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Aliphatic amines in Antarctic CR2, CM2, and CM1/2 carbonaceous chondrites

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Abstract

Meteoritic water-soluble organic compounds provide a unique record of the processes that occurred during the formation of the solar system and the chemistry preceding the origins of life on Earth. We have investigated the molecular distribution, compound-specific δ^{13}C isotopic ratios and enantiomeric compositions of aliphatic monoamines present in the hot acid–water extracts of the carbonaceous chondrites LAP 02342 (CR2), GRA 95229 (CR2), LON 94101 (CM2), LEW 90500 (CM2), and ALH 83100 (CM1/2). Analyses of the concentration of monoamines in these meteorites revealed: (a) the CR2 chondrites studied here contain higher concentrations of monoamines relative to the analyzed CM2 chondrites; (b) the concentration of monoamines decreases with increasing carbon number; and (c) isopropylamine is the most abundant monoamine in these CR2 chondrites, while methylamine is the most abundant amine species in these CM2 and CM1/2 chondrites. The δ^{13}C values of monoamines in CR2 chondrite do not correlate with the number of carbon atoms; however, in CM2 and CM1/2 chondrites, the ^{13}C enrichment decreases with increasing monoamine carbon number. The δ^{13}C values of methylamine in CR2 chondrites ranged from −1 to +10‰, while in CM2 and CM1/2 chondrites the δ^{13}C values of methylamine ranged from +41 to +59‰. We also observed racemic compositions of *sec*-butylamine, 3-methyl-2-butylamine, and *sec*-pentylamine in the studied carbonaceous chondrites. Additionally, we compared the abundance and δ^{13}C isotopic composition of monoamines to those of their structurally related amino acids. We found that monoamines are less abundant than amino acids in CR2 chondrites, with the opposite being true in CM2 and CM1/2 chondrites. We used these collective data to evaluate different primordial synthetic pathways for monoamines in carbonaceous chondrites and to understand the potential common origins these molecules may share with meteoritic amino acids.

Keywords: Meteoritic amines; Aliphatic amines; Carbonaceous chondrites; Antarctic meteorites; Astrochemistry; Astrobiology

1. INTRODUCTION

The study of the organic compounds from carbonaceous chondrites provides valuable insights into the available chemical inventory at the birth of the solar system, the subsequent processing that occurred inside asteroid parent bodies, and the organic chemistry preceding the origins of life on Earth (Oró, 1961; Anders, 1989; Pizzarello et al., 2006). Carbonaceous chondrites are thought to originate from water-rich asteroids and can contain up to 5 wt.% organic carbon (Wetherill and Chapman, 1988). Among the eight groups of carbonaceous chondrites (Sears and Dodd, 1988), the moderately aqueously altered CR (Renazzo-like) and CM (Mighei-like) type 2 meteorites contain the most abundant and diverse suites of water-soluble organic compounds (Cronin and Moore, 1971; Pizzarello

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and Cronin, 2000; Glavin et al., 2006, 2011; Martins et al., 2007; Pizzarello et al., 2008; Callahan et al., 2011).

Meteoritic amino acids have been extensively studied (see reviews and references therein: Cronin and Chang, 1993; Botta et al., 2002; Burton et al., 2012; Cobb and Pudritz, 2014; Elsila et al., 2016). Isotopic ratios, structural diversity, and enantiomeric compositions provide information about the formation mechanisms of extraterrestrial organic compounds (Epstein et al., 1987; Engel and Macko, 1997; Pizzarello and Cronin, 2000; Elsila et al., 2012). Amino acids in CR2 and CM2 carbonaceous chondrites are typically enriched in D, ^{13}C, and ^{15}N (Martins et al., 2007; Elsila et al., 2012), relative to their terrestrial counterparts, suggesting that the formation of these compounds or their precursor molecules occurred in cold interstellar environments (Sandford et al., 2001; Robert, 2003). The α-H-α-amino acids are the most abundant amino acid species in CR2, CM2, and CM1/2 chondrites (Cronin and Pizzarello, 1983; Martins et al., 2007; Pizzarello et al., 2008; Glavin and Dworkin, 2009; Pizzarello and Holmes, 2009; Glavin et al., 2011). The enantiomeric composition of abiotically produced amino acids is racemic, in contrast to the homochirality (almost exclusively L-enantiomers) found in biological systems on Earth. A few meteoritic amino acids, most notably isovaline, have been found to exhibit an L-enantiomeric excess (L-*ee*; Cronin and Pizzarello, 1997; Pizzarello et al., 2003; Glavin et al., 2011; Burton et al., 2013). Isovaline is an α-methyl-α-amino acid that is not abundant in Earth's biosphere and is not prone to rapid racemization under aqueous conditions (Pollock et al., 1975). It has been proposed that the development of homochirality on Earth may have occurred not as a random process but instead as a consequence of the delivery of L-enantioenriched amino acids to the early Earth (Engel and Macko, 1997; Cronin and Pizzarello, 1997; Pizzarello et al., 2003; Glavin and Dworkin, 2009).

