Low total abundances and a predominance of *n*-ω-amino acids in enstatite chondrites: Implications for thermal stability of amino acids in the inner solar system

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Abstract–Investigating the organic contents of enstatite chondrite meteorites may offer insights into both early inner solar system and early Earth chemistry. Enstatite chondrite meteorites have highly reduced and anhydrous compositions, and their bulk isotopic compositions closely resemble terrestrial values, suggesting that their parent body asteroids accreted within the inner protoplanetary disk and were a primary contributor during Earth's late accretion (Javoy, 1995; Piani et al., 2020). Here, we present the first report of amino acids in enstatite chondrite meteorite samples. Three EH3 meteorites were analyzed (Dominion Range [DOM] 14021, Larkman Nunatak [LAR] 12001, and Larkman Nunatak 06252). The acid-hydrolyzed water extracts of the meteorites contained low abundances (1.5–215.9 pmol g^{-1}) of *n*-ω-amino acids (glycine, β-alanine, γ-amino-*n*-butyric acid [γ-ABA], δ-amino-*n*-valeric acid [δ-AVA], and ε-amino-*n*-caproic acid [ε-ACA]), but amino acids were not present above detection limits in the nonhydrolyzed samples. The low amino acid abundances and the predominance of *n*-ω-amino acids resemble amino acid distributions previously observed for thermally altered chondrites. These results suggest that the parent body asteroid was not conducive to the synthesis and/or preservation of α-amino acids, or free amino acids in general, and that EH3 chondrite-like material may not have been a primary contributor of diverse or abundant free amino acids to the early Earth.

INTRODUCTION

Enstatite chondrite meteorites or E-type chondrites (hereinafter referred to as "E chondrites") are a distinct meteorite group defined by several unique properties including their highly chemically reduced and anhydrous compositions. The mineralogy of E chondrites consists of reduced, nearly FeO-free, silicate (essentially pure enstatite pyroxene [$MgSiO_3$]), Si-bearing kamacite (Fe, Ni metal), troilite (FeS), and a wide range of sulfide, nitride, phosphide, and silicide minerals that are characteristic of extremely reducing formation conditions (Anders, 1964; El Goresy, 1988; Gannoun et al., 2011; Keil, 1989; Kimura et al., 2005; Lin & El Goresy, 2002; Mason, 1966; Weisberg & Kimura, 2012). E chondrites lack hydrous minerals that would otherwise be indicative of parent body aqueous alteration, and they have low

water contents (0.08–0.54 wt% H_2O; Piani et al., 2020) relative to other chondrite meteorites (e.g., 7.2–9.1 wt% H_2O for Orgueil [CI], Alais [CI], and Murchison [CM2]; Piani et al., 2020). Collectively, these observations suggest that the parent body asteroids of E chondrites accreted within the innermost portion of the protoplanetary disk. Therefore, the compositions of E chondrites may serve as chemical records of the inner solar system during its formation.

Not only are E chondrites potentially derived from the same vicinity as the terrestrial planets but they are also considered candidates for the building materials of Earth (Javoy, 1995; Piani et al., 2020; Warren, 2011). E chondrites have bulk oxygen isotope compositions that can be plotted on, or nearly along, the terrestrial fractionation line (Clayton et al., 1976, 1984; Javoy, 1995; Javoy et al., 2010), suggesting that they are

potential remnants of the building blocks of the terrestrial planets. Models of Earth's accretion estimate that chemically reduced meteorites similar in composition to E chondrites comprised, at minimum, half of Earth's accreted material, with an increasing contribution toward the later stages of accretion (Brasser et al., 2018; Dauphas, 2017; Mah & Brasser, 2021). As such, investigating the organic composition of E chondrites may not only provide important insights into the chemistry of the inner protoplanetary disk but also information about the organic inventory of the Earth without the delivery of hydrated and organic-rich carbonaceous asteroids.

E chondrite meteorites are rich in carbon (0.15–0.70 wt%; Belsky & Kaplan, 1970; Grady et al., 1986) and previous studies have described the analysis of graphite, insoluble organic matter, and light hydrocarbons in a few thermally altered E chondrites (e.g., Belsky & Kaplan, 1970; Cody et al., 2008; Remusat et al., 2012). However, to our knowledge, water-soluble organic compounds such as amino acids have not yet been investigated in E chondrites. Amino acids are the monomers of proteins in terrestrial biology and are a common target class of water-soluble organic compounds in meteorite analyses due to their ubiquity in biology, numerous routes of abiotic synthesis, structural variation, and the availability of sensitive analytical methods to measure these species. By investigating the amino acid content of meteorite samples, we learn about the possible syntheses and preservation mechanisms of these molecules within asteroid parent bodies and the potential exogenous origins of amino acids on the prebiotic Earth. The bulk of our current knowledge of meteoritic amino acids is based on studies of carbonaceous (C) chondrite meteorite samples. To date, 96 different aliphatic amino acids have been named in the Murchison CM2 carbonaceous chondrites and appear to exhibit complete structural diversity (Glavin et al., 2018), though the distribution and abundances of amino acids vary widely between different C chondrite groups (Burton et al., 2012; Elsila et al., 2016; Glavin et al., 2018; Martins et al., 2007; Pizzarello et al., 2006). Comparative studies within and across C chondrite groups have shown that a variety of factors, including the mineralogy, aqueous and thermal alteration history, and post-fall terrestrial contamination, can influence the amino acid chemistry of a sample (Elsila et al., 2016; Glavin et al., 2011, 2020). Expanding our amino acid database with analyses of E chondrite samples opens a new window to study the prebiotic chemistry of the inner solar system specifically, and allows us to assess the influence of thermal alteration, reduced oxidation state, high metal contents, and lack of aqueous alteration on the synthesis and preservation of amino acids. Furthermore, if E

chondrite-like material did, in fact, comprise the bulk of the impactor population during Earth's late accretion, the present study offers new insights into whether that process would have concomitantly delivered a significant abundance of prebiotic organic matter to the early Earth, or if a reservoir of water-rich objects, such as comets, was necessary to deliver organic matter.

E chondrites are categorized into two distinct subgroups, EH and EL chondrites, which are generally thought to be derived from two distinct parent body asteroids, based on differences in trace element abundances that reflect distinct nebular processing (Keil, 1989). EH chondrites also differ from the EL chondrites in that they tend to have smaller chondrules, lower abundances of enstatite, higher abundances of sulfides, and more silicon-rich and nickel-poor metal compositions (Krot et al., 2014). Although the parent bodies of E chondrites are unknown (Greenwood et al., 2020), E chondrites possess spectral and density similarities to M-type asteroids (Chapman & Salisbury, 1973; Shepard et al., 2010), such as Lutetia (Vernazza et al., 2011) and 16 Psyche, the target of NASA's upcoming Psyche mission (Elkins-Tanton et al., 2020; Landsman et al., 2018; Lupishko & Belskaya, 1989).

Like all chondrites, EH and EL meteorites are assigned a petrologic type, a number specifying the degree of alteration experienced within the parent body asteroid (Van Schmus & Wood, 1967; Weisberg et al., 2006). E chondrite petrologic types range between 3 and 6, indicating varying thermal alteration histories, with petrologic type 3 representing the least altered materials, and petrologic type 6 representing the most thermally altered. In the present study, we have investigated the amino acid content of three EH meteorites of petrologic type 3, in order to study EH chondrite samples that have experienced relatively low temperatures for this chondrite group (Kimura et al., 2005; Quirico et al., 2011; Zhang & Sears, 1996). We selected Dominion Range (DOM) 14021, Larkman Nunatak (LAR) 12001, and LAR 06252 for this study since there is sufficient mass available for destructive analyses of these specimens, and these meteorites exhibit relatively minor weathering and/or fracturing. Reduced weathering/fracturing minimizes the potential impact of terrestrial contamination derived from the fall and recovery, as the internal mass of the meteorites tend to be better protected from terrestrial contamination.

