

## IN-SITU ORGANIC COMPOUND ANALYSIS OF THE METEORITE SURFACE BY DESORPTION ELECTROSPRAY IONIZATION COUPLED WITH AN ORBITRAP MASS SPECTROMETER.

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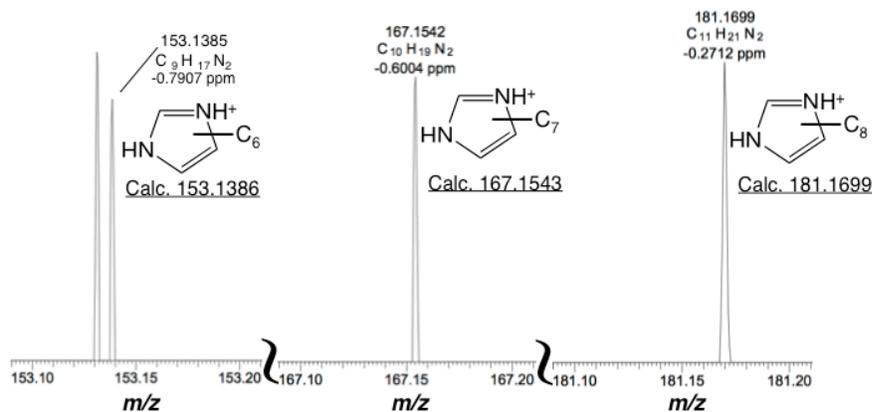
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**Introduction:** Carbonaceous chondrites contain a wide variety of organic compounds, which have been generally identified by mass spectrometry (MS) coupled with gas or liquid chromatography (GC or LC) using the solvent extracts of powdered samples. In-situ analysis of organic compounds for extraterrestrial materials has been performed by a few methods including two-step laser MS [1]. However, these methods are applicable to volatile compounds such as polycyclic aromatic hydrocarbons, and difficult to analyze polar compounds particularly for high-molecular compounds. A high-resolution MS (HRMS) analysis revealed more than hundred of thousands ion peaks consisting of CHO, CHNO and CHNOS in elemental compositions from the various solvent-extracts from the Murchison meteorite [2], even though the CH and CHN compositions were not reported. Recently, abundant CHN compositions were identified in the methanol extract of Murchison using LC-HRMS [3], in which two homologous series of alkylated pyridines were predominant. In this study, in-situ analysis of organic compounds on the meteorite surface was performed by desorption electrospray ionization (DESI) [4] coupled with HRMS.

**Methods:** The carbonaceous chondrites including Murray (CM2) were examined in this study. The small meteorite fragments (~ a few mm) were obtained by chipping. The relatively flat samples bearing the fresh surface were embedded on an indium (In) plate and subjected to DESI-HRMS analysis using a DESI ion source (Omni Spray Ion Source 2-D, Prosolia) coupled with a hybrid quadrupole-Orbitrap mass spectrometer (Q-Exactive Plus, Thermo Scientific). A DESI spray solution was MeOH at a flow rate of 1.5  $\mu$ L/min. The nebulizer N<sub>2</sub> gas pressure was set at 100 psi and the spray solution was electrically charged to ~3 kV. The positive ions were collected in full scan mode ( $m/z$  100-500) with mass resolution of 70,000 or 140,000 ( $m/\Delta m$  at  $m/z$  200). DESI-MS imaging was conducted using a motorized x-y stage with spatial resolution of ~50  $\times$  50  $\mu$ m.

**Results and Discussion:** Large amounts of ion peaks ranging from  $m/z$  100 to 500 were detected from the surface of Murray. They included both indigenous and contamination signals, because many peaks with the same  $m/z$  were observed from the surface of the background (In plate). However, indigenous peaks of meteorite origin were discriminated from the background using the ultrahigh mass resolution. Alkylated imidazole homologs (C<sub>n</sub>H<sub>2n-1</sub>N<sub>2</sub>) were identified (Fig. 1), which were found as a major component in the MeOH extract of the bulk sample. The DESI imaging revealed that the alkyimidazoles occurred in the matrix, probably being associated with clay minerals. This study indicates that DESI-HRMS is an effective method to identify polar organic compounds on the surface of extraterrestrial materials. Further analytical developments (e.g. sample preparation, composition of spray solvents and spatial resolution) is promising to characterize the organic compound distribution in meteorites.



**Fig. 1.** High-resolution mass spectra of alkylated imidazole homologs (C<sub>n</sub>H<sub>2n-1</sub>N<sub>2</sub><sup>+</sup>; n=9-11) detected from the surface of the Murray meteorite by DESI-HRMS. Note that the alkylated-imidazole was protonated as [M+H]<sup>+</sup>. The observed exact mass matched with the corresponding calculated value within 1 ppm in mass precision.

**References:** [1] Clemett S. J. et al. 1993. *Science* 262:721–725. [2] Schmitt-Kopplin P. et al. 2010. *Proceedings of the National Academy of Sciences* 107:2763-2768. [3] Yamashita Y. and Naraoka H. 2014. *Geochemical Journal* 48: 519-525. [4] Takats Z. et al. 2004. *Science* 306: 471–473.