Aliphatic monoamines (hereafter called "amines") are organic compounds that share analogous structural backbones with amino acids; however, amines in carbonaceous chondrites have been far less studied than amino acids. Extraterrestrial methylamine and ethylamine were detected in samples collected from the coma of comet Wild 2 from the Stardust sample return mission (Sandford et al., 2006; Glavin et al., 2008), and more recently from the surface of comet 67P/Churyumov-Gerasimenko (Goesmann et al., 2015). Additionally, the abundances of various amines extracted from the CM2 Murchison meteorite and from eight Antarctic CR2 meteorites have been reported (Jungclaus et al., 1976; Pizzarello et al., 1994, 2012; Pizzarello and Holmes, 2009; Pizzarello and Yarnes, 2016). Most of these amine detections, however, lacked isotopic and enantiomeric measurements, leaving an important gap in the understanding of the formation of meteoritic organics and the alterations these compounds may have experienced inside the parent body. Recently, we reported the compound-specific δ^{13}C isotopic composition of amines in the Murchison meteorite and linked the origins of amines and amino acids to the same primordial carbon pool (Aponte et al., 2014a). The comparison of the isotopic ratios of meteoritic amines and amino acids in carbonaceous chondrites of different classes may provide important insights into the primordial origins of complex organic matter in space and to the chemical processing that happened inside the parent body (Aponte et al., 2015). Additionally, the enantiomeric compositions of chiral amines may constrain the origins of enantiomeric excesses in meteoritic amino acids, an important unanswered question for the emergence and development of Earth's homochiral life.

In this report, we investigated the molecular, isotopic, and enantiomeric compositions of amines in the Antarctic carbonaceous chondrites La Paz Icefield (LAP) 02342 (CR2), Graves Nunataks (GRA) 95229 (CR2), Lonewolf Nunataks (LON) 94101 (CM2), Lewis Cliffs (LEW) 90500 (CM2), and Allan Hills (ALH) 83100 (CM1/2), using gas chromatography coupled with mass spectrometry and isotope-ratio mass spectrometry (GC–MS/IRMS). The δ^{13}C isotopic ratios of amines in these meteorites have not been previously reported; the enantiomeric composition of *sec*-butylamine has been previously reported but not discussed in depth (Aponte et al., 2015). Additionally, we analyzed the amino acid abundances and δ^{13}C isotopic ratios in LON 94101, LEW 90500, and ALH 83100 from the same sample used for amine analysis, to directly compare the data on amines and amino acids while minimizing effects of potential sample heterogeneity. Our results provide information on the prebiotic synthesis of amines and amino acids and on the origins of homochirality on Earth.

2. MATERIALS AND METHODS

2.1. Materials

Standards and reagents were purchased from Alfa Aesar or Sigma–Aldrich and used without further purification except as noted below. All glassware and sample handling tools used for the meteorite samples were rinsed with Millipore Direct Q3 UV water (18.2 MΩ, 3 ppb total organic carbon; hereafter referred to as "water") wrapped in aluminum foil, and then heated in a muffle furnace at 500 °C overnight. We used HPLC grade dichloromethane (DCM), semi-conductor grade NaOH, and 6 M HCl (doubly distilled). Silica gels were bought from SiliCycle (Silia*Bond*®, 40–63 μm particle size) and cleaned using methanol and DCM followed by drying under vacuum. (*S*)-(–)-*N*-(trifluoroacetyl)pyrrolidine-2-carbonyl chloride (*S*-TPC, 97% *ee*) was purchased from Sigma Aldrich. Details of the sources of specific five carbon (C_5) amino acids used as standards are available elsewhere (Glavin and Dworkin, 2009).

2.2. Meteorite samples and extraction procedure

Analyses of meteoritic amines were preformed according to previously published methods (Aponte et al., 2014a, 2015). Meteorite samples, obtained from interior chips that did not contain any visual evidence of fusion crust, were provided from the Antarctic meteorite collection at the NASA Johnson Space Center. All meteorites were individually crushed into fine powders and homogenized using a porcelain mortar