DETERMINATION OF TRACE-ELEMENT BULK COMPOSITION OF EQUILIBRATED ORDINARY CHONDRITE METEORITE SAMPLES BY LA-ICP-MS USING VARIOUS REFERENCE MATERIALS.

A.V. Andronikov[1], D.S. Lauretta[1], H.C. Connolly Jr.[1,2,3], and I.E. Andronikova[1], [1]Lunar and Planetary Laboratory, University of Arizona, 1629 E. University Ave., Tucson, AZ 85721, USA (andron@lpl.arizona.edu), [2]Dept. Physical Sci., Kingsborough Community College of CUNY, Brooklyn NY USA and Dept. of Earth and Environmental Sciences, The Graduate Center of CUNY New York, NY USA; [3]Dept. of Earth and Planetary Sciences American Museum of Natural History New York, NY 10024, USA.

Introduction: In September 2016, a mission to return pristine sample of asteroid material (OSIRIS-REx) will be launched to the near Earth asteroid 1999RQ36. This asteroid is a B type and is thought to be compositionally similar to carbonaceous chondrites (CC) [1]. One of the objectives of the preparation stage of the mission is to compile a spectral library of CC analog meteorites to the asteroid. A transitional target in this work is to determine precise bulk composition of CC to be used for further spectral analyses. Since CC are known to contain relatively abundant organic material [2], they are tough to dissolve by conventional acid digestion for further ICP-MS analysis. One technique for obtaining a bulk composition of material that does not involve the dissolution of samples is LA-ICP-MS. We report on our results using LA-ICP-MS to determine bulk compositions of chondrites.

Material: We used samples of more abundant equilibrated ordinary chondrites (EOC) as a proof of concept for further analyses of rare CC. We analyzed L4 Gold Basin, L5 Sierra Colorada, and L6 Broken Hill. Pulverized material of each sample was pressed to pellets for the LA-ICP-MS analyses. As reference materials (RM) for laser ablation (LA), we applied NIST-610 and NIST-612 synthetic glasses, BCR-2G, BHVO-2G and BIR-1G USGS natural basalt glasses, and a pellet prepared from pulverized material of carbonaceous CV3 Allende meteorite (the composition is certified by the Smithsonian Institute). All sample preparