DEVELOPMENT OF A NEW CLOSED SYSTEM SAMPLE CRUSHER FOR ANALYZING HYPERVOLATILE ORGANICS IN CARBONACEOUS CHONDrites AND BENNU SAMPLES. Y. Huang¹ (yongsong_huang@brown.edu), E. Santos¹, B. Kim¹, M. R. Alexandre¹, R. Milliken¹, P.R. Heck², Y. Zheng³, D. P. Glavin³, J. P. Dworkin⁴, H. C. Connolly Jr⁵,⁶, D. S. Lauretta⁷, ¹DEEPS, Brown University, Providence, RI, USA, ²Robert A. Pritzker Center for Meteoritics and Polar Studies, Negaunee Integrative Research Center, Field Museum of Natural History, Chicago, IL, USA, ³NASA Goddard Space Flight Center, Greenbelt, MD, USA; ⁴Department of Geology, Rowan University, Glassboro, NJ, USA; ⁵Department of Earth and Planetary Science, American Museum of Natural History, New York, NY, USA, ⁶Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, USA.

Introduction: Samples collected from the surface of the carbonaceous B-type asteroid Bennu and returned to Earth by the Origins, Spectral Interpretation, Resource Identification, and Security–Regolith Explorer (OSIRIS-REx) mission offer pristine materials for organic characterization. One hypothesis in the OSIRIS-REx Sample Analysis Plan [1] is that asteroid Bennu contains significant interstellar components. A fundamental scientific question is to what extent the volatile organic compounds, especially the hydridolite C₇ to C₈ alkanes or alkenes are formed in interstellar clouds, the presolar molecular cloud, the solar nebula, and/or parent bodies. Argument against their interstellar origin centers around the difficulty for these compounds to survive the collapse phase and formation of the solar nebula due to their high volatility [2].

The most definitive evidence for their interstellar origin would be their δD values, as it is well known that hydrogen-bearing molecules in dense interstellar clouds are highly enriched in deuterium, resulting from the strong isotopic fractionation that accompanies ion-molecule reactions taking place at the very low temperatures characteristic of such clouds [2]. Yuen et al reported δ¹³C values of C₁ to C₃ n-alkanes [3]. However, C isotopic data alone is insufficient to demonstrate an origin from interstellar clouds. Butterworth et al. [4] attempted to determine δD of methane in Murchison by subtracting the ¹³C/¹²C ratio from the CH₄ mass 17/16 ratio to measure methane δD and obtained a value of +77±50 ‰. However, there is no demonstration so far (e.g., by using methane with known δD values) that such approach can obtain reliable H isotopic compositions.

Samples: Two Murchison fragments from the Field Museum of Natural History in Chicago (~0.5 g and ~0.6 g) were used for gas chromatography-mass spectrometry (GC-MS) and GC-isotope ratio mass spectrometry (IRMS) analyses, respectively. The Bennu sample fragment will be studied in the same way as Murchison.

Analytical methods: Sample fragments were crushed using a newly designed closed system sample crusher made of stainless steel. The crusher was modified from that designed for analyzing volatile hydrocarbons in fluid inclusions in Earth rocks [5]. To avoid organic contamination, expanded Teflon™ was used to replace rubber gaskets. After loading the samples into the crusher, the sample was crushed with up to 5 tonnes of pressure, with intermittent piston rotation and vibration. Volatile gases were subsequently purged into GCMS and GCIRMS. A Frontier Lab MicroJet liquid nitrogen cryotrap was used to trap volatiles and hypervolatiles. Subsequently, the trapped gasses were separated using a Porabond GC column (50m x 0.32mm x 5µm) with the following oven program: 30 °C (15 min), 2 °C/min to 150 °C (5 min), 20 °C/min to 280 °C (25 min).

Results: Volatile organic compounds found include C₁ to C₆ straight chain and branched alkanes and alkenes, benzene, C₁ to C₃ alcohols, C₂ to C₃ aldehyde and ketones, C₁ sulfur compounds and tetrahydrofuran. Though the hypervolatiles could not be totally chromatographically resolved, we were able to measure δD on Murchison methane since co-eluting species (e.g., CO, N₂) do not contain H atoms. Variable peak intensities were achieved for other volatiles, but only those with intensities higher than 300 mV are shown in Fig.1, along with their δD values.

Discussion: All C₁ to C₄ alkanes and alkenes have positive δD values. Of the three C₄ alkane and alkene measurements, the branched 2-methyl propane has ~190 ‰ higher δD value than the butane and but-2-ene. Methane has the highest δD value among all hydrocarbons we measured. The isotopic pattern is consistent with those observed previously in carbon isotopic values, with shorter chain length or branched compounds showing more enriched C isotopic values than their counterparts [3]. It is the first time that compound specific δD values of C₁ and C₃ alkanes and alkenes were measured. Our data suggest that methane (the most volatile compound among all organic compounds in the universe) in Bennu, at least partially, is of interstellar origin.

Acknowledgments: This research is funded by NASA grant 80NSSC22K1691 and under award NNH09ZDA007O and contract NNM10AA11C and the TAWANI Foundation.
