

Challenging analyses of organic content in Saharan carbonaceous chondrites. Y. Osawa¹ and S. Pizzarello², ¹Department of Earth and Planetary Sciences, Kyushu University, ²Department of Chemistry and Biochemistry, Arizona State University.

Introduction:

Much of our knowledge about meteorite organics has been obtained from analyses of meteorites from Antarctica [1], due to its preservative environment for most organic compounds (cryogenic and dry). On the other hand, very little study of organics in hot desert meteorites have been conducted to date and the fate of both soluble and insoluble meteorite organics in such extreme environment is not very well known. Several meteorites are continuously found in hot desert regions and in the current study we analyzed the organic content in four different carbonaceous chondrites collected in the Sahara desert in Northwest Africa: NWA3340 (CM2-an.), NWA5028 (C3-ung.), NWA5028 (likely CR2), and another meteorite tentatively classified as NWA5376 (CM2). Here we report the results of molecular analyses of amino acids and insoluble organic matter (IOM) in these samples.

Samples and Methods:

All meteorite samples came from Morocco, were purchased from local dealers and housed cleanly in the Center of Meteorite Study at Arizona State University prior to the analyses. They were grinded into powder and the weight of each powder were: 1.01g of NWA3340, 2.48g of NWA5028, 0.96g of NWA5765 and 0.56g of NWA5958. The water extraction was performed at 100°C for 24h in evacuated vials with ~4 mL of triple distilled water, followed by the separation of amino acids from neutral and acidic compounds by eluting the extracts through a cation exchange column (BIORAD AG-50, x4) using in successive steps water and Ammonium hydroxide. The basic eluate was dried, esterified with isopropanol 1.5N HCl at 100°C for 1h, dried and the residue again reacted with trifluoroacetic anhydride (TFAA) in dichloromethane (1:4, v:v) at room temperature for half hour. Subsequently, gas chromatography-mass spectrometry (GC-MS) was employed for the molecular analyses of amino acid derivatives [e.g., 2]. The powder of NWA3340 and NWA5028 which were sufficient in amount for the IOM analyses were extracted with solvent, dried, further extracted with 6N HCl at room temperature for 24h and, after removal of the extract, with C₂S at room temperature for several minutes. The extracted powders were then kept in a HF/HCl/H₂O (28:50:34, v:v) solution at 40°C for a week with stirring. The resulting IOM amounts obtained were about 10mg and 60mg for NWA3340 and NWA5028, respectively; approximately 10mg of each were analyzed by Nuclear Magnetic Resonance (NMR)

experiments for their molecular characterization.

Results and Discussion:

NWA3340, NWA5028 and NWA5376 were found to contain mainly contaminant amino acids, indicating their exposure to active terrestrial process, e.g. bacterial contamination. Only one sample, NWA5958, displayed less contamination and contained a few non- α -amino acids; we detected glycine, β -alanine and γ -aminobutyric acid (γ -ABA) as well as L- and D-alanine (Fig. 1). L- and D-alanine were not found as a racemic mixture, as in most uncontaminated carbonaceous chondrite analyzed so far, however, D-alanine is rare in the biosphere and it is possible that D-alanine and an equal amount of L-alanine are indigenous in this meteorite. The possibility of an indigenous D-alanine would also suggest that all or part of glycine could be of extraterrestrial origin. Non- α -amino acids are less common in Earth's biosphere so that β -amino acid and γ -ABA may be indigenous as well. Moreover it was previously reported that non- α -amino acids are more stable than α -species [3] and could be considered 'survival' compounds, however, it should be kept in mind that β -alanine has been found in bacteria and could be a byproduct of contaminant glutamic acid decarboxylation. It is apparent that more labile compounds such as amino acids are easier to be broken down or leached from meteorites, therefore, the fact that NWA5958 seems to still contain indigenous amino acids implies that our sample was the least altered of all meteorites analyzed in this study.

