SMELLS LIKE TEEN SPIRIT: VOLATILE ORGANIC COMPOUNDS IN CARBONACEOUS CHONDRITES.

J. C. Aponte[1,*], F. Séguin[1,2], A. J. Siguelnitzky[1,3], J. P. Dworkin[1], J. E. Elsila[1], D. P. Glavin[1], H. C. Connolly Jr.[4,5,6] and D. S. Lauretta[4], [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771, [2]The Catholic University of America, Washington D.C. 20064, [3]Sig Engineering LLC, Laurel, Maryland 20707, [4]Lunar and Planetary Laboratory, University of Arizona, Tucson, Arizona 85721, [5]Rowan University, Glassboro, New Jersey 08028, [6]American Museum of Natural History, New York, NY 10016. *Email: Jose.C.Aponte@nasa.gov

Introduction: Volatile organic compounds (VOCs) are free organic molecules that may evaporate or sublimate at standard temperature and pressure. Formed through a series of chemical mechanisms involving processes such as ion/neutral surface-chemistry synthesis on pre-solar icy dust grains [1], VOCs have been trapped inside meteoritic matrixes and are part of the molecular inventory of our primitive solar system [2-4]. Like soluble and insoluble organic matter (SOM and IOM), VOCs have remained unaltered by biological and geological processes since their formation early in solar system. Evaluating their abundance and molecular distributions offers key insights into the chemistry and processes that occurred during the early stages of solar system formation and the effects of parent body processing.

Analytical methods: The analysis and compound-specific isotopic analysis (CSIA) of meteoritic SOM are commonly done by crushing a meteorite chip and extracting the SOM using polar and non-polar solvents [5]. It is expected that an undetermined amount of pressure, and thus, heat, is applied to the meteorite chip during sample powdering, and therefore, sample crushing may lead to VOCs loss [6]. Further, crushing a meteorite sample could result in the partial thermal degradation of labile SOM and IOM leading to the potential formation of VOCs as decomposition products (e.g., methane, CO_2). Thus, to avoid these drawbacks associated with typical protocols used for the study of meteoritic organics, we designed and custom-build a front-end meteorite disaggregation and extraction unit that can powder the meteorite sample at cold temperatures by disaggregation after a series of freeze-thaw cycles (using liquid nitrogen) while effectively trapping native meteoritic VOCs. This setup allows the study of VOCs and will help us understand the VOC inventory samples from asteroid Bennu brought back to Earth by NASA's OSIRIS-REx mission.

We tested our setup for ^{13}C isotope fractionation in the extract headspace during volatile desorption after freeze-thaw cycling. By comparing the isotopic values of a range of solvents (e.g., methanol, acetone, diethyl ether, etc.) in water versus those values obtained after direct injection on compounds, we found that the $\delta^{13}C$ isotopic values for direct GC injections and those for the freeze-thaw apparatus desorption agree within error, suggesting that only modest and, in some cases, not statistically significant $\delta^{13}C$ isotopic fractionations are recorded when desorbing the organics using the freeze-thaw apparatus. From those experiments using solvents we noted that water-soluble VOCs are not fully desorbed from the water even at 60 °C and 100 °C and that successive extraction and desorption cycles are possible without significantly affecting their ^{13}C-isotope values. This observation suggests that isotopic fractionation of organic VOCs is not extensive under freeze-thaw conditions, however, the abundance of the compounds we found do not represent the total concentration of a given species in the meteorite samples and that an undetermined portion of any given compound may still be retained in the aqueous extract. Therefore, our results should be considered as referential lower limits.

Results and Discussion: Using the freeze-thaw disaggregation setup for the analysis of the Murchison meteorite allowed the identification, quantification, and CSIA of 24 VOCs including molecules containing 1-10 carbon atoms including aldehydes/ketones, and aromatic compounds such as alkylbenzenes and naphthalene. Because CO and CH_4 cannot be cryogenically trapped using a liquid nitrogen bath as they flow under reduced pressures [3], we did not attempt to analyze CO and CH_4 as individual species. Instead, these gases flowed through the oxidation reactor and were converted to CO_2 for analysis. Although the concentration individual species in the CO+CH_4 mixture cannot be disentangled using our current setup, we detected ~1 μmol/g of CO+CH_4 in Murchison, which equates to concentrations that are about three orders of magnitude higher of those previously reported for CO and/or CH_4 in Murchison [3,4]. We also observed large quantities of CO_2 released from the meteorite extract with $\delta^{13}C$ values linking its origins to dissolved carbonates in the sample. This analysis is planned on a sample from asteroid Bennu delivered to Earth by the OSIRIS-REx mission.

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