

NON-TARGETTED ANALYSES ON SOLUBLE ORGANIC COMPOUNDS IN CHONDRITES.J.Isa¹ and F.-R. Orthous-Daunay¹ and H.Naraoka²¹Univ. Grenoble Alpes, CNRS, IPAG (CS 40700 38058 Grenoble Cedex 9, France. isaj@univ-grenoble-alpes.fr)²Kyushu University, (744 Motoooka, Nishi-ku, Fukuoka 819-0395 Japan)

Introduction: The solar system origin and subsequent evolution of organic matter are still not well understood. Inorganic chondritic components, bulk elemental compositions, and the petrography of chondrites group reflect different accretionary components. Also, the petrological observations of alterations/metamorphism in the chondrites shows evidence of the geological evolution since accretion and of the parent body processes that result in the variety of rock types we see today across chondrite groups. The fact that the vast majority of organic compounds are subject to reactions that lead to synthesis, degradation, and alteration during geological processes helps to explain why the overall picture of organic compound distribution is still unclear. Although the majority of organics in chondrites are large, insoluble organic compounds and soluble organic compounds (SOCs) such as the ones that are essential for life have been identified in meteorites and are of great interest to the origin of life in the universe. Targeted analyses have successfully identified a wide variety of pre-biotic organic compounds in meteorites [1]. Non-targeted analyses have started revealing the complexity of SOCs including the discovery of a new type of metalorganic [2,3]. In order to comprehensively study SOCs in meteorites including carbonaceous and non-carbonaceous chondrites, we have applied non-targeted analyses on the solvent extracts from chondrites and measured them by using the nano-ESI direct-infusion with a high-resolution Orbitrap mass spectrometer.

Measurements and data processing: We have studied CR, CM, LL, and R chondrites from Antarctic meteorites, (MIL 090657, EET 96029, Y-793596, and PRE 95404). Each meteorite was subsequently extracted by solvent (hexane, dichloromethane, methanol, and 100 °C water). The methanol extracted organics were analyzed using the high-resolution Orbitrap mass spectrometer at Kyushu University. After we acquired the spectra, we utilized post processing data analysis tools developed in-house (R programming language and Igor) to study the Orbitrap data. The analysis used the mzR package in the Bioconductor tool kit and Proteowizard software to convert the data format from vendor raw data to mzML mass spectrometer data [4]. The Igor-based software was also used for the data analyses. The post-processing includes mass-drift correction, peak detection, blank subtractions, and noise rejection.

Results: Chemical formulae were heuristically assigned for individual peaks in the Orbitrap data and we have been able to identify the major compounds found in the CM chondrite extract by using the positive ion modes. The CM extract contains N-bearing organic compounds that are similar to and consistent with the organic compounds found in a methanol extract from the Murchison meteorite. In our CM chondrite analysis, we were able to assign approximately 60% of major peaks that were detected as singly plus charged $C_nH_nN_nO_n$ compounds to within 5 ppm of mass precision between m/z 300 and 750. For this data reduction, we used the following assumptions: 1) ion intensity consistent with the $^{12}C/^{13}C$ isotope pattern; 2) select singly charged state compounds or m/z of doubly charged state compounds are multiplied by two; and 3) reasonable H/C, N/C, and O/C ratios that are 0.1-6, 0-4, and 0-3 (by atomic weight), respectively. Among the assigned $C_nH_nN_nO_n$ compounds, approximately 20% of compounds were assigned as $C_nH_nN_n$. In contrast to CM analyses, very few peaks were detected from LL extract. The LL data set is not large enough to demonstrate the characteristics of chemical formulae. In contrast, a significantly complex spectrum was obtained from the R chondrite extract. In order to decode the complex spectra, we performed some filtering: 1) subtracted peaks that appeared in the CM and LL analyses; 2) made subsets for peaks of singly charged ions and doubly charged ions; and 3) selected the data which only have ion intensities consistent with the $^{12}C/^{13}C$ isotope pattern. After the subtraction of CM and LL spectra, nearly 5000 unique peaks were detected in the R chondrite spectra in the m/z range of 50 to 750. However, only about 50 peaks remained after selection steps 2) and 3) were applied. One of the remaining peaks can be assigned with the elemental pattern of $C_nH_nN_nS_n$. The results suggest that this complex spectrum includes compounds consisting of multiple hetero-elements possibly besides N, O, and S. We will develop new tools to identify such elements. We are in the process of performing CR chondrite data analysis and data reduction for the negative mode analyses. We will present results outlining major differences in organic compound distributions amongst the different chondrite groups.

References: [1] Naraoka H, et al., ACS Earth Space Chem. 2017;1:540-550 [2] Schmitt-Kopplin, P., Proceedings of the National Academy of Sciences, 107(7), 2763-2768. [3] Ruf, A. et al., (2017) Proceedings of the National Academy of Sciences, 114(11), 2819-2824. [4] Chambers, M. C. et al., (2012) Nature biotechnology, 30(10), 918.