In addition to the amino acid analyses, the NMR experiment on NWA3340's IOM revealed that this material was not much depleted of sp³ carbon compared to other carbon-rich chondrite IOMs analyzed previously (Fig. 2). A large loss of sp³ carbon in the insoluble macromolecule of carbonaceous chondrites is considered as one of the effects of low temperature alteration in their asteroidal parent body [4]. From our data, we should assume that this IOM was not altered extensively after its residence in the Saharan environment. On the other hand, we found the IOM of NWA5028 to contain very little alkyl hydrogen, even less than found in the IOM of a CR2 chondrite after hydrothermal treatment (S. Pizzarello 2011, Fig. 3). Likewise sp³ carbon, alkyl hydrogen is easily removed from IOM by pre-terrestrial alteration or planetary processing. Our result thus indicates a quite intense alteration on NWA5028 parent body, in the desert condition, or both.

Our investigation revealed that the Saharan conditions are severe for meteoritic amino acids and, likely, could be for other labile compounds e.g. alkyl hydrocarbons. However, at least one sample still contained extraterrestrial amino acids that appear to have survived these conditions. Although there are variations of the extent to which each meteorite stone is altered in the desert, meteorite IOMs are less susceptible to the terrestrial processing and could still retain primitive organic material.

References:

[1] Sephton M. A. (2002) *Nat. Prod. Rep.*, 19, 292-311. [2] Pizzarello S. et al (2012) *Proc. Natl. Acad. Sci. USA*, 109, 11949-11954. [3] Monroe A. A. and Pizzarello S. (2011) *Geochim. Cosmochim. Acta*, 75, 7585-7595. [4] Cody G. D. and Alexander C. M. O'D. (2005) *Geochim. Cosmochim. Acta*, 69, 1085-1097. [5] Pizzarello S. et al (2011) *Proc. Natl. Acad. Sci. USA*, 108, 4303-4306.

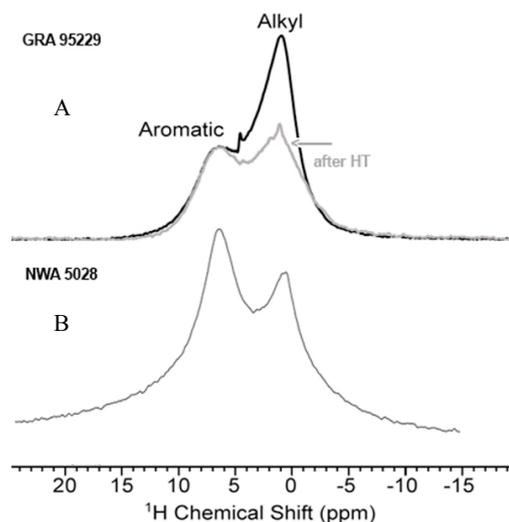


Fig. 3. ^1H Solid-state NMR spectra of GRA-IOM before (black) and after (gray) hydrothermal treatment [5] (A) and of untreated NWA5028-IOM from this study (B).

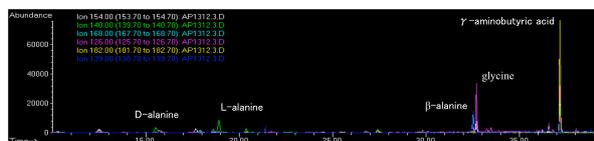


Fig. 1. The chromatogram of NWA5958 (GC-MS). Glycine, DL-alanine, β -alanine and γ -aminobutyric acid were observed in the water extract.

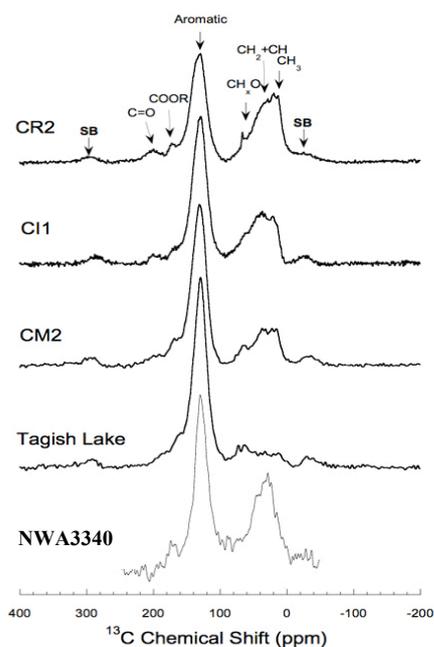


Fig. 2. VA ^1H - ^{13}C CP MAS NMR spectra of the insoluble residues derived from EET92042 (CR2), Orgueil (CI1), Murchison (CM2), Tagish Lake [4] and NWA3340 in this study