MATERIALS AND METHODS

Chemicals and Reagents

All glassware and tools were wrapped in aluminum foil and heated at >500 °C for a minimum of 6 h before

use in order to remove organic contamination. All vials were capped with PTFE-lined lids. Standards and reagents were purchased from Sigma-Aldrich and Fisher Scientific. Ultrapure water (Millipore Milli-Q Integral 10, 18.2 MΩ, ≤3 ppb total organic carbon; hereafter referred to as "ultrapure water") was used. Stock amino acid solutions were prepared by mixing individual standards (97–99% purity) in ultrapure water. The o-phthaldialdehyde/N-acetyl-L-cysteine (OPA/NAC) reagent used for amino acid derivatization was prepared by mixing 300 μL 0.1 M OPA in methanol, and then adding 670 μL 0.1 M sodium borate buffer (pH 9) and 30 μL 1 M NAC. A 0.1 M hydrazine solution was prepared by double vacuum distillation of anhydrous hydrazine (98% purity) and subsequent dilution in ultrapure water. The ammonium formate buffer used for the ultra-high-performance liquid chromatography with fluorescence detection and time-of-flight mass spectrometry (LC-FD/ToF-MS) analyses was prepared by ammonium hydroxide titration of a 50 mM formic acid solution to pH 8. Details regarding the preparation of solutions and the sources of specific five-carbon (C_5) amino acids used as standards are available in Glavin et al. (2006, 2011, 2020).

Sample Preparation and Amino Acid Extraction

Interior samples of three EH3 meteorites (DOM 14021, 2.0 g; LAR 12001, 2.2 g; LAR 06252, 2.5 g) were provided by the Antarctic meteorite curator at the NASA Johnson Space Center. The samples were prepared for amino acid extraction within a positive pressure ISO 5 HEPA-filtered laminar flow hood in an ISO ≤8 white room. The DOM 14021 and LAR 12001 chips did not show any visible signs of weathering, while one of the LAR 06252 chips appeared to exhibit minor weathering, as evidenced by a small amount of white mineral and minor rusting on the surface of the sample. The individual meteorite samples were powdered using ceramic mortars and pestles, and all three meteorites, especially LAR 12001, were highly indurated and resistant to powdering. The powdered samples were subdivided into ~500 mg aliquots in flame-sealed glass ampoules, each containing 1 mL of ultrapure water. To monitor background levels of amino acids in the method, two procedural blanks were also carried through the meteorite extraction procedure and sample work-up: one solvent blank, containing no mineral component, and one mineral analog blank, consisting of ~500 mg of clean serpentine mineral powder (heated >6 h at 500 °C prior to the extraction step to drive off organics). All sealed ampoules were then heated in an oven set at 100 °C for 24 h.

Isolation and Analysis of Amino Acids

Following the hot water extraction step, the aqueous extracts were separated from the meteorite residues by centrifugation. The residues were rinsed with ultrapure water (3 × 0.5 mL) and centrifuged after each addition of 0.5 mL ultrapure water and all of the rinses were combined with the aqueous extract. For each sample, the extract was divided into two equal portions: one portion for the analysis of "free" amino acids and one portion carried through an acid-vapor hydrolysis step (6 M double-distilled HCl [ddHCl], 150 °C for 3 h) to measure the "total" amino acid content (free plus acid-hydrolyzable). Unhydrolyzed and acid-hydrolyzed extracts were redissolved in ultrapure water, desalted using cation-exchange resins, and derivatized using OPA/NAC, following protocols described elsewhere (Glavin et al., 2006, 2011). The derivatized amino acids were analyzed via LC-FD/ToF-MS using a Waters ACQUITY H Class UPLC with UV fluorescence detector and a Waters Xevo G2 XS ToF-MS. The instrument parameters and analytical conditions used were the same as those described elsewhere (Glavin et al., 2020). For the Xevo mass calibrations, an automatically applied lock mass of a fragment (278.1141 Da) of Leucine Enkephalin (0.09 μM in 50/50 acetonitrile/water with 0.1% formic acid) with a scan time of 1 s every 120 s was used. The capillary voltage was set to 1.2 kV. The amino acids and their enantiomeric ratios were quantified from the peak areas generated from both UV fluorescence (UPLC-FD, λex = 340 nm, λem = 450 nm) and ToF-MS chromatograms by plotting the accurate mass to within 10 ppm of the theoretical m/z value of each OPA/NAC derivative over the elution time as described previously (Glavin et al., 2020). The reported amino acid abundances are the average value of three separate LC-FD/ToF-MS measurements. The errors given are based on the standard deviation of the average value of three separate measurements. Amino acid abundances are blank corrected to account for trace levels of contamination present in the blanks.

