

Indigenous aliphatic amines in the aqueously altered Orgueil meteorite

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Abstract—The CI1 Orgueil meteorite is a highly aqueously altered carbonaceous chondrite. It has been extensively studied, and despite its extensive degree of aqueous alteration and some documented instances of contamination, several indigenous organic compounds including amino acids, carboxylic acids, and nucleobases have been detected in its carbon-rich matrix. We recently developed a novel gas chromatographic method for the enantiomeric and compound-specific isotopic analyses of meteoritic aliphatic monoamines in extracts and have now applied this method to investigate the monoamine content in Orgueil. We detected 12 amines in Orgueil, with concentrations ranging from 1.1 to 332 nmol g^{−1} of meteorite and compared this amine content in Orgueil with that of the CM2 Murchison meteorite, which experienced less parent-body aqueous alteration. Methylamine is four times more abundant in Orgueil than in Murchison. As with other species, the amine content in Orgueil extracts shows less structural diversity than that in Murchison extracts. We measured the compound-specific stable carbon isotopic ratios ($\delta^{13}\text{C}$) for 5 of the 12 monoamines detected in Orgueil and found a range of $\delta^{13}\text{C}$ values from −20 to +59‰. These $\delta^{13}\text{C}$ values fall into the range of other meteoritic organic compounds, although they are ¹³C-depleted relative to their counterparts extracted from the Murchison meteorite. In addition, we measured the enantiomeric composition for the chiral monoamines (*R*)- and (*S*)-*sec*-butylamine in Orgueil, and found it was racemic within experimental error, in contrast with the L-enantiomeric excess found for its amino acid structural analog isovaline. The racemic nature of *sec*-butylamine in Orgueil was comparable to that previously observed in Murchison, and to other CM2 and CR2 carbonaceous chondrites measured in this work (ALH 83100 [CM1/2], LON 94101 [CM2], LEW 90500 [CM2], LAP 02342 [CR2], and GRA 95229 [CR2]). These results allow us to place some constraints on the effects of aqueous alteration observed over the monoamine concentrations in Orgueil and Murchison, and to evaluate the primordial synthetic relationships between meteoritic monoamines and amino acids.

INTRODUCTION

The Orgueil meteorite is an observed fall that occurred on May 14, 1864 (Nagy et al. 1961), and constitutes the largest CI chondrite ever recovered and the most extensively studied (see Gounelle and Zolensky [2014] and references therein). Like all known CI chondrites, it is classified as alteration type 1, which indicates extensive aqueous processing inside its parent body. Orgueil is an organic-rich carbonaceous chondrite that contains ~3.5 wt% carbon and 9–14 wt% water in

its matrix (Lodders [2003] and references therein). Its initially reported organic composition was controversial; early reports of extraterrestrial organic compounds generated by life (Claus and Nagy 1961; Nagy et al. 1962; Fitch and Anders 1963; Meinschein et al. 1963) were later shown to be products of contamination by terrestrial hydrocarbons and pollen (Anders et al. 1964; Oró et al. 1966; Oró and Nooner 1967; Nagy 1975; Sephton et al. 2001; Watson et al. 2003). Further analyses, however, demonstrated the presence of indigenous organic compounds in Orgueil, including

amino acids and nucleobases (Lawless et al. 1972; Stoks and Schwartz 1979; Ehrenfreund et al. 2001; Martins et al. 2006; Glavin and Dworkin 2009; Callahan et al. 2011). Aliphatic monoamines (hereafter referred to as “amines”) have not been previously analyzed in the Orgueil meteorite, leaving an important gap in the study of the organic composition of this meteorite.

Amines are volatile organic compounds that can be oxidized under aqueous conditions to amides, imines, nitriles, aldehydes, and other related compounds in the presence of oxygen and transition metal ions (Kim et al. 2008; Chanda and Fokin 2009; Roy et al. 2012). Orgueil is a water-rich carbonaceous chondrite that contains a large suite of transition metals (Anders and Ebihara 1982; Lodders 2003); thus, although structurally analogous organic compounds such as amino acids have been previously reported from Orgueil (Lawless et al. 1972; Ehrenfreund et al. 2001; Glavin and Dworkin 2009), it might be expected that the concentration of amines surviving inside Orgueil would be low due to the potential catalytic effects of transition metals in the destruction of organics (Murahashi 1995; Soulé et al. 2011; Largeton 2013). We have recently developed an analytical method to study the abundance, molecular distribution, and $\delta^{13}\text{C}$ isotopic composition of meteoritic amines and applied it to the Murchison meteorite (Aponte et al. 2014a). In this work, we report our analysis of amines in Orgueil using the same technique.

CI chondrites show a distinctive organic content in relation to other carbonaceous chondrites (Ehrenfreund et al. 2001; Martins et al. 2006; Callahan et al. 2011). However, because all CI chondrites are extensively aqueously altered, it is challenging to separate the effects of aqueous alteration from the inherent parent body differences in this comparison. Therefore, we became interested in understanding the amine content in Orgueil and how it compared to chondrites with lower water content and aqueous alteration histories. Amines have been previously reported in CR carbonaceous chondrites from petrologic types 1–3 (Pizzarello and Holmes 2009; Pizzarello et al. 2012); however, the isotopic ratios of the reported amines were not determined, making it difficult to eliminate terrestrial contamination as their origin. In addition, amines have been detected in the Tagish Lake meteorite (C2-ungrouped chondrite), but the identities, concentrations, and isotopic compositions were not reported (Pizzarello et al. 2001). From these studies, however, it may be observed that the most aqueously altered meteorites have the least abundant amines. Orgueil and the CM type 2 Murchison meteorite have experienced mild degrees of thermal processing below 150 °C (Clayton and Mayeda 1999; Bullock et al. 2005; Brearley 2006);

thus, differences in their organic composition may have arisen from either differences in their parent bodies or the larger degree of aqueous alteration observed in Orgueil. We have compared the Orgueil amine data with that from the Murchison meteorite in this study both to evaluate the effects of aqueous alteration in the molecular, isotopic, and enantiomeric compositions of amines and to shed light on the characteristics of the CI parent body and the chemical processes relevant to its organic content.

The isotopic composition of meteoritic aliphatic compounds is a product of their precursor molecules and formation pathways; thus, it provides clues about their primordial synthetic histories (Yuen et al. 1984). The $\delta^{13}\text{C}$ composition of meteoritic amines combined with the meteorite alteration history is useful in constraining their original formation to specific synthetic routes predicted by observed isotopic trends. The amine ^{13}C abundance has only been previously measured for amines in the Murchison meteorite, showing an inverse relationship between the ^{13}C abundance and the amine molecular weight (Aponte et al. 2014a). This isotopic trend has been previously observed for amino acids in Murchison (Engel et al. 1990; Pizzarello et al. 1994, 2004; Elsila et al. 2012) and may suggest that meteoritic amines and amino acids were formed from precursor molecules that amplified isotopic fractionation through a chain-elongation mechanism (Yuen et al. 1984).

A primordial synthetic relationship between meteoritic amines and amino acids has also been suggested based on their molecular architecture (Pizzarello 2002; Pizzarello et al. 2006; Hudson et al. 2009; Aponte et al. 2014a). These compound classes share similar structural aliphatic backbones; for example, methylamine and ethylamine are structurally analogous to glycine and α - and β -alanine, respectively, while the backbone of *n*-propylamine is shared by α -amino-*n*-butyric and γ -amino-*n*-butyric acids. In addition, branched meteoritic amines and amino acids may share similar chiral centers such as those found in *sec*-butylamine and isovaline. A link between the origins of biological homochirality on Earth and the nonterrestrial L-enantiomeric excess (L-*ee*) found for isovaline in Orgueil and Murchison has been previously suggested (Cronin and Pizzarello 1997; Pizzarello et al. 2003; Glavin and Dworkin 2009). Thus, investigating the distribution and enantiomeric composition of amines may provide clues about the primordial synthetic mechanisms of amino acids and the origins of the *ee* of L-isovaline.

