonaceous chondrites of the Ornans type: A metamorphic sequence. *Geochimica et Cosmochimica Acta* 41:477–449.
- Michel-Levy CM and Lautie A 1981 Microanalysis by Raman spectroscopy of carbon in the Tieschitz chondrite. *Nature* 292:321–322.
- Pearson VK, Sephton MA, Kearsley AT, Bland PA, Franchi IA, Gilmour I 2002 Clay mineral-organic matter relationships in the early solar system. *Meteoritics & Planetary Science* 37:1829–1833.
- Pearson VK, Sephton MA, Franchi IA, Gibson JM, and Gilmour I 2006 Carbon and nitrogen in carbonaceous chondrites: Elemental abundances and stable isotopic compositions. *Meteoritics & Planetary Science* 41:1899–1918.
- Pizzarello S, Cooper GW, and Flynn GJ 2006 The nature and distribution of the organic material in carbonaceous chondrites and interplanetary dust particles In *Meteorites and the Early Solar System II* (eds. Lauretta DS and McSween HY), pp 625–651. University of Arizona Press: Tucson, AZ.
- Pizzarello S and Holmes W 2009 Nitrogen-containing compounds in two CR2 meteorites: ¹⁵N composition, molecular distribution and precursor molecules. *Geochimica et Cosmochimica Acta* 73:2150–2162.
- Remusat L, Guan Y, Wang Y and Eiler JM 2010 Accretion and preservation of D-rich organic particles in carbonaceous chondrites: Evidence for important transport in the early solar system nebula. *The Astrophysical Journal* 713:1048–1058.
- Remusat L, Piani L and Bernard S 2016 Thermal recalcitrance of the organic D-rich component of ordinary chondrites. *Earth and Planetary Science Letters* 435:36–44.
- Righter K and Neff KE 2007 Temperature and oxygen fugacity constraints on CK and R chondrites and implications for water and oxidation in the early solar system. *Polar Science* 1: 25–44.
- Scott ERD and Jones RH 1990 Disentangling nebular and asteroidal features of CO3 carbonaceous chondrite meteorites. *Geochimica et Cosmochimica Acta* 54, 2485–2502.
- Sears DWG and Dodd RT 1988 Overview and classification of meteorites In *Meteorites and the Early Solar System* (ed. Kerridge JF and Matthews MS), pp. 3–31. University of Arizona Press: Tucson, AZ.
- Sephton MA 2002 Organic compounds in carbonaceous meteorites. *Natural Product Reports* 19:292–311. [PubMed: 12137279]
- Schrader DL and Davidson J 2017 CM and CO chondrites: A common parent body or asteroidal neighbors? Insights from chondrule silicates. *Geochimica et Cosmochimica Acta*. In press.
- Wasson JT, Isa J, and Rubin AE 2013 Compositional and petrographic similarities of CV and CK chondrites: A single group with variations in textures and volatile concentrations attributable to impact heating, crushing and oxidation. *Geochimica et Cosmochimica Acta* 108:45–62.
- Wiik HB 1956 The chemical composition of some stony meteorites. *Geochimica et Cosmochimica Acta* 9:279–289.
- Weisberg MK, Prinz M, Clayton RN, and Mayeda TK 1997 CV3 chondrites: Three subgroups, not two. *Meteoritics & Planetary Science* 32: A138–A139.
- Wetherill GW and Chapman CR (1988) Asteroids and meteorites In *Meteorites and the Early Solar System* (ed. Kerridge JF and Matthews MS), pp. 35–67. University of Arizona Press: Tucson, AZ.

Figure 1.

Positive electron impact GC-MS chromatogram (extracted at $m/z = 165$ – 168 ; 28–38 min region) of *S*-TPC-derivatized acid-vapor hydrolyzed amine extract of CO3, CV3, CK4 and CK5 carbonaceous chondrites, procedural blank, and standards used. The identities of the peaks are presented in Table 1 (structures are shown in Figure S1). U: unidentified compound, P: Phthalate. Difference in retention times may be due to variability in the carrier gas composition and potential column degradation over extensive usage.

Figure 2.