RESULTS AND DISCUSSION

Detection of Amino Acids in the Acid-Hydrolyzed Extracts

Nonhydrolyzed and acid-hydrolyzed extracts from each sample were analyzed to investigate the presence of amino acids that are readily extractable in water, and amino acids generated or liberated from chemical precursors or sequestered amino groups (e.g., HCN, peptides, lactams, hydantoins, etc.) during acid hydrolysis, respectively. The nonhydrolyzed extracts

Table 1. Summary of averaged, blank-corrected amino acid abundances in 6 M ddHCl-hydrolyzed ("total") hot water extracts of three EH3 meteorites (in pmol g^{-1}), and in an Antarctic ice sample from the northern Graves Nunataks region (in fmol g^{-1}, converted from pptr values; Burton et al., 2012).

	DOM 14021 (EH3)	LAR 12001 (EH3)	LAR 06252 (EH3)	Antarctic ice (fmol g^{-1}; Burton et al., 2012)
D-aspartic acid	<0.1	<0.1	<0.1	0.1
L-aspartic acid	<0.1	<0.1	<0.1	0.1
D-glutamic acid	<0.1	<0.1	<0.1	0.1
L-glutamic acid	<0.1	<0.1	<0.1	<0.1
D-serine	<0.1	<0.1	<0.1	<0.1
L-serine	<0.1	<0.1	<0.1	0.5
D-threonine	<0.1	<0.1	<0.1	n.d.
L-threonine	<0.1	<0.1	<0.1	n.d.
Glycine	<0.1	<0.1	3.6 ± 0.7	0.4
β-alanine	2.7 ± 0.3	<0.1	10.7 ± 0.4	<0.1
D-alanine	<0.1	<0.1	<0.1	0.1
L-alanine	<0.1	<0.1	<0.1	0.6
γ-amino-n-butyric acid (γ-ABA)	9.9 ± 0.7	7.4 ± 0.1	48.7 ± 0.2	<0.1
D-β-amino-n-butyric acid (D-β-ABA)	<0.1	<0.1	<0.1	<0.1
L-β-amino-n-butyric acid (L-β-ABA)	<0.1	<0.1	<0.1	<0.1
α-aminoisobutyric acid (α-AIB)	<0.1	<0.1	<0.1	<0.1
D,L-α-amino-n-butyric acid (D,L-α-ABA)	<0.1	<0.1	<0.1	<0.1
ε-amino-n-caproic acid (ε-ACA)	59.9 ± 0.2	27.6 ± 3.0	215.9 ± 0.1	<0.1
3-amino-2,2-dimethylpropanoic acid (3-a-2,2-dmpa)	<0.1	<0.1	<0.1	<0.1
D,L-4-aminopentanoic acid (D,L-4-apa)	<0.1	<0.1	<0.1	<0.1
D,L-4-amino-3-methylbutanoic acid (D,L-4-a-3-mba)	<0.1	<0.1	<0.1	<0.1
D,L-3-amino-2-methylbutanoic acid (D,L-3-a-2-mba)	<0.1	<0.1	<0.1	<0.1
D,L-3-amino-2-ethylpropanoic acid (D,L-3-a-2-epa)	<0.1	<0.1	<0.1	<0.1
δ-aminovaleric acid (δ-AVA)	<0.1	<0.1	1.5 ± 0.1	<0.1
D,L-4-amino-2-methylbutanoic acid (D,L-4-a-2-mba)	<0.1	<0.1	<0.1	<0.1
3-amino-3-methylbutanoic acid (3-a-3-mba)	<0.1	<0.1	<0.1	n.d.
D-2-amino-2-methylbutanoic acid (D-isovaline)	<0.1	<0.1	<0.1	<0.1
L-2-amino-2-methylbutanoic acid (L-isovaline)	<0.1	<0.1	<0.1	<0.1
D,L-3-aminopentanoic acid (D,L-3-apa)	<0.1	<0.1	<0.1	<0.1
D-2-amino-3-methylbutanoic acid (D-valine)	<0.1	<0.1	<0.1	<0.1
L-2-amino-3-methylbutanoic acid (L-valine)	<0.1	<0.1	<0.1	<0.1
D-2-aminopentanoic acid (D-norvaline)	<0.1	<0.1	<0.1	<0.1
L-2-aminopentanoic acid (L-norvaline)	<0.1	<0.1	<0.1	<0.1
Total	76.0 ± 0.7	36.5 ± 3.2	280.5 ± 1.4	4.2

n.d. = not determined.