In this study we measured the abundance, distribution, enantiomeric, and ^{13}C -isotopic composition of amines in Orgueil for the first time, and compared those distributions with those of amino acids previously

found in Orgueil and both amines and amino acids reported from Murchison (Ehrenfreund et al. 2001; Glavin and Dworkin 2009; Aponte et al. 2014a), providing new insights into the prebiotic synthesis of these classes of organic compounds.

MATERIALS AND METHODS

Materials and Reagents

All glassware and sample handling tools used for the meteorite samples were rinsed with Millipore Direct Q3 UV ultrapure water (18.2M Ω , 3 ppb total organic carbon; hereafter referred to as “water”), wrapped in aluminum foil, and then pyrolyzed in air at 500 °C overnight. Semiconductor grade sodium hydroxide (NaOH), (*S*)-(-)-*N*-(trifluoroacetyl)pyrrolidine-2-carbonyl chloride (*S*-TPC, 97% *ee*), and hydrochloric acid (HCl) were purchased from Sigma-Aldrich; we diluted and doubly distilled the HCl prior to use. Anhydrous sodium sulfate (Na₂SO₄) was pyrolyzed before use to remove organic contamination. Amine standards and reagents were obtained from Sigma-Aldrich and Alfa Aesar and used without further purification. Triazabicyclodecene and aminopropyl silica gels (Si-TBD and Si-NH₂, respectively) were bought from SiliCycle (SiliaBond[®], 40–63 μ m particle size) and cleaned using HPLC grade methanol and dichloromethane (DCM) followed by drying under vacuum.

Meteorite Extraction Procedures and Derivatization

We previously showed that the abundance of amines in Murchison is increased after hydrolysis and that our hydrolysis and workup method do not affect the isotopic and enantiomeric compositions of amines in a standard mixture (Aponte et al. 2014a). In light of the expected low abundances of amines in Orgueil due to the extensive degree of aqueous alteration and low organic content previously reported for this chondrite (Ehrenfreund et al. 2001), we analyzed only its total amine content (all amines found in either free form or released from precursors upon acid-vapor hydrolysis), rather than both the total and free amines, as previously analyzed in Murchison (Aponte et al. 2014a). We studied a piece of Orgueil (931.6 mg extracted) obtained from the Musée National, Paris. The sample, which did not show any visual evidence of fusion crust, was powdered using a mortar and pestle in a positive pressure HEPA-filtered laminar flow hood, and separated into four portions (~230 mg each). Each portion was extracted at 100 °C for 24 h inside a flame-sealed glass ampoule containing 1 mL of 0.5 M HCl. Extracts were separated from residues by centrifugation

and removed to a test tube; sample residues were rinsed with water (2 \times 0.5 mL) and the rinses combined with the aqueous acid portion, and 1 mL of 6 M HCl was added to the solution. 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 8 M NaOH; the aqueous layer was then separated by centrifugation and the solid residue rinsed with water (2 \times 4 mL). The aqueous portions were combined, reacidified using 1 mL of 6 M HCl, and dried under reduced pressure. The residues were redissolved in 2 mL of 1 M NaOH and extracted using DCM (3 \times 1 mL). The combined DCM extracts were passed through a plug of anhydrous Na₂SO₄, rinsed once with 0.5 mL of DCM, and derivatized by stirring with 50 mg of Si-TBD and 50 μ L of 0.1 M *S*-TPC for 1 h at room temperature. After that time, 50 mg Si-NH₂ were added to the mixture, and stirred for 30 min at room temperature (see Aponte et al. [2014a] for further details about the derivatization protocol). The slurry was filtered, rinsed with ~3 mL of DCM, dried under flowing nitrogen gas then dissolved in 70 μ L of ethyl acetate prior to GC analyses. A procedural blank (used to quantify the concentration of amines present in the derivatization reagent) and a pyrolyzed serpentine blank (as analogous mineral material to Orgueil) were subjected to the same procedures. We measured the enantiomeric composition of *sec*-butylamine in samples of the CM2 and CR2 carbonaceous chondrites ALH 83100 (parent 63, specific 283, 15.1 g; CM1/2), LON 94101 (parent 6, specific 83, 8.0 g; CM2), LEW 90500 (parent 9, specific 83, 9.4 g; CM2), LAP 02342 (parent 0, specific 45, 411.2 mg; CR2), and GRA 95229 (parent 0, specific 119, 675.1 mg; CR2) provided from the Antarctic meteorite collection at NASA Johnson Space Center, for comparison to that found in Orgueil; the extraction methods used for these samples were identical to those of Orgueil.

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 \times 0.25 mm I.D. \times 0.25 μ m film thickness Chirasil L-Val capillary columns (Agilent) using an oven program set as follows: initial temperature was 40 °C, ramped at 12 °C min⁻¹ to 140 °C, ramped at 2 °C min⁻¹ to 150 °C and held for 4 min, ramped at 2 °C min⁻¹ to 158 °C and held for 15 min, and ramped at 20 °C min⁻¹ to 200 °C with a final hold of 20 min (UHP helium was used as carrier gas at 1.4 mL min⁻¹ 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. 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; $m/z = 165.5$ – 168.5 was used for compounds 1, 2, 4–8, 10, 11, 13–14, 18, and 20–25; while compound 3 was extracted at $m/z = 222.5$ – 225.5 ; $m/z = 234.5$ – 238.5 for compounds 12, 15–16, and 19; $m/z = 98.5$ – 100.5 for compound 9; and $m/z = 112.5$ – 114.5 for compound 17 (Table 1). The $\delta^{13}\text{C}$ values of the eluting compounds were obtained after injection of three pulses of precalibrated CO_2 ($\delta^{13}\text{C} = -24.23\text{‰}$ VPDB) into the IRMS and computation using Thermo Isodat 2.5 software, using previously published methodology (Aponte et al. 2014a).

RESULTS AND DISCUSSION

Molecular Distribution and Abundance of Amines

The organic content in the Orgueil meteorite has been largely depleted, likely due to its extensive degree of aqueous processing (Ehrenfreund et al. 2001; Botta et al. 2002; Glavin and Dworkin 2009; Burton et al. 2014). This is the first time amines have been reported from the Orgueil meteorite; Fig. 1 shows the GC-MS ion chromatogram (Fig. S1 shows a full GC-MS chromatogram) of representative injections from Orgueil, the pyrolyzed serpentine, and a mixture of amine standards. Table 1 presents the concentrations of amines in Orgueil, Murchison, and blank (structures are shown in Figs. 2 and S2). The serpentine blank contained low to moderate concentrations of isopropylamine, methylamine, dimethylamine, *tert*-pentylamine, and *n*-propylamine (1.2, 1.6, 15.1, 1.0, and 3.2 nmol g^{-1} of meteorite, respectively). These values represent potential contamination levels from our extraction and derivatization reagents and protocols. We detected 12 amines in total in the Orgueil sample, including all C1–C3 structural isomers, and chiral C4 (*R*)- and (*S*)-*sec*-butylamine; however, only 10 of those compounds may be indigenous to Orgueil. Those compounds include methylamine, isopropylamine, and *n*-propylamine, which are more abundant in Orgueil than in the serpentine blank; and *tert*-butylamine, ethylamine, ethylmethylamine, (*R*)- and (*S*)-*sec*-butylamine, diethylamine, and *n*-butylamine, which are not present in the serpentine blank. Dimethylamine and

tert-pentylamine may be absent in the meteorite as their abundances are similar to those in the serpentine blank within experimental error.

Similar to Murchison, methylamine and ethylamine were the most abundant amines found in Orgueil, representing 84% and 7% of its total amine content, respectively. For comparison, methylamine and ethylamine constituted 54% and 15%, respectively, of the total amine content in Murchison. Methylamine is highly abundant in Orgueil, with a concentration of 331 nmol g^{-1} , almost four times higher than that observed in Murchison (85 nmol g^{-1}) and about twice the total amine content of Murchison (157 nmol g^{-1}). Orgueil experienced more parent-body aqueous alteration than Murchison, which has been suggested to be highly detrimental to the abundance of meteoritic organic compounds (Ehrenfreund et al. 2001; Glavin and Dworkin 2009; Burton et al. 2014). Further, transition metals such as those present in carbonaceous chondrites can potentially catalyze oxidation reactions through aqueous processes, transforming amines into more polar compounds inside the Orgueil parent body (Murahashi 1995; Soulé et al. 2011; Largeton 2013); therefore, finding higher amounts of methylamine in Orgueil relative to Murchison was an unexpected result.

In contrast to the molecular diversity of amines seen in the Murchison meteorite, Orgueil contained an incomplete suite of structural isomers for C4 and C5 amines. The nondetection of higher molecular weight isomers in Orgueil cannot be explained by the $\sim 10\times$ lower mass extracted (we extracted ~ 1 g of Orgueil, but 13 g of Murchison; Aponte et al. 2014a), and may suggest that either these compounds were present below our limits of detection (0.7 nmol g^{-1} of meteorite), or that indeed those higher molecular weight isomers are not present in Orgueil. Nonetheless, even if higher molecular weight amines were present below our detection limits, Orgueil and Murchison would still show large molecular differences due to the larger relative abundance of methylamine in Orgueil. These differences in abundances and structural diversity may be inherited signatures of the original formation and processes of the different parent bodies of the CI and CM chondrites, or these differences may reflect the effects of the increased aqueous alteration of the CI1 chondrite (Cody and Alexander 2005). Because there are no CI2 chondrites, and there is a very limited amount of available CM1 chondrites for study, it is challenging to assess whether the differences between Orgueil and Murchison reflect primarily parent body differences or they are representative of the more extensive aqueous alteration that occurred in Orgueil.

Gaseous methylamine (-6°C boiling point) trapped inside Orgueil's matrix (either dissolved in water or

Table 1. Concentrations of amines in nmol g⁻¹ of meteorite samples and serpentine blank.

Cmpd Number	Amine	Serpentine Blank ^a	Orgueil (CI1) ^a	Murchison (CM2) ^{a,b}
1	<i>tert</i> -butylamine	< 0.7	1.3 ± 0.2	2.6 ± 0.3
2	Isopropylamine	1.2 ± 0.1	5.1 ± 0.1	7.9 ± 0.6
3	Methylamine	1.6 ± 0.02	331.5 ± 0.5	85.1 ± 7.8
4	Dimethylamine	15.1 ± 2.6	13.0 ± 4.9	2.7 ± 0.4
5	Ethylamine	< 0.7	27.3 ± 2.4	24.1 ± 2.8
6	<i>tert</i> -pentylamine	1.0 ± 0.01	1.1 ± 0.2	1.7 ± 0.2
7	Ethylmethylamine	< 0.7	2.3 ± 0.4	1.5 ± 0.2
8	(<i>R</i>)- <i>sec</i> -butylamine	< 0.7	2.4 ± 0.3	5.3 ± 0.6
9	Diethylamine	< 0.7	3.2 ± 0.4	0.8 ± 0.1
10	(<i>S</i>)- <i>sec</i> -butylamine	< 0.7	2.5 ± 0.3	5.0 ± 0.6
11	<i>n</i> -propylamine	3.2 ± 0.04	4.8 ± 0.04	6.4 ± 0.7
12	(<i>R</i>)-3-methyl-2-butylamine	< 0.7	< 0.7	2.1 ± 0.3
13	Methylpropylamine	< 0.7	< 0.7	1.0 ± 0.2
14	Isobutylamine	< 0.7	< 0.7	1.6 ± 0.2
15	(<i>R</i>)- <i>sec</i> -pentylamine	< 0.7	< 0.7	1.4 ± 0.2
16	(<i>S</i>)-3-methyl-2-butylamine	< 0.7	< 0.7	2.4 ± 0.3
17	Ethylpropylamine	< 0.7	< 0.7	0.2 ± 0.02
18	3-pentylamine	< 0.7	< 0.7	0.9 ± 0.1
19	(<i>S</i>)- <i>sec</i> -pentylamine	< 0.7	< 0.7	1.3 ± 0.3
20	<i>n</i> -butylamine	< 0.7	1.4 ± 0.1	1.1 ± 0.1
21	(<i>R,S</i>)-2-methylbutylamine	< 0.7	< 0.7	0.7 ± 0.1
22	Isopentylamine	< 0.7	< 0.7	0.1 ± 0.01
23	<i>n</i> -pentylamine	< 0.7	< 0.7	0.3 ± 0.02
24	Pyrrolidine	< 0.7	< 0.7	0.5 ± 0.05
25	<i>n</i> -Hexylamine	< 0.7	< 0.7	0.2 ± 0.02
Total abundance		22.0	395.9	156.9

^aCompounds identified by comparison with elution time and mass spectra of standards; values are the average of three measurements; errors shown are standard deviations.

^bData taken from: Aponte et al. (2014a, 2014b).

adsorbed in mineral grains) could have been lost to evaporation either through degassing mechanisms during its residence time on Earth (over 150 yr) or after pulverization of the sample before starting our extraction protocol. Therefore, the methylamine detected in our measurements may have been present inside Orgueil in the form of a stable transition metal chelate, or as an unbound ammonium salt (under appropriate pH conditions). Alternatively, methylamine may have been produced from species containing hydrolyzable methyl moieties in their structures, such as amides, during our extraction protocol. Methylamine is produced from gas-phase and grain surface processes in interstellar molecular clouds (Kaifu et al. 1974; Halfen et al. 2013), and it has been found in comet-exposed material from the Stardust sample return mission to comet Wild 2 (Sandford et al. 2006; Glavin et al. 2008). In addition, the formation of methylamine has been previously observed from shock and spark discharge synthesis studies (Johnson et al. 2008; Parker et al. 2011; Koziol and Goldman 2015), and it has been found in simulated aerosols, which may reflect complex synthetic processes occurring in an organic-rich

atmosphere such as that of Titan (Lavvas et al. 2008; Cable et al. 2014). Thus, methylamine is a ubiquitous species that can be formed from smaller precursors (e.g., CO, NH₃, HCN), or from the decomposition of larger molecules through thermal and ionizing processes (UV or proton irradiation). A thorough discussion of the multiple routes capable of yielding methylamine, however, is beyond the scope of this manuscript. Regardless of the original molecular form and synthesis of methylamine, its high concentration in Orgueil shows that even more than 150 yr after this meteorite was collected, highly volatile organic species may be extractable from its matrix or liberated upon hydrolysis, as was previously observed in amines extracted from Murchison.

It is difficult to invoke selective processes such as aqueous alteration to explain the depletion of more complex amine species relative to methylamine in Orgueil. Therefore, we explain the large abundance of methylamine with three hypotheses that are not mutually exclusive (1) aqueous processes inside Orgueil's parent body and hydrolysis upon meteorite extraction may have resulted in the production of methylamine out

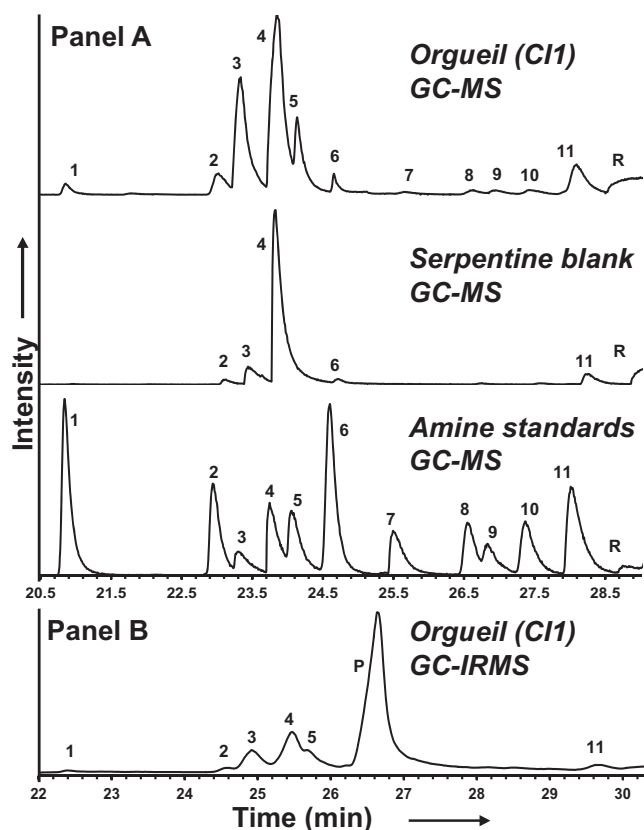


Fig. 1. Panel A shows a positive electron-impact GC-MS chromatogram (extracted at $m/z = 165.5\text{--}168.5$; 20.5–28.8 min region) of *S*-TPC-derivatized acid-vapor hydrolyzed amine extract of Orgueil, *S*-TPC-derivatized acid-vapor-hydrolyzed serpentine blank, and *S*-TPC-derivatized mixture of amine standards. Panel B shows the GC-IRMS chromatogram obtained at $m/z = 44$ ($^{12}\text{CO}_2$ peak) obtained and measured during carbon compound-specific isotope analysis. The identities of the peaks are presented in Table 1 and their structures are shown in Fig. 2. R = reagent contaminant, P = phthalate.

