

NON-TARGETED ULTRAHIGH-RESOLUTION MASS SPECTROMETRY OF SOLUBLE ORGANIC MOLECULES IN SAMPLE RETURNED FROM ASTEROID BENNU. Ph. Schmitt-Kopplin^{1,2,3*}, M. Liss¹, M. Harir¹, D. P. Glavin⁴, J. P. Dworkin⁴, H. C. Connolly Jr.^{5,6,7}, and D. S. Lauretta⁶. ¹Technical University Munich TUM, Weihenstephan, Freising, Germany, ²Helmholtz Munich, Oberschleissheim, Germany, ³Max Planck Institute for Extraterrestrial Physics, MPE, Garching, Germany, ⁴NASA Goddard Space Flight Center, Greenbelt, MD, USA, ⁵Rowan University, Glassboro, NJ, USA, ⁶Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, USA. ⁷American Museum of Natural History, New York, NY, USA. *Email: schmitt-kopplin@tum.de.

Introduction: The surface material of the carbonaceous B-type asteroid Bennu was recovered during the touch-down sampling by NASA's Origins, Spectral Interpretation, Resource Identification, and Security–Regolith Explorer (OSIRIS-REx) spacecraft and delivered to Earth in September 2024. OSIRIS-REx mission collected samples from Bennu, providing a unique opportunity to study the composition and history of this asteroid. Especially the detailed analysis of organic matter (soluble SOM and insoluble IOM) plays a crucial role in understanding the presence of prebiotic organic compounds on Bennu. Samples from carbonaceous chondrites and from B-type asteroids such as Bennu can be considered as valuable chemical archives of the chemistry and its molecular evolution in the early phases of solar system formation. Here we present the first results on the methanol soluble organic matter (SOM) from a 3.3 mg aggregate sample of Bennu using ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectroscopy (FTICR/MS) [1–3].

The goals of this SOM analysis [4] using ultrahigh-resolution mass spectrometry were to profile organic compounds with the elements C, H, N, O, S, and Mg from the Bennu samples, and to compare these organic signatures to those from meteorites and JAXA's Hayabusa2 Ryugu samples. Such analysis enabled us already to evaluate possible alteration processes that may have occurred on Ryugu (temperature and shock stresses, water alteration) leading to organic matter preservation or specific transformations (e.g., sulfurizations) [5].

Samples: An aggregate sample (OREX-800031-0) scooped from inside the OSIRIS-REx sample collector weighing ~55 mg and consisting of a mixture of fine- to intermediate-sized particles was sealed in a N₂ glovebox at NASA Johnson Space Center and shipped to NASA Goddard Space Flight Center (GSFC) where it was subsampled in air for multiple analyses [6], including a 3.3 mg portion (OREX-803006-0) used for this study. A similar mass of the CM2 carbonaceous chondrite Murchison and a blank baked silica prepared at GSFC were also analyzed in this study.

Experimental Methods: We gently crushed the particles in a agate mortar with 400 µL methanol. The slurry was centrifuged and the 400 µL supernatant used for analysis. FTICR/MS equipped with a 12 Tesla superconducting magnet at the Helmholtz Center Munich

was used in direct sample injection with negative and positive electrospray ionization modes (ESI(-), ESI(+)) as well as in positive atmospheric pressure photoionization (APPI(+)). Detailed description of the analysis and data evaluation was described earlier [1, 3, 5].

Results and Discussion: The tens of thousands of signals obtained in ESI(-), ESI(+)- and APPI(+)-FTICR-MS were calibrated, filtered, converted, and cumulative assigned into more than 11.000 elementary compositions consisting of C, H, N, O, and/or S. Having analyzed similarly more than hundred carbonaceous meteorite samples with known thermal and water alteration history, the chemical profiles could be compared and integrated with known metadata on parent body history with AI and chemometrics procedures. As for meteorite and Ryugu SOM, the mass spectrometric data show a continuum of elementary compositions in the C, H, N, O, and S space reflecting the chemosynthetic pathways involved. Only few organomagnesium compounds (CHOMg, CHOSMg, CHONMg) were found in the Bennu aggregate; this likely reflects the relatively low/medium-temperature processes on the Bennu parent body [2, 3]. While the Ryugu sample showed the importance of sulfur chemistry similar to CI meteorites and Tarda [5] in ESI(-)-FTICR/MS, Bennu's soluble organic composition is specifically S-poor and more N-rich with abundant oxygenized nitrogen chemistry closer to Murchison CM2. The electrospray ionization showed very polar, nitrogen and oxygen rich compounds, while the photoionization enabled the profiling of substituted polyaromatic hydrocarbons with less nitrogen compounds than described earlier in Ryugu [5].

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