represent the "free" water-soluble amino acid content of the meteorite, while the acid-hydrolyzed extracts represent the "total" amino acid content ("free" amino acids + "precursors"). Low abundances of amino acids were detected in all three hydrolyzed meteorite extracts (Table 1) while the nonhydrolyzed extracts did not contain amino acids above background levels. The hydrolyzed procedural blanks contained trace amounts of glycine (50 pmol), L-alanine (1 pmol), and β-alanine (4 pmol) and their abundances were subtracted from the meteoritic amino acid measurements. Free amino acids were not detected in any of the three E chondrite samples. While an absence of free amino acids is unusual for extracts of meteorites from other classes, it is not uncommon for there to be a relatively high

abundance of amino acids in acid-hydrolyzed meteorite extracts. Total amino acid abundances within acid-hydrolyzed samples are often a factor of two higher than that of nonhydrolyzed samples (Burton et al., 2012, 2013, 2015; Glavin et al., 2011, 2020; Simkus et al., 2019), indicating that a significant portion of amino acids in chondrites are bound as labile precursors or synthesized via acid hydrolysis through reactions between volatile organics. This observation, combined with the low overall abundances in the E chondrite samples, suggests that the abundance of free water-soluble amino acids, if present, may have fallen below detection limits. The lack of detection of free amino acids in the E chondrite samples could also indicate that the parent body conditions were not favorable for

amino acid syntheses and/or preservation, or favored the cyclization or polymerization of these species. Since the formation of such bound species results in the loss of a water molecule, perhaps the low water activity on the parent body favored such compounds.

Low Total Abundances and a Predominance of n-ω-Amino Acids

The relative abundances of individual amino acids detected in the E chondrite samples resembled the amino acid distributions previously observed for thermally altered R and CK chondrites (Burton et al., 2015), ureilites, CV chondrites, and CO chondrites (Burton et al., 2012), and thermally altered CI chondrites (Burton et al., 2014). More specifically, the amino acid compositions observed in the current study primarily consisted of straight-chain, terminal-amine amino acids (n-ω-amino acids) generally exhibiting a trend of decreasing abundance in the order of: ε-amino-n-caproic acid (ε-ACA) > γ-amino-n-butyric acid (γ-ABA) > β-alanine > glycine > δ-amino-n-valeric acid (δ-AVA). Despite this resemblance in amino acid distributions, the abundances that we measured for the E chondrite samples are exceptionally low, with total abundances over 10-fold lower than the most amino acid-depleted R chondrite and thermally altered CI chondrite previously analyzed (Burton et al., 2014, 2015). Our ability to detect such low abundances of amino acids in the present study is partly due to the relatively high sample masses (~2 g each) that were analyzed. The fact that the E chondrite samples are so depleted in amino acids relative to these other chondrite groups suggests that their parent body conditions may have been particularly unfavorable for the synthesis and/or preservation of these compounds. The consistent dominance of n-ω-amino acids in thermally altered meteorites points toward a relationship between thermal metamorphism and the predominance of these structures. Although the dominance of n-ω-amino acids was similar, the thermally altered meteorites contained higher relative amounts of free amino acids (8–100%) compared to the lack of free amino acids observed in E chondrites (Burton et al., 2012). This suggests that the formation mechanisms may be different and that the low water abundance alone is not responsible for the absence of detectable free amino acids in the nonhydrolyzed EH chondrites analyzed here. The apparent absence of free amino acids in E chondrites, in contrast to other thermally altered chondrites, could be partially attributed to the highly reducing, high-temperature conditions of the inner solar system and potentially insufficient accreted volatile molecules within the parent bodies.

Given the high temperatures (<400 °C, Kimura et al., 2005; <550–600 °C, Quirico et al., 2011) that EH3