of other organic species (e.g., hydrogen cyanide, methylamides, formaldehyde, complex macromolecules, etc.); (2) Orgueil's CI parent body formed inside a more methylamine-rich region relative to the formation region of Murchison's CM parent body; or (3) the time and environment where the CM parent body accreted may have favored the necessary cosmochemical conditions for the development of longer chain molecules, which may have not been favored at the time and location where the CI parent body formed.

Cometary Origins of Amines

The high water-to-rock ratio, abundance of hydrated minerals (Campins and Swindle 1998; Lodders and Osborne 1999), distinctive oxygen isotopes of the CI1 chondrites (Clayton and Mayeda 1999), and

reconstructed orbit and atmospheric trajectory of Orgueil (Gounelle et al. 2006) have led to the suggestions that their parent body may have been a comet fragment or an extinct cometary nuclei (Campins and Swindle 1998; Lodders and Osborne 1999; Gounelle et al. 2006). This hypothesis is also supported by the similar D/H ratios reported between Orgueil and comet Hartley 2 (103P/Hartley 2; Hartogh et al. 2011). Methylamine and ethylamine have been observed in comet-exposed material from the Stardust sample-return mission to comet Wild 2; the higher abundance of these compounds in comet-exposed material compared to nonexposed samples suggested that they were nonterrestrial in origin (Sandford et al. 2006; Glavin et al. 2008). The relative abundances of methylamine and ethylamine in Orgueil are very different from the abundance of the amines seen in the cometary sample. Glavin et al. (2008) found approximately equal concentrations of methylamine and ethylamine in Stardust comet-exposed aerogel and attributed their presence to the decomposition of submicron particles or gas formed by impact heating during collection. In Orgueil, however, methylamine is 25 times more abundant than ethylamine. These differences in the molecular abundances may be attributed to inherent sample differences; comet-exposed material analyzed from Stardust-sampled volatiles outgassing in the coma, while the Orgueil meteorite samples analyzed a fragment of its parent body. Additionally, the extraction and processing of samples from the Stardust sample were optimized for the analyses of amino acids, which may have affected the efficiency of amine detection (Glavin et al. 2008). Thus, it is not possible from these amine measurements to determine if the Orgueil parent body was a comet with similar amine composition to Wild 2.

Molecular Relationship of Amines and Amino Acids

The amines in this study were detected after extraction and acid-vapor hydrolysis of a fragment from the same Orgueil piece previously used to quantify the abundance of amino acids (Glavin and Dworkin 2009; Glavin et al. 2011); therefore, sample heterogeneity may have only a modest effect on our comparison of amines and amino acids. Amines are structurally related to amino acids, with both compound classes sharing similar aliphatic backbones (Fig. 2). Amino acids, however, contain one or more additional functional groups, which results in a larger number of possible structural isomers relative to amines. In order to investigate the potential synthetic relationships of amines and amino acids in Orgueil, we compared the abundances of the amines with all of their structurally

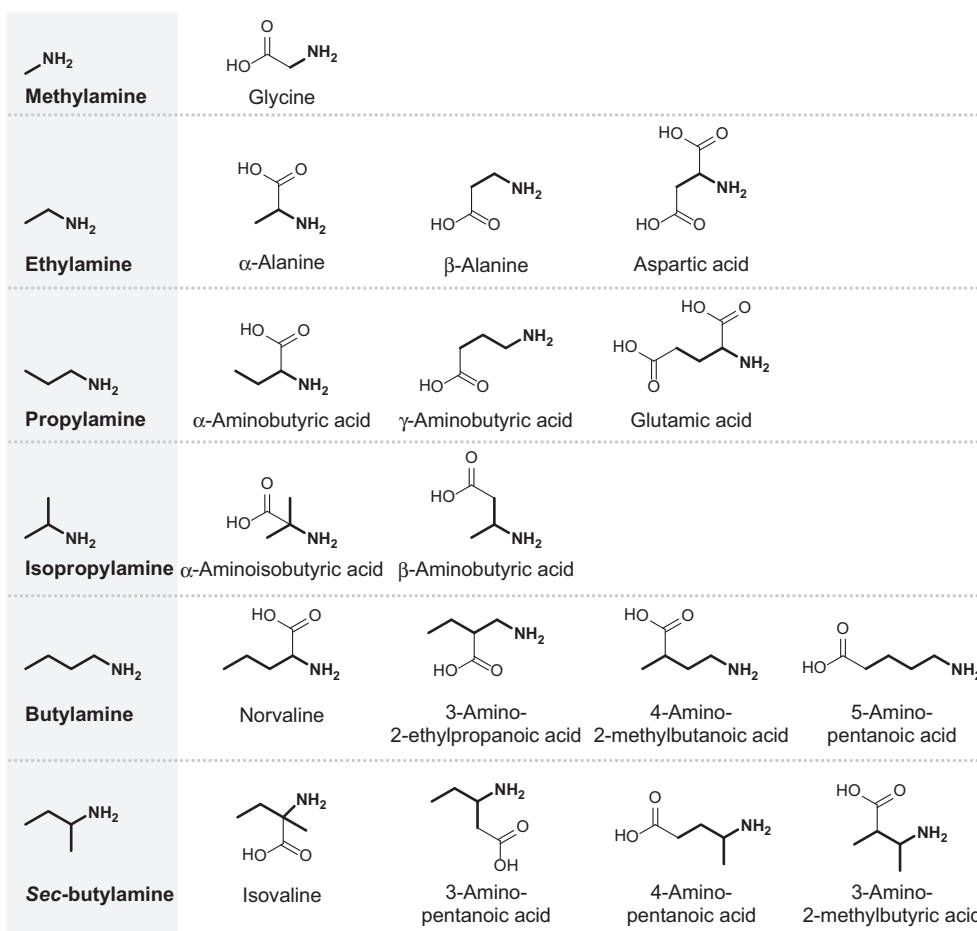


Fig. 2. Structures of amines and amino acids sharing the same aliphatic backbones.

analogous amino acid, and we have compared those results to the amine and amino acid ratios found in Murchison (Table 2, Fig. 3) (Glavin and Dworkin 2009).

Figure 2 shows the molecular structures of amines and amino acids sharing the same aliphatic backbones. Methylamine and glycine share the same aliphatic root, but the amine is 29 times more abundant than the amino acid. Ethylamine is present within similar concentrations to β -alanine, which is the most abundant amino acid in Orgueil (Table 2). Furthermore, the concentration of each of the amines in Orgueil (ethylamine, *n*-propylamine, and *n*-butylamine) is higher than that of their structurally analogous α -H- α -amino acids (R-CH(NH₂)-COOH; α -alanine and aspartic acid; α -aminobutyric acid and glutamic acid; and norvaline, respectively), as shown by the amine to α -H- α -amino acid ratios plotted in Fig. 3A. In addition, the relative abundances of amines compared to their structurally analogous α -H- α -amino acids are lower in Murchison than in Orgueil. In contrast, the ratio of the amine to the other structurally analogous amino acids (β , γ , or δ -

amino acids and α -alkyl- α -amino acids; “non- α -amino acids”) in both Orgueil and Murchison is <1 for four of the five amines for which we have measurements of these types of analogous amino acids and <2 for the fifth (Fig. 3B), and these ratios do not show a clear distinction between the two meteorites. The higher acidity of the α hydrogen atom in the α -H- α -amino acids may cause these compounds to be more sensitive to decomposition and/or synthetic reactions (e.g., decarboxylation and deamination or the reverse) than the less polar amines, β , γ , or δ -amino acids, and α -alkyl- α -amino acids, leading to the lower relative abundances of the α -H- α -amino acids.

