INSOLUBLE CYANIDE IN CI, CM, CR, CO, AND CV CARBONACEOUS CHONDRITES. J. C. Aponte[1,*], S. Kolibas[2], H. L. McLain[1,3,4], J. P. Dworkin[1], J. E. Elsila[1], D. P. Glavin[1]. [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA, [2]Ohio State University, Columbus, OH 43210, USA, [3]Catholic University of America, Washington DC 20064, USA, [4]Center for Research and Exploration in Space Science and Technology, NASA/GSFC, Greenbelt, MD 20771, USA. *Email: Jose.C.Aponte@nasa.gov.

Introduction: Aliphatic amino acids have been unambiguously detected in carbonaceous chondrites and because of their importance to life on Earth and their astrobiological relevance, their extraterrestrial origins remain heavily discussed [1,2]. Although no consensus on the origin of chondritic amino acids has been reached, it is assumed that at least a portion of these compounds originated from precursor molecules, either indigenous to the asteroid parent body or from contaminants that reacted during the meteorite extraction and acid hydrolysis processes used for analysis in the laboratory [3]. One potential precursor of amino acids in carbonaceous chondrites is hydrogen cyanide (HCN) or its inorganic form, cyanide anion (CN⁻) [4,5]. Therefore, measuring the concentration of HCN and CN⁻ in carbonaceous chondrites is key to understanding the potential parent-daughter relationship between cyanide species and aliphatic amino acids [e.g., 6,7].

The analysis of cyanide in carbonaceous chondrites is important to understanding the primitive pool of starting materials available for prebiotic organic synthesis during parent body processing and in the early Earth [8,9]. Work in our laboratory has led to the development of a method for the analysis of HCN and CN⁻ in hot-water extracts and acid-digested distillates of extraterrestrial samples [10,11]. Cyanide has been found in carbonaceous chondrites in concentrations ranging from < 0.1 to 2500 nmol of cyanide per gram of meteorite [10-12], and experiments have shown that HCN is hydrolysable to amino acids under the conditions used for the workup of extraterrestrial sample extracts [4,5,13] suggesting that at least a portion of the amino acids detected in extraterrestrial samples may have originated from the hydrolysis of HCN during sample extraction.

Analytical Methods: In this work, we analyzed ~200 mg of carbonaceous chondrite residues from the CI, CM, CR, CO, and CV subtypes (Table 1). These samples were first extracted using a 3:2 mixture of dichloromethane (DCM) and methanol to remove all neutral soluble compounds (e.g., PAHS, alkanes, esters, etc.), and the mineral residues left were subjected to acid-hydrolysis using a MicroDIST distillation apparatus (Lachat Instruments) using previously published methods [10,11]. After distillation, an aliquot of 50 µL of acid-released cyanide distillate was derivatized using 50 µL of 10 mM sodium borate buffer

(pH = 9), 50 µL of 1 mM naphthalene-2,3-dicarboxaldehyde (NDA) solution in methanol, and 50 µL of 0.1M glycine in water (Scheme 1), reacted at room temperature for 30 min, and analyzed by ultrahigh performance liquid chromatography with UV fluorescence and quadrupole time-of-flight mass spectrometry detection (LC-FD/Q-ToF-MS).

Table 1. Insoluble cyanide (nmol/g of material) in the meteorite samples analyzed in this work. Aqueously altered meteorites are shown in blue, thermally metamorphosed meteorites shown in red, and meteorites with varying degrees of aqueous and thermal alteration are shown in black.

Meteorite	Type[a]	mg Distilled	nmol/g Cyanide
Orgueil	CI1.1	200.6	< 0.01
SCO 06043	CM1.1	200.6	< 0.01
ALH 83100	CM1.1	203.5	0.4 ± 0.1
LAP 02333	CM1.5	190.6	44.8 ± 1.7
GRA 98005	CM1.6	200.9	< 0.01
LEW 90500	CM1.6	208.9	3.9 ± 0.2
Murchison	CM1.6	202.1	< 0.01
LON 94101	CM1.8	201.6	1.9 ± 0.1
LEW 85311	CM1.9	190.2	134.2 ± 1.7
EET 96029	CM2.7	201.6	0.3 ± 0.1
WIS 91600	CM2-an	201.1	0.6 ± 0.1
GRO 03116	CR2	197.4	< 0.01
GRO 17063	CR2	190.3	< 0.01
PCA 91082	CR2.3	199.7	< 0.01
MIL 090001	CR2-an	203.3	< 0.01
BUC 10933	CR2-an	207.4	< 0.01
GRA 06100	CR2-an	207.6	< 0.01
ALH 83108	CO3.5	203.1	< 0.01
ALH 77003	CO3.6	201.4	< 0.01
Allende	CV3.6	203.5	< 0.01
MET 01017	CV3-an	200.6	< 0.01

[a]Meteorite groups are arranged according to their approximate aqueous and thermal alteration [14-16].