meteorites may have experienced during parent body thermal alteration, the predominance of non-α-amino acids in the acid-hydrolyzed extracts analyzed here could reflect a preferential preservation of amino acid derivatives with higher thermal stabilities. For instance, for the C_4 amino acids, it has been shown that γ-ABA has a relatively low decarboxylation rate at elevated temperatures in aqueous solution, in comparison to α- and β-amino-n-butyric acid (Li & Brill, 2003a). The higher abundances of γ-ABA and nondetection of α-ABA and β-ABA in the E chondrite samples may be attributable to this difference in thermal stability. Likewise, non-α-amino acids that are capable of converting to lactam derivatives (such as γ-ABA and δ-AVA) are relatively stable at elevated temperatures up to 400 °C and are potentially preferentially preserved in metamorphosed parent bodies (Burton et al., 2012; Cooper & Cronin, 1995; Islam et al., 2001, 2003; Li & Brill, 2003b). The absence of common α-amino acids could also indicate that Strecker cyanohydrin synthesis was not a dominant mechanism for amino acid synthesis in the E chondrite parent body asteroids and that reactions such as Michael addition of β-amino acids, or Fischer–Tropsch type reactions, may have played a more significant role (Elsila et al., 2016). Perhaps, the predominance of bound n-ω-amino acids could have resulted from Fischer–Tropsch type reactions associated with a high-pressure impact event, as has been previously proposed for other meteorites such as the Martian meteorite Roberts Massif (RBT) 04262 (Callahan et al., 2013).

The low abundances of amino acids in the E chondrite samples, relative to chondrites that contain mineralogical evidence of aqueous alteration (Burton et al., 2014; Elsila et al., 2016; Glavin et al., 2018), may demonstrate the significant role that water–rock interactions play in generating meteoritic amino acids. The low amino acid contents and the absence of detectable free amino acids could also be indicative of the destructive effects of parent body thermal alteration on amino acids and/or their precursors (e.g., aldehydes, ketones, ammonia, and cyanide). Other factors could have influenced the potential for amino acid synthesis in these samples, including the highly reduced mineral assemblages, low abundances of matrix minerals, high metal contents, and low porosities (Macke et al., 2010; Weisberg & Kimura, 2012); determining how each of these factors alone could have affected prebiotic organic synthesis would require additional focused studies. E chondrites bear some resemblance to CB and CH chondrites, in terms of their high metal contents, high abundances of chondrules, low abundances of calcium-aluminum inclusions and amoeboid olivine aggregates, and low volumes of matrix minerals (background fine-grained minerals, as opposed to chondrules or inclusions), relative to other chondrite groups (Krot et al., 2014; Scott
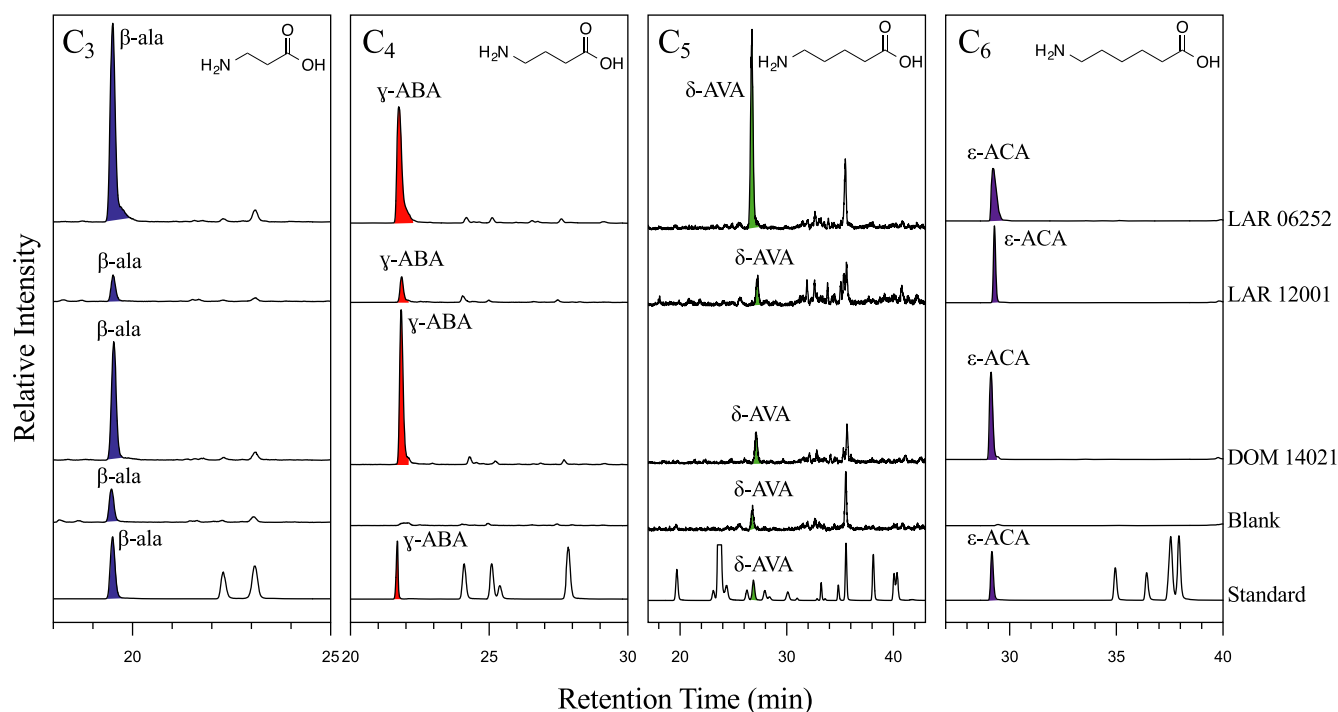
Fig. 1. Representative LC-ToF-MS single ion chromatograms of 6 M ddHCl-hydrolyzed EH3 chondrite samples, a procedural blank, and an amino acid standard mixture. The four panels illustrate chromatograms for C_3 (m/z = 351.1015), C_4 (m/z = 365.1171), C_5 (m/z = 379.1328), and C_6 (m/z = 393.1484) amino acids. Meteorites and blanks are ratioed to be the same mass on column. The standards are ratioed arbitrarily. (Color figure can be viewed at wileyonlinelibrary.com.)