Various hypotheses may be proposed to explain the observed abundances of amines and amino acids in Orgueil and Murchison, for example (1) the amine to amino acid ratio may have been originally higher in the CI parent body compared to the CM parent body, (2) amino acid precursors (e.g., carbonyl compounds and cyanide ion) were less abundant in relation to potential amine precursors (e.g., ammonia and alcohols) in Orgueil, (3) amines were used as feedstock to form

Table 2. Concentrations of meteoritic amines and their structurally related amino acids^a in nmol g⁻¹ of meteorite.

Compound	Orgueil (CI1)	Murchison (CM2)
Methylamine	331.5 ± 0.5	85.1 ± 7.7
Glycine	11.5 ± 6.0	26.6 ± 1.6
Ethylamine	27.3 ± 2.4	24.1 ± 2.8
D-alanine	0.9 ± 0.2	7.0 ± 0.1
L-alanine	1.1 ± 0.2	7.4 ± 0.9
β-alanine	30.7 ± 7.6	15.9 ± 1.8
D-aspartic acid	0.5 ± 0.3	1.0 ± 0.1
L-aspartic acid	0.5 ± 0.2	1.1 ± 0.1
<i>n</i> -Propylamine	4.8 ± 0.04	6.4 ± 0.7
D,L-α-aminobutyric acid	0.7 ± 0.5	3.9 ± 1.5
γ-aminobutyric acid	2.7 ± 1.3	14.2 ± 2.1
D-glutamic acid	0.4 ± 0.1	2.9 ± 0.4
L-glutamic acid	0.7 ± 0.2	3.0 ± 0.4
Isopropylamine	5.1 ± 0.1	7.9 ± 0.6
α-aminoisobutyric acid	3.3 ± 1.4	30.9 ± 6.0
D-β-aminobutyric acid	2.1 ± 1.1	2.3 ± 0.2
L-β-aminobutyric acid	1.8 ± 0.6	2.5 ± 0.1
<i>n</i> -Butylamine	1.4 ± 0.1	1.1 ± 0.1
D-norvaline	0.11 ± 0.01	0.15 ± 0.02
L-norvaline	0.12 ± 0.01	0.16 ± 0.02
D,L-3-amino-2-ethylpropanoic acid	1.5 ± 0.1	0.3 ± 0.02
D,L-4-amino-2-methylbutanoic acid	1.5 ± 0.1	0.6 ± 0.07
D,L-5-aminopentanoic acid	1.2 ± 0.2	0.4 ± 0.04
(<i>R</i>)- <i>sec</i> -butylamine	2.4 ± 0.3	5.3 ± 0.6
(<i>S</i>)- <i>sec</i> -butylamine	2.5 ± 0.3	5.0 ± 0.6
D-isovaline	0.3 ± 0.03	8.5 ± 0.4
L-isovaline	0.4 ± 0.02	12.3 ± 0.6
D,L-3-aminopentanoic acid	1.5 ± 0.1	1.3 ± 0.2
D,L-4-aminopentanoic acid	4.4 ± 0.2	0.7 ± 0.1
D,L- and <i>allo</i> -3-amino-2-methylbutyric acid	0.5 ± 0.03	0.2 ± 0.04

^aValues taken from: Glavin and Dworkin (2009).

larger species and this process was inhibited in Orgueil compared to Murchison, (4) the decomposition of larger and more complex organics (e.g., insoluble organic matter; Cody and Alexander 2005) through extended aqueous processes yielded more amines than amino acids, or e) the increased relative destruction of polar amino acids compared to amines was greater in Orgueil because of the higher level of aqueous alteration it experienced compared to Murchison.

In addition, it is also possible that amines in Orgueil originated from the systematic decomposition through decarboxylation of their corresponding amino acids (especially α-H-α-amino acids) inside the parent body. This seems unlikely to account for the high methylamine content, however, as the exclusive synthesis of methylamine through this synthetic route would have required the decomposition of a vast amount of glycine, with a required initial concentration that would have been at least 30 times higher than that currently observed in Orgueil. Furthermore, we have not seen decomposition of glycine to methylamine

during acid-vapor hydrolysis during our workup. Therefore, it is more likely that methylamine was either originally more abundant than glycine inside Orgueil, or that it originated mainly from the hydrolysis and consumption of species other than glycine (e.g., methylamides in grain-size macromolecules) throughout parent body alterations or during our extraction procedure.

Indeed, based on the assumptions that either amines were formed from decarboxylation of amino acids, or amino acids formed through the CO₂ addition to amines, a measurable correlation in their corresponding abundances would be expected; however, except for methylamine, the abundances of amines and amino acids in Orgueil and Murchison seem to lack a clear relationship. The absence of a direct relationship between the abundances of meteoritic amines and amino acids may suggest that aqueous processes inside the parent body may favor the decomposition of amino acids through deamination over decarboxylation. The spontaneous deamination of amines should be more

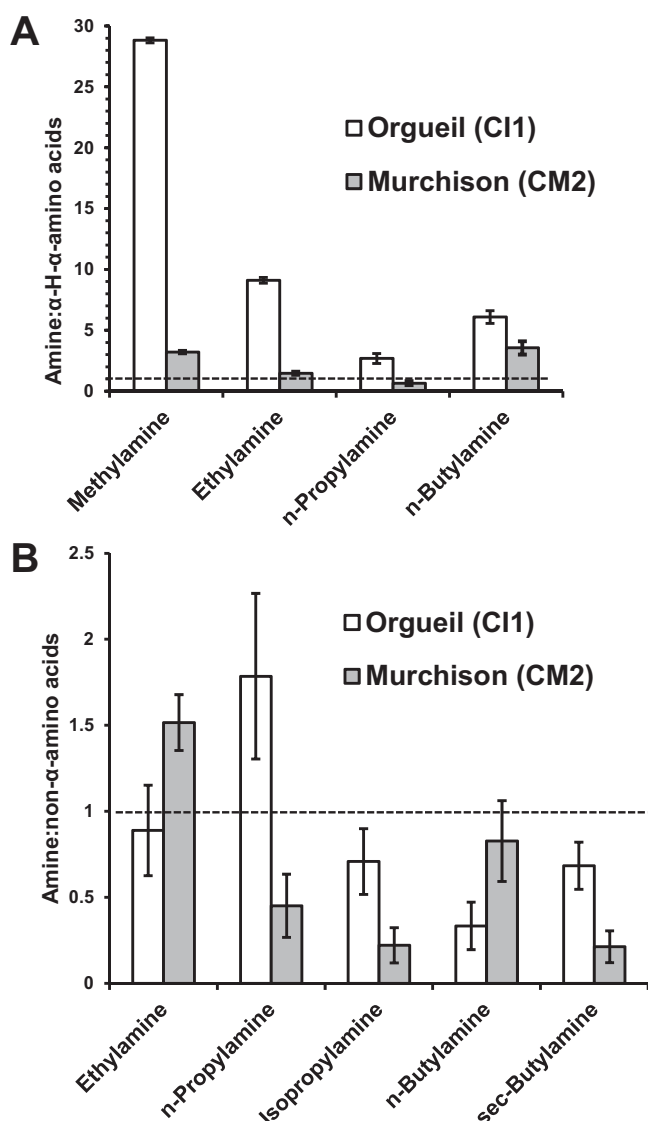


Fig. 3. Relative abundances of amines and amino acids from Orgueil and Murchison. A) Ratio of amine abundance to structurally analogous α -H- α -amino acids abundance. B) Ratio of amine abundance to β , γ , and δ -amino acids and α -alkyl-amino acids (non- α -amino acids) abundance. Abundances taken from Table 2. A dashed line is shown for a ratio of 1:1.

favorable than decarboxylation (Alexandrova and Jorgensen 2011); thus, it would be expected that amino acid decarboxylation may not significantly contribute to the production of amines in meteorites. It remains to be seen, however, if the presence of other inorganic and organic species in chondrites could affect the relative likelihood of deamination and decarboxylation reactions.

