

NITROGEN FUNCTIONAL CHEMISTRY OF ORGANIC GRAINS IN CR CHONDRITES AND IDPs.C. Vollmer¹, J. Leitner², H. Busemann³, N. H. Spring⁴, D. Kepaptsoglou⁵, Q. M. Ramasse⁵, and P. Hoppe²¹Universität Münster, Inst. f. Mineralogie, Corrensstr. 24, 48149 Münster, Germany, christian.vollmer@wwu.de,²Max-Planck-Institut für Chemie, Hahn-Meitner-Weg 1, 55128 Mainz, Germany, ³ETH Zürich, Institut für Geochemie und Petrologie, Clausiusstr. 25, Zürich, CH, ⁴University of Alberta, Earth and Atmospheric Sciences, Edmonton, Canada, ⁵SuperSTEM Laboratory, Keckwick Lane, Daresbury, UK.

Introduction: The provenance of the most pristine biomolecules, e.g., amino acids or nucleobases, on the early Earth is still a matter of debate [e.g., 1]. Starting from very simple interstellar CHON-bearing species such as CO₂, H₂CO (formaldehyde), HCN, or NH₃, complex polymerization reactions can either occur in the interstellar medium or the solar nebula, e.g., by irradiation of coated dust grains, on cometary or asteroidal parent bodies by aqueous alteration, or by reactions on Earth in the atmosphere or at mineral interfaces in hydrothermal systems. Disentangling these complex modification processes is important to understand the evolution of the first pristine relevant biomolecules [see, e.g., 2, for a recent review].

Samples and Methods: Extraterrestrial samples that have not suffered severe thermal overprint such as petrologic type 2-3 carbonaceous chondrites or interplanetary dust particles (IDPs) are suitable candidates to search for pristine biomolecules. These samples contain on average several wt.% of organic C mainly in the form of kerogen-like molecules (“insoluble organic matter”, IOM) that can be isotopically anomalous, most notably in H or N. The origins of these anomalies are usually attributed to fractionation reactions in cold environments [e.g., 3], but recent ideas suggest that they might also be explained by high temperature solar nebula processes [4] or hydrothermal reactions on asteroidal bodies [5] in the case of nitrogen. The aim of this study is to locate organic matter in these samples “in-situ” by electron microscopy (SEM) and NanoSIMS techniques and to characterize the functional chemistry, specifically of nitrogen, and mineralogy by low voltage (60 kV) high resolution scanning transmission electron microscopy (STEM) combined with electron energy loss spectroscopy (EELS). This approach is less representative than bulk analyses on extracted organic matter performed since decades, but provides important information on unprocessed, single grains within their petrographic context.

Results and Discussion: Results on organic grains from CR chondrites Renazzo and Elephant Moraine (EET) 92161 and several IDPs from the L2006 collector confirm our previous findings that the polymerization of aromatic rings in the CR grains is increased compared to the IDP grains, probably due to subtle fluid-induced reactions on the CR parent body [6]. These polycyclic aromatic hydrocarbons are not directly relevant to early lifeforms, but could have served as scaffolds for the first primitive cell membranes [7]. Other functional groups observed by EELS at the C-K edge include several types of C-O bonding environments (ketones, aldehydes, carboxylic acids) that may act as precursors for α -amino acids via Strecker synthesis reactions [8] or for complex sugars via formose reactions [9]. Carbonate bonding is prevalent in the CR as well as in the IDP samples, not always as discrete calcite grains, but dispersed within the organic matter, which underlines the importance of fluids for organic synthesis reactions. Furthermore, we could document strong nitrogen functionality (C-N nitrile/imine or imidazole and NH_x amine bonding) in the CR grains, but so far not in the IDP organics. This may indicate the importance of fluids for advancing polymerization and stabilization reactions of N-compounds or the presence of functionally different primary nitrogen reservoirs sampled by cometary and asteroidal samples. Nitrogen functionality is of particular importance, as for example nitrile/imine and amine bonding environments are precursors of amino acids, whereas N-heterocycles such as imidazole are important constituents of nucleobases. Recent analyses by N-XANES on bulk samples of Tagish Lake organics have demonstrated as well that N-K edge functionality can be fitted by different amounts of amine and imine/nitrile or imidazole functional groups [10]. This supports recent ideas that aqueous complexation reactions starting from NH₂-bonding environments were catalyzed on meteorites parent bodies to form biorelevant molecules such as certain amino acids and nucleobases [11].

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