& Krot, 2014). Previous analyses of CB and CH chondrite samples revealed amino acid distributions similar to those observed here (i.e., a predominance of non-α-amino acids; Burton et al., 2013). However, the CB/CH chondrite samples contained amino acids in abundances (CB: 5–47 nmol g^{-1}; CH: 167–221 nmol g^{-1}; Burton et al., 2013) that were several orders of magnitude more abundant than the E chondrite values reported here (37–281 pmol g^{-1}). The relatively high abundances of amino acids measured for CB/CH chondrites may demonstrate the important role of mineral–fluid interactions for prebiotic organic synthesis; CB/CH chondrites tend to have slightly higher matrix volumes (<5 vol%), including hydrated matrix minerals and clasts (Greshake et al., 2002; Krot et al., 2014), while matrix volumes of E chondrites are exceptionally low (<0.1 vol%) and anhydrous (Krot et al., 2014). Thus, it is likely that catalytic reactions on hydrated matrix mineral surfaces that are absent in E chondrites may have played a role in yielding relatively higher abundances of amino acids in CB and CH chondrites.

Potential Terrestrial Origins of ε-ACA

There are two sources that need to be evaluated as potential terrestrial origins for the amino acids identified in this study (1) the environment of the original fall site, including sample collection and storage processes, and (2) the methodology for sample extraction and analysis in the laboratory. Stable isotopic analyses (δD, and in some cases $\delta^{13}C$) can serve as a means to support or refute extraterrestrial origins; however, isotopic measurements were not possible in this study due to the low amino acid abundances. Likewise, the analysis of chirality to look for L-excesses of protein amino acids that would be expected in biologically contaminated samples was impossible with the exception of a small amount of L-alanine (1 pmol), because only achiral amino acids were detected. Our assessment of the origins of amino acids in these E chondrite samples, therefore, primarily relies on comparisons to blanks and previous meteorite analyses. Our analyses of procedural blanks in parallel with the E chondrite samples provided confidence that the methodology was not a significant source of amino acids. The amino acid content of the E chondrite samples is clearly distinguishable from the procedural blanks by the predominance of n-ω-amino acids in the meteorites (Fig. 1), ruling out the laboratory as a source of these compounds. The predominance of n-ω-amino acids in these Antarctic E chondrite samples is also distinctly different from the composition of Antarctic

ice previously collected and analyzed by Burton et al. (2012) (Table 1). The n-ω-amino acids, β-alanine, γ-ABA, δ-AVA, and ε-ACA were not detectable above 0.08–0.1 fmol g^{-1} (0.01 pptr) levels in the Antarctic ice samples (Burton et al., 2012), in contrast to the amino acid abundances measured here for E chondrites (1.5–215.9 pmol g^{-1}). The protein amino acids, aspartic acid, glutamic acid, serine, alanine, and valine were present between 0.07 and 0.6 fmol g^{-1} (0.01 and 0.05 pptr, respectively) in the Antarctic ice samples (Burton et al., 2012), but were absent in the E chondrite samples studied here. These distinct differences in amino acid distributions suggest that the fall and collection site is unlikely to have been a significant source of n-ω-amino acids to the meteorite samples.