One important similarity in the molecular distribution of meteoritic amines and amino acids in Orgueil and Murchison is their general decrease in molecular abundance with increasing molecular weight.

This trend has also been observed for monocarboxylic acids in Murchison and other meteorites (Table 2; Yuen and Kvenvolden 1973; Huang et al. 2005; Aponte et al. 2011), and may suggest a common synthetic mechanism for aliphatic chains in these meteoritic organic compounds.

$\delta^{13}\text{C}$ Compound-Specific Isotopic Analyses of Amines in Orgueil

Amino acid contamination from landing sites and infiltration of microbiota (fungi or bacteria) are the most likely and unavoidable sources of terrestrial contamination in carbonaceous chondrites (Bada et al. 1998; Toporski and Steele 2007; Elsila et al. 2011). Although Orgueil was a recovered “fresh fall,” meaning it had a short period of time in contact with its landing site, this meteorite has been exposed to Earth’s biosphere for over 150 yr, and evidence of at least some terrestrial contamination during storage and handling has been reported (Anders et al. 1964; Nagy 1975; Sephton et al. 2001; Watson et al. 2003). Most extraterrestrial organic compounds show distinctive stable isotopic compositions (D/H , $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$) that are enriched in the heavier isotopes relative to terrestrial sources. Therefore, compound-specific isotopic analyses are particularly useful to characterize the origin of meteoritic organics as extraterrestrial and to provide information about their prebiotic synthetic mechanisms (Engel et al. 1990; Pizzarello et al. 1994, 2004; Elsila et al. 2011, 2012).

Amines appear to be ubiquitous in marine environments (Van Neste et al. 1987; Wang and Lee 1990); however, to the best of our knowledge, no compound-specific carbon isotopic analyses have been reported from terrestrial sources of these molecules. Out of the 12 amines found in Orgueil, there were sufficient abundances to measure the $\delta^{13}\text{C}$ compositions of 5 of them (Table 3). Relative to the $\delta^{13}\text{C}$ values found in the serpentine blank, the amines found in Orgueil showed an overall ^{13}C -enrichment, which suggests these molecules are not the result of terrestrial contamination and instead may have formed in cold interstellar environments (Sandford et al. 2001; Robert 2003). As previously mentioned, the derivatization reagent used in our experiments was contaminated with trace amounts of amines; therefore, the $\delta^{13}\text{C}$ values presented here should be considered as a lower limit for extraterrestrial amines in Orgueil. The $\delta^{13}\text{C}$ isotopic measurements of dimethylamine and *n*-propylamine were likely the most affected given their low abundance in Orgueil; even with trace contamination, isopropylamine and methylamine were substantially ^{13}C -enriched relative to terrestrial nitrogen-containing organics (e.g., amino

acids and anilines; Scott et al. 2006; Larsen et al. 2009; Elsila et al. 2011; Skarpeli-Liati et al. 2011) which supports their interstellar origin. In contrast, ethylamine was not observed in our blanks; however, this compound partially coeluted with dimethylamine, which may have a large effect on the isotopic value we report here.

In addition to the contrasting molecular distributions of amines in Orgueil and Murchison, we observed that the amines in Orgueil were depleted in ^{13}C relative to the amines found in Murchison. The isotopic analyses of the amines found in Murchison showed an inverse relationship between increasing aliphatic chain length and $\delta^{13}\text{C}$ ratios, which we attributed to a chain-elongation mechanism in which larger compounds form out of more reactive ^{12}C -rich smaller molecules (Yuen et al. 1984; Sephton and Gilmour 2001). The lower molecular diversity of Orgueil makes it difficult to assess whether the same relationship holds true in this meteorite; however, judging from the similar within-error $\delta^{13}\text{C}$ values for methylamine and ethylamine, it appears that the chain-elongation mechanism observed in Murchison may not have been in place for the synthesis of these amines in Orgueil (Table 3). However, the absence of a correlation between increasing carbon number and the $\delta^{13}\text{C}$ ratios of amines is consistent with observations of other organic compounds such as alkanes and aromatic molecules released by the pyrolysis of macromolecular materials from Orgueil (Sephton and Gilmour 2001).

The molecular and isotopic differences in organic compounds in Orgueil and Murchison have been previously explained by two not mutually exclusive arguments (1) the different cosmochemical environments where the CI and CM parent bodies originally accreted and (2) the larger degrees of aqueous alteration experienced by Orgueil (Ehrenfreund et al. 2001). The cosmochemical conditions at the time and place of the parent body accretion remain unknown; however, the $\delta^{13}\text{C}$ isotopic data found for amines could support either of these two hypotheses and provide further clues about the primordial synthetic origins of meteoritic organics. Amines inside Orgueil's parent body could have formed in a ^{13}C -depleted environment relative to the cosmochemical environment where amines inside Murchison's parent body formed, or the amines in Orgueil could have formed out of different carbon pools than that of amines in Murchison. Amines may be formed from reductive amination of carbonyl compounds (including carbon monoxide for methylamine), or from hydrogenation of nitriles and imines; moreover, amines may be produced from the hydrolysis of amides, and from the addition of ammonia to alkenes, carboxylic acids and alcohols in

Table 3. $\delta^{13}\text{C}$ values (‰VPDB) of meteoritic amines and their structurally related amino acids in the samples.

Compound	Serpentine Blank ^a	Orgueil (CI1) ^a	Murchison (CM2)
Methylamine	-39 ± 23	43 ± 10^b	129 ± 7^c
Glycine	—	22^d	13 ± 3^f
Ethylamine	n.d.	$59 \pm 10^{b,c}$	80 ± 2^e
D-alanine	—	n.a.	38 ± 10^f
L-alanine	—	n.a.	40 ± 9^f
β -alanine	—	18^d	10 ± 6^f
n-propylamine	-31 ± 4	-20 ± 5^b	40 ± 1^e
Isopropylamine	-17 ± 7	10 ± 3^b	42 ± 1^e
Dimethylamine	-48 ± 6	-6 ± 10^b	$23 \pm 5^{b,e}$

n.a. = not available in the literature; n.d. = compound was not detected in the sample.

^aValues are the average of three measurements; errors shown are standard deviations.

^bIncludes contribution from the derivatization reagent (see Table 1).

^cThis compound partially coelutes with dimethylamine.

^dValues taken from: Ehrenfreund et al. (2001).

^eValues taken from: Aponte et al. (2014a).

^fValues taken from: Elsila et al. (2012).

acid media, and transition metal catalysts (Tielens and Hagen 1982; Charnley et al. 2004; Theule et al. 2011; Elsila et al. 2012). None of these reactions should change the carbon isotopic ratios between precursors and the resulting amines, because there are no modifications to carbon-carbon bonds. If these reactions happened through the aqueous processes inside Orgueil's parent body, resulting in a higher abundance of ^{13}C -depleted amines relative to those in Murchison, then the lighter $\delta^{13}\text{C}$ values of the amines in Orgueil would suggest that the molecular precursors of amines were also originally ^{13}C -depleted. Future isotopic analyses of potential amine precursors from Orgueil and other carbonaceous chondrites are needed to understand the abiotic origins of amines.

$\delta^{13}\text{C}$ Isotopic Analyses of Amines in Relation to Amino Acids

Our isotopic data can be used to explore the synthetic relationship between meteoritic amines and amino acids. The only $\delta^{13}\text{C}$ isotopic values known for amino acids in Orgueil correspond to glycine and β -alanine (+22‰ and +18‰, respectively; Ehrenfreund et al. 2001), which are analogs of methylamine (+43‰) and ethylamine (+59‰; Table 3), respectively. Terrestrial contamination cannot explain the large isotopic difference (>21‰) between meteoritic amines and amino acids in Orgueil; therefore, we should consider other fractionation processes.