Scheme 1. Reaction scheme for the derivatization of cyanide by NDA and glycine [10,11].
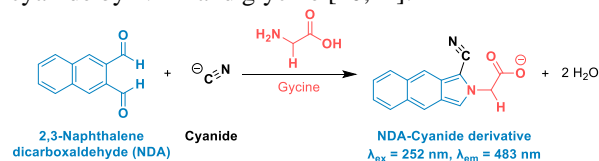
Results and Discussion: This work shows the detection of insoluble cyanide in mineral residues of DCM-methanol extracted carbonaceous chondrites. Low concentrations of distilled CN^- ranging from below our limits of detection (0.01 nmol/g of meteorite) to 0.6 nmol/g of meteorite were found in the extensively aqueously altered chondrites like Orgueil (CI1.1), SCO 06043 (CM1.1), and ALH 83100 (CM1.1), as well as in the thermally metamorphosed meteorites EET 96029 (CM2.7), WIS 91600 (CM2-an), ALH 83108 (CO3.5), ALH 77003 (CO3.6), Allende (CV3.6), and MET 01017 (CV3-an). However, the concentration of CN^- varied greatly in the remaining CM chondrites and were only found below detection limits in all the CR meteorites studied here.

The highest concentrations of CN^- were found in LAP 02333 (CM1.5) and LEW 85311 (CM1.8); however, these values remain low as the concentrations of LEW 85311 we found were about twenty times lower than those previously reported for the same meteorite [10]. Indeed, using accurate mass spectrometry measurements and isotope fragmentation patterns, iron cyanocarbonyl complexes $[Fe^{II}(CN)_5(CO)]^{3-}$ and $[Fe^{II}(CN)_4(CO)_2]^{2-}$ and not ferrocyanide or ferricyanide were suspected to contribute as much as 70% of the total acid-releasable CN^- in LEW 85311 [10].

Insoluble CN^- have been previously reported from Muchison and other CM2 type chondrites including LEW 85311 [10-12] in concentrations ranging from 8 to 63 nmol/g of meteorite. The absence of insoluble cyanide in the Murchison sample we analyzed could reflect meteorite heterogeneity, and/or it may be an indication that the insoluble cyanide distilled was not initially only present as ferro- and ferricyanides $(Fe(CN)_6]^{X-})$, but potentially as iron cyanocarbonyl complexes $(Fe(CN)_X(CO)_Y)$ [10] or other transition metal organocyanides, which may be methanol/DCM soluble and may have been lost during the organic-solvent extraction pretreatment done here.

CN^- was not observed above detection limits in all CR2 type chondrites we studied. Similar to the Murchison sample studied here, these results may suggest that the cyanide organometallic complexes in CR2 meteorites may be of a solvent-soluble nature or that these compounds were simply not present in the CR2 parent body. The amino acid concentration in GRO 17063 and GRO 03116 have not been measured before; however, concentrations of up to 930 nmol of amino acids/g of meteorite were reported from PCA 91082 (CR2) [17]. The absence of distilled CN^- in the CR2 samples we evaluated are in line with the absence or low concentrations of nucleobases and purines in CR2 chondrites despite their elevated amino acid content [18], and with the absence of CN^- previously found for GRA 06100 [10].

Conclusions: Comparing our search for insoluble cyanide species in meteorite residues previously subjected to organic solvent extraction against those result from unextracted samples [e.g., 10], suggest that if present, the meteoritic organometallic cyanide complexes may be represented by a wide range of molecular structures with varying degrees of aqueous and organic solvent solubilities. Future analyses of meteoritic cyanide and synthetic species may provide insights into the chemical inventory at the formation of the solar system and through the aqueous and thermal processing that has occurred in the asteroid parent bodies, shedding light on the potential link between cyanide and its derivatives (e.g., amino acids).

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