The most abundant amino acid detected for all three samples was ε-ACA, which is also the degradation product upon acid hydrolysis of samples containing the nylon-6 polymer (Dworkin et al., 2018; Glavin et al., 2006). This potential terrestrial source is an important consideration for interpreting amino acid data in cases where samples have been exposed to nylon-6 during collection, storage, and/or analysis. All meteorite samples collected in Antarctica by the Antarctic Search for Meteorites (ANSMET) team were initially stored in nylon bags. Once nylon was identified as a potential source of terrestrial amino acids (Glavin et al., 2006) and after testing different bagging materials in 2008 (Dworkin et al., 2018), ANSMET replaced the nylon sample collection materials with polytetrafluoroethylene (PTFE, e.g., Teflon™; Righter, personal communication). Today, ANSMET collects all recovered meteorites in PTFE bags, in which they are transferred to NASA's Johnson Space Center (JSC) to be dried and processed in nitrogen cabinets for storage. While C chondrites and Martian meteorites are stored long-term in PTFE bags, other meteorite types that are not typically targeted for soluble organic analyses, such as E chondrites, are stored dry in nylon bags. The risk of contamination from the nylon bags would be lower for dried meteorite samples because nylon is spread through contact transfer, which becomes more efficient when wet conditions exist (Dworkin et al., 2018). However, it is worth considering whether trace levels of nylon-6 polymer could still be transferred to the meteorites during the process of storing dried meteorites in nylon bags. LAR 06252 was collected in Antarctica in 2006. At that point in time, meteorites were collected and stored in nylon bags. The LAR06252 sample was, therefore, exposed to nylon both before and after the meteorite was desiccated. In contrast, LAR 12001 and DOM 14021, collected in 2012 and 2014, respectively, had minimal exposure to nylon-6, which may help explain the relatively lower ε-ACA abundances measured in these two samples.

CONCLUSIONS

Three EH3 chondrite samples (DOM 14021, LAR 12001, and LAR 06252) were analyzed to determine their free and bound amino acid contents. All three meteorites were found to contain extremely low abundances of bound amino acids and only a small suite of n-ω-amino acids were identified as indigenous to the samples. The absence of free amino acids in these samples suggests that the conditions within the E chondrite parent body or bodies were not optimal for the synthesis and/or preservation of amino acids in their free form. The amino acid distributions observed here for the E chondrite samples resemble those of other thermally altered chondrite groups, in terms of low total abundances and the predominance of n-ω-amino acids (Burton et al., 2012, 2015). The predominance of bound n-ω-amino acids in the E chondrite samples may reflect a greater preservation of larger derivatives (e.g., peptides, complexes, etc.) due to the possibly higher stabilities of these structures under elevated temperatures and/or pressures.

These results suggest that EH3-like material bombarding the early Earth would have contributed lower abundances of amino acids (or their precursors) per mass of meteorite, in comparison to most other chondrite types analyzed to date. The implication of this finding is that, if meteoritic delivery of amino acids constituted a significant source of amino acids or their precursors to the early Earth, materials like those from the E chondrites studied here are unlikely to have been a major contributor. Rather, other chondrite groups such as C chondrites would have had the potential to deliver much larger quantities of prebiotic organic matter. We do consider, however, that the organic compositions of EH3 meteorites are not necessarily representative of all E chondrites, and that the low abundances of amino acids detected here do not rule out all E chondrites as significant sources of amino acids on the early Earth. The two groups of E chondrites (EH and EL chondrites), for instance, could contain entirely different total abundances and distributions of amino acids, and they may not be equally relevant to Earth's late accretion (e.g., Mah & Brasser, 2021). Further investigation of E chondrite organic matter by conducting amino acid analyses of EL samples specifically would be important to fully assess the potential influence of E chondrite-like material on the chemistry of the early Earth. The present study offers valuable new insights into the organic content of a chondrite group previously unstudied for soluble organic matter, and demonstrates

the importance of early solar system dynamics for understanding implications for Earth's prebiotic chemistry.

Data Availability Statement—The data that supports the findings of this study are available in the supplementary material of this article.

Editorial Handling—Dr. Scott Sandford

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SUPPORTING INFORMATION

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

Data S1. Data points for Figure 1.