Chemical processes resulting in the interconversion of amines and amino acids would affect their observed isotopic values. Amino acids can be formed from the addition of carbon dioxide (CO_2) or hydrogen cyanide (HCN ; the cyanide or nitrile moiety turns into a carboxylic acid moiety upon aqueous hydrolysis) to an amine; inversely, amines may result from decarboxylation of amino acids or from the loss of a nitrile ion (CN^-) from amino nitriles (Pizzarello 2002; Pizzarello et al. 2006; Hudson et al. 2009; Aponte et al. 2014a). Amino acids are ^{13}C -depleted relative to amines in Orgueil and Murchison (Table 3), suggesting either (1) that at some point during the formation of amino acids, a ^{12}C -rich source that was not incorporated in the amines aliphatic chain was added to the amino acid aliphatic chain, or (2) that the amine precursor, either an amino acid or amino nitrile, lost a ^{12}C -rich moiety ($^{12}\text{CO}_2$ or $^{12}\text{CN}^-$, respectively).

The $\delta^{13}\text{C}$ values for CO_2 and HCN created before accretion of the parent body are unknown; however, the $\delta^{13}\text{C}$ values for CO_2 ($+29.1 \pm 0.2$ ‰; Yuen et al. 1984) and HCN ($+5.3 \pm 2.3$ ‰; Pizzarello 2014) have been reported from Murchison. These isotopic values constrain the synthetic relationship between amines and amino acids found in Murchison, and may also potentially apply for methylamine, ethylamine, glycine, and β -alanine in Orgueil (*n*-propylamine, isopropylamine, and dimethylamine were partially contaminated from the derivatization reagent and their $\delta^{13}\text{C}$ values in Orgueil fall below those $\delta^{13}\text{C}$ meteoritic values of CO_2 and HCN , while the $\delta^{13}\text{C}$ values for D,L- α -alanine in Orgueil remain unknown). Considering the meteoritic $\delta^{13}\text{C}$ values of CO_2 and HCN in Murchison, the addition of CO_2 or HCN to an amino acid precursor (e.g., amines and other compounds such as carbonyl compounds and imines), or the loss of CO_2 or CN^- from an amino acid to form an amine inside the parent body, would result in ^{13}C -depleted amino acid products relative to their precursor molecules. Therefore, these synthetic mechanisms are in agreement with either of the amine/amino acid parent–daughter relationships described above.

Nonetheless, it is also possible that meteoritic amines and amino acids are not related through the chemical processes described above, but rather formed from distinctive precursors such as carbonyl compounds, imines, and nitriles. Unfortunately, without carbon isotopic data on these various potential precursor molecules, it is impossible to attribute the isotopic differences between amines and amino acids to different precursor pools. Isotopic studies of other meteoritic molecules, and observations of the isotopic values of interstellar CO_2 or HCN , will further aid the understanding of the origins of these and other meteoritic organic compounds.

Enantiomeric Analyses of *sec*-Butylamine

We measured the abundances of the enantiomers (*R*)- and (*S*)-*sec*-butylamine. This is the first time that the enantiomeric composition of chiral compounds other than amino acids has been investigated in Orgueil. Figure 4 presents the gas chromatogram of (*R*)- and (*S*)-*sec*-butylamine (compounds 8 and 10) monitored at $m/z = 165.5$ – 168.5 and the mass spectra of these peaks in Orgueil and standards. The low abundance of (*R*)- and (*S*)-*sec*-butylamine is reflected in the higher signal-to-noise ratio and in the mass spectral fragmentation patterns. In addition, trace amounts of an unknown phthalate become clear at $m/z = 149$ (Fig. 4); this phthalate, however, is present throughout the mass chromatogram and does not have a quantitative impact on the determination of the abundance nor the enantiomeric composition of the amines in Orgueil.

The amino acid literature uses D- and L-notations based on analogy with glyceraldehyde; (*R*)-*sec*-butylamine is structurally analogous to L-isovaline, and similarly (*S*)-*sec*-butylamine to D-isovaline. We wanted to investigate if the process that resulted in the L-*ee* reported for isovaline had similar effects on left-handed (*S*)-*sec*-butylamine. Table 4 presents the enantiomeric composition (*R/S* enantiomeric ratios and S_{ee}) of (*R*)- and (*S*)-*sec*-butylamine extracted from Orgueil and from Murchison; for comparison, we also present the enantiomeric composition previously reported for the structurally analogous amino acids D- and L-isovaline (Glavin and Dworkin 2009; Glavin et al. 2011; Aponte et al. 2014a). In contrast to the enantiomeric excess reported for L-isovaline extracted from Orgueil (Glavin and Dworkin 2009), we found (*R*)- and (*S*)-*sec*-butylamine as a racemic mixture within experimental errors in our experiments (Table 4). Our relatively large experimental uncertainties result from the low abundances of *sec*-butylamine in Orgueil, the low number of replicates ($n = 3$), and the low sensitivity of GC-MS measurements relative to other chromatographic methods such as the ultrahigh performance liquid chromatography coupled to fluorescence detection and time-of-flight mass spectrometry used to quantify enantiomeric excesses in isovaline (Glavin and Dworkin 2009). The racemic composition of these amines is consistent with the racemic composition of (*R*)- and (*S*)-*sec*-butylamine and aliphatic monocarboxylic acids found in Murchison (Aponte et al. 2014a, 2014b). Furthermore, motivated by the contrasting racemic nature of *sec*-butylamine and the large enantiomeric excesses found for L-isovaline in Orgueil and Murchison, we explored the enantiomeric composition of *sec*-butylamine in the CM2 and CR2 carbonaceous chondrites ALH 83100 (CM1/2), LON

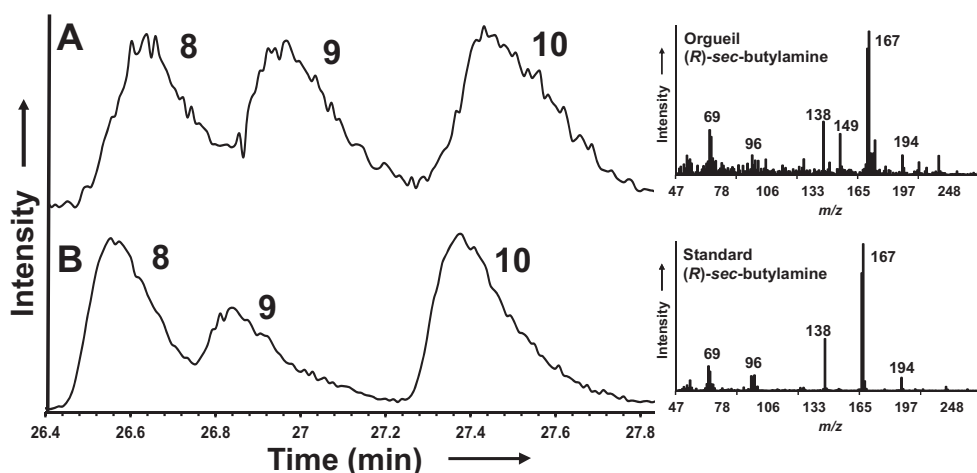


Fig. 4. Partial electron-impact GC-MS chromatogram of *S*-TPC-derivatized (*R*- and (*S*)-*sec*-butylamine (compounds 8 and 10, respectively; 26.4–27.9 min region) extracted at $m/z = 165.5$ – 168.5 . A) Acid-vapor-hydrolyzed extract of Orgueil, B) racemic standards. Insets show the simultaneously collected mass spectra for peak 8 and (*R*)-*sec*-butylamine standard; the $m/z = 149$ peak corresponds to a common plasticizer (phthalate) that is ubiquitously present throughout the chromatograph and which characteristic m/z ratio becomes more apparent as the amount of analyte (amine) is lower.

Table 4. Enantiomeric compositions of *sec*-butylamine (*R*/*S* and S_{ee}) and isovaline (*D*/*L* and L_{ee}) extracted from Orgueil and Murchison carbonaceous chondrites.