Total abundance of amines in acid-hydrolyzed hot water extracts of CO3, CV3, CK4 and CK5 carbonaceous chondrites. Meteorites are arranged according to their aqueous and thermal alteration (Alexander et al. 2013). For comparison, amine abundances in CI1, CM1/2, CM2, and CR2 meteorites have been included in the graph (values taken from Aponte et al. 2014, 2015, 2016).

Composition of Matrix Olivines in CV and CK Chondrites

Figure 3.

Compositions of matrix olivines in LAP 02206 (n=20), GRA 06101 (n=16), ALH 85002 (n=13), and EET 92002 (n=13) measured in individual grains using focused-beam electron microprobe analysis. The mean fayalite contents are as follows: LAP 02206 (Fa₄₄), GRA 06101 (Fa₄₅), ALH 85002 (Fa₃₁), and EET 92002 (Fa₃₂). Arrows represent compositional ranges obtained in previous studies. Fayalite contents for the CK chondrites are Fa₃₀₋₃₃ (Kallemeyn et al. 1991). Fayalite contents for Allende are Fa₄₅₋₅₅ (Abreu and Brearley 2003).

Figure 4.

Back scattered electron (BSE), Z-contrast electron micrographs from CV 3.7 LAP 02206 and GRA 06101. (a) Mosaic of the LAP 02206 section used for this study. Note that the boundary between matrix and chondrules is clearly observable. (b) Type I chondrule in LAP 02206 surrounded by fine-grained fayalitic olivine matrix. (c) Type II chondrule in LAP 02206 showing significant compositional integration with the surrounding matrix. (d) Close-up image of typical fine-grained matrix in LAP 02206. Matrix is dominated by equilibrated, elongated 10–50 micron, fayalitic olivine grains, with lesser amounts of nepheline and opaques, including Fe-sulfides and oxides. (e) Type I chondrule in LAP 02206 surrounded by fine-grained fayalitic olivine matrix. The margins of this chondrule show evidence of Fe-

diffusion from the matrix. (f) Matrix in GRA 06101 resembles matrix in LAP 02206 in terms of size and range of chemical composition.

Figure 5. Back scattered (Z-contrast) electron micrographs from CK4 ALH 85002 and CK5 EET 92002. (a) Mosaic of the ALH 85002 section used for this study. The boundaries between matrix and chondrules are not observable at this magnification. (b) Chondrule in ALH 85002. It is unclear if this is a type I or type II chondrule, as its chemical composition has equilibrated with the surrounding matrix. (c) Large chondrule in EET 92002. Small chondrules are no longer apparent in EET 92002. As in the case of ALH 85002, it is unclear if this chondrule is a type I or type II chondrule. (d) Matrix in EET 92002, showing bands with fayalitic olivine and with plagioclase composition. Individual grains are no longer apparent.

Figure 6.

Molecular distributions of amines in acid-hydrolyzed hot water extracts of carbonaceous chondrites from various petrologic types. Structural distributions are shown as relative abundances of isomers of methylamine (C₁), ethylamine (C₂), and all structural isomers of propylamine (C₃), butylamine (C₄), and pentylamine (C₅); values taken from Aponte et al. 2014, 2015, 2016.

Table 1.

Blank-corrected concentrations of amines from hot-water acid-hydrolyzed extracts of CO3, CV3, CK4 and CK5 meteorites, values in nmol/g of meteorite.^a