Meteorite	<i>Sec</i> -butylamine ^a		Isovaline ^b	
	(<i>R</i> / <i>S</i>)	S_{ee} (%)	(<i>D</i> / <i>L</i>)	L_{ee} (%)
Orgueil (CI1)	0.95 ± 0.06	3.4 ± 2.2	0.73 ± 0.07	15.2 ± 4.0
Murchison (CM2)	1.00 ± 0.01	1.0 ± 2.2	0.61 ± 0.09	17.2 ± 6.7
ALH 83100 (CM1/2)	0.99 ± 0.02	1.0 ± 1.5	n.a.	n.a.
LON 94101 (CM2) ^c	0.99 ± 0.02	1.0 ± 1.4	0.95 ± 0.08	2.4 ± 4.1
LEW 90500 (CM2)	0.98 ± 0.03	1.4 ± 4.4	0.94 ± 0.03	3.3 ± 1.8
LAP 02342 (CR2)	0.99 ± 0.01	0.8 ± 2.3	n.a.	n.a.
GRA 95229 (CR2)	1.00 ± 0.01	1.0 ± 2.8	n.a.	n.a.

n.a.: Not available in the literature.

^aEnantiomeric ratios, enantiomeric excess (ee), and standard deviations are based on three separate measurements from single ion gas chromatograms extracted at $m/z = 165.5$ – 168.5 for *sec*-butylamine. Ratios and S_{ee} have been corrected against injections of racemic standards to account for instrument response. The enantiomeric excesses of (*S*)-*sec*-butylamine were propagated through the equation: S_{ee} (%) = $([S] - [R]) / ([S] + [R]) \times 100$.

^bValues taken from: Glavin and Dworkin 2009; and Glavin et al. 2011.

^cLON 94101 is paired with LON 94102 (Glavin et al. 2011).

94101 (CM2), LEW 90500 (CM2), LAP 02342 (CR2), and GRA 95229 (CR2), finding that *sec*-butylamine is also present as a racemic mixture in these meteorites (Table 4; more detailed analysis of the amine content of the CR2 and CM2 meteorites will be forthcoming in a manuscript currently in preparation).

The synthetic relationships between *sec*-butylamine and isovaline have been previously discussed (Aponte et al. 2014a). Although (*R*)- and (*S*)-*sec*-butylamine are approximately half as abundant in Orgueil as in Murchison, in both meteorites, these compounds are the most abundant of the C4 amine constitutional isomers (Table 1). Similarly, isovaline is more abundant than its structural C5 α -amino isomers valine and norvaline

inside Orgueil and Murchison (Glavin and Dworkin 2009). These similarities in relative molecular abundances of meteoritic *sec*-butylamine and isovaline suggest a possible connection in the formation of their structural aliphatic backbones. However, without being able to compare the ^{13}C isotopic composition of (*R*)- and (*S*)-*sec*-butylamine extracted from Orgueil to those present in Murchison, it is difficult to determine if they were originally synthesized from a common carbon pool and if the amines derive from the amino acids or vice versa.

The low acidity of both the α -methyl group of isovaline (Pollock et al. 1975) and the α -hydrogen present in *sec*-butylamine ($\text{p}K_a = 40$; Bordwell et al.

1981) make these compounds highly resistant to racemization. Therefore, as the racemization rate on the parent body would be expected to be low, any large enantiomeric excesses in (*R*)- or (*S*)-*sec*-butylamine that occurred before their incorporation into the parent body should have been preserved and been observable in our sample. Our detection of racemic *sec*-butylamine suggests that there was no such large enantiomeric excess prior to accretion. However, it is possible that a small enantiomeric excess (within our experimental error) could have been induced into *sec*-butylamine or other amino acid precursors (carbonyl compounds, amino nitriles, imines, etc.) or even to the amino acids themselves through either destructive or synthetic physical processes such as ultraviolet circularly polarized light before the accretion of the parent body (Takano et al. 2007; De Marcellus et al. 2011; Meinert et al. 2014; Modica et al. 2014). This small excess could have then been amplified on the parent body to the larger observed isovaline excess (Pizzarello and Cronin 2000). Such amplification could occur preferentially in amino acids compared to amines because of their most basic molecular difference; that is, although *sec*-butylamine and isovaline share identical aliphatic chains, the α -carboxylic acid group present on the amino acid, which is replaced with an α -H on the amine, substantially increases the polarity and water solubility of amino acids. It is possible that higher polarity and water solubility aided as-yet-unknown processes or autocatalytic reactions that amplified an original but small amino acid asymmetry (Soai et al. 1995; Blackmond 2004; Pizzarello and Weber 2004), especially inside water-rich meteorites such as Orgueil. Future studies aimed at observing small enantiomeric excesses in *sec*-butylamine and those evaluating potential amplification mechanisms inside the parent body may provide further clues on the primordial synthesis and development of these prebiotic compounds.

CONCLUSION

We investigated the origins of the amines in Orgueil based on their molecular, isotopic, and enantiomeric compositions and in relation to the amines and amino acids found in the less aqueously altered Murchison meteorite. In contrast to the high molecular diversity found in Murchison, amines in Orgueil showed a high abundance of methylamine and an incomplete structural diversity for C4 and C5 isomers, suggesting that (1) aqueous processes inside Orgueil resulted in the production of larger amounts of methylamine relative to other amine species, (2) Orgueil's parent body formed in a methylamine-rich region, or (3) the environment

where the CM parent body accreted favored the formation of longer chain amines. In addition, amines in Orgueil were found in higher concentrations than the sum of their α -H- α -amino acid structural analogs, which may have resulted from their lower water solubility and higher stability to aqueous processes inside Orgueil's parent body. The $\delta^{13}\text{C}$ values for amines in Orgueil fell into the range expected for compounds formed in cold interstellar environments, but were ^{13}C -depleted relative to those found in Murchison. In both Orgueil and Murchison, amines were enriched in ^{13}C compared to their amino acid structural analogs. These isotopic dissimilarities between amines in Orgueil and Murchison suggest that chain elongation under kinetic control was not the main synthetic mechanism for the formation of amines in Orgueil and that the precursors of amines inside Orgueil (nitriles, carbonyl compounds, imines, etc.) should also be ^{13}C -depleted compared to those in Murchison. The isotopic contrast between amines and amino acids in these two meteorites may be a reflection of the different chemical compositions of the environments where their parent bodies were originally accreted, and of the chemical processes which may have resulted in the isotopic fractionation of amines in Orgueil. However, it is also possible that amines and amino acids formed out of different carbon pools, and without the isotopic data for the full suite of amines and amino acids it is challenging to assess their parent-daughter synthetic relationships. Finally, the racemic composition of (*R*)- and (*S*)-*sec*-butylamine contrasts with the enantiomeric enrichment of L-isovaline observed in Orgueil; however, the lower polarity and solubility of amines may explain their lack of enantiomeric excess and suggest the abiotic enantiomeric enrichment of amino acids resulted from their higher susceptibility to aqueous processes. Additional future analyses of the molecular, isotopic, and enantiomeric composition of meteoritic amines and their structural analogs in carbonaceous chondrites will aid the understanding of the abiotic formation of organic compounds.

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SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article:

Fig S1: Positive electron impact GC-MS chromatogram (extracted at $m/z = 46$ – 320 ; 20 – 44 min region) of *S*-TPC-derivatized acid-vapor hydrolyzed amine extract of Orgueil, *S*-TPC-derivatized acid-vapor-hydrolyzed serpentine blank, and *S*-TPC-derivatized mixture of amine standards. Peak identifications: 1, *tert*-butylamine; 2, isopropylamine; 3, methylamine; 4, dimethylamine; 5, ethylamine; 6, *tert*-pentylamine; 7,

ethylmethylamine; 8, (*R*)-*sec*-butylamine; 9, diethylamine; 10, (*S*)-*sec*-butylamine; 11, *n*-propylamine; 12, (*R*)-3-methyl-2-butylamine; 13, methylpropylamine; 14, isobutylamine; 15, (*R*)-*sec*-pentylamine; 16, (*S*)-3-methyl-2-butylamine; 17, ethylpropylamine; 18, 3-pentylamine; 19, (*S*)-*sec*-pentylamine; 20, *n*-butylamine; 21, (*R,S*)-2-methylbutylamine; 22, isopentylamine; 23, *n*-pentylamine; 24, pyrrolidine; 25, *n*-hexylamine; P: phthalate; R: reagent contaminant (*S*-TPC acid); U: unknown compound; S: molecular sulfur.

Fig S2: Structures of aliphatic amines listed in Table 1.