Cmpd	Amine	DOM 08006 (C03.00)	MIL 05013 (C03.01)	LAP 02206 (CV3.7)	GRA 06101 (CV3.7)	Allende (CV3.6)	ALH 85002 (CK4)	EET 92002 (CK5.00)
1	<i>tert</i> -Butylamine	0.068 ± 0.002	0.030 ± 0.003	0.041 ± 0.001	<i>b</i>	0.07 ± 0.01	<i>b</i>	<i>b</i>
2	<i>iso</i> -propylamine	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.74 ± 0.17 ^c	<i>b</i>	<i>b</i>
3	Methylamine	3.31 ± 0.24 ^c	0.91 ± 0.05 ^c	0.88 ± 0.02 ^c	0.93 ± 0.01 ^c	1.54 ± 0.04 ^c	1.18 ± 0.03 ^c	1.21 ± 0.15 ^c
4	Dimethylamine	0.19 ± 0.02	<i>b</i>	<i>b</i>	<i>b</i>	0.50 ± 0.04	<i>b</i>	<i>b</i>
5	Ethylamine	0.21 ± 0.02 ^c	0.11 ± 0.01 ^c	0.10 ± 0.01 ^c	0.117 ± 0.001 ^c	0.068 ± 0.002 ^c	0.16 ± 0.01 ^c	0.51 ± 0.07 ^c
6	<i>tert</i> -Pentylamine	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.07 ± 0.01	<i>b</i>	<i>b</i>
7	Ethylmethylamine	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.095 ± 0.001	<i>b</i>	<i>b</i>
8	(<i>R</i>)- <i>sec</i> -Butylamine	<i>b</i>	0.060 ± 0.002	0.081 ± 0.002	0.085 ± 0.001	0.088 ± 0.001	<i>b</i>	0.08 ± 0.01
9	Diethylamine	<i>b</i>	<i>b</i>	0.04 ± 0.01	0.040 ± 0.001	0.051 ± 0.003	<i>b</i>	0.07 ± 0.01
10	(<i>S</i>)- <i>sec</i> -Butylamine	<i>b</i>	0.060 ± 0.002	0.074 ± 0.001	0.078 ± 0.001	0.090 ± 0.001	<i>b</i>	0.083 ± 0.004
11	<i>n</i> -Propylamine	0.17 ± 0.01 ^c	0.075 ± 0.003 ^c	<i>b</i>	0.12 ± 0.01 ^c	<i>b</i>	0.19 ± 0.02 ^c	0.38 ± 0.02 ^c
Total amine abundance		4.0 ± 0.3	1.3 ± 0.1	1.2 ± 0.04	1.4 ± 0.02	3.3 ± 0.3	1.5 ± 0.1	2.3 ± 0.3

^aCompounds identified by comparison with elution time and mass spectra of standards. Compounds 12–25 shown in Figure S1, were looked for, but not found in the meteorites analyzed.

^bValues fell below our detection limits (0.01 nmol/g meteorite).

^cMay contain trace amounts of amine present in the derivatization reagent.

Table 2.

Summary of the petrologic characteristics of the carbonaceous chondrites studied. Note that there are disagreements in the petrologic types and temperature ranges assigned to CV and CK meteorites.

	DOM 08006	MIL 05013	LAP 02206	GRA 06101	Allende	ALH 85002	EET 92102
Petrologic type	$\delta_{\text{C03.00}}$	$\delta_{\text{C03.01}}$	$\delta_{\text{CV}_{\text{oxA}} 3}$ >3.2–3.6	$\delta_{\text{CV}_{\text{oxA}} 3}$ >3.2–3.6	CV _{oxA} 3.2–3.6*	CK4	CK5
Pairing group	DOM 08004	MIL 03377	N/A	N/A	Fall	ALH 82135	EET 87507
Terrestrial weathering			B	B	N/A	A	A/Be
Estimated temperature (°C)	< 100°C	< 100°C	400–600°C	400–600°C	400–600°C	300–658°C	300–658°C
Main alteration effect	None	None	Aqueous/Thermal	Aqueous/Thermal	Aqueous/Thermal	Thermal	Thermal
Degree of aqueous alteration	Minimal	Minimal	Moderate	Moderate	Moderate	None	None
Degree of thermal metamorphism	None	None	Moderate	Moderate	Moderate	Extensive	Very extensive
Matrix volume (vol.%)	30–40	30–40	34–50	34–50	34–50	66–74	65–79
Matrix dominant materials	Amorphous silicates, olivine	Amorphous silicates, olivine	Ferroan olivine	Ferroan olivine	Olivine Fa _{45–55}	Ferroan olivine, plagioclase	Ferroan olivine, plagioclase

* Guimon et al. (1995), Bonal et al. (2006), respectively.

δ_{Davidson} et al. (2014).

δ_{Based} on compositional variations in matrix olivine compositions; this work.

δ_{Matrix} volumes reported here for all meteorites, with the exception of Allende, are the ranges observed for each group. Kallenemeyn et al. (1991). Nittler et al. (2013). Wasson et al. (2013).

$\delta_{\text{Temperatures}}$ are assigned based on more extensive equilibration in matrix olivine compositions in comparison with CV Allende.

δ_{Ito} and Messenger (2010).

δ_{Estimate} for CK meteorites from Righter and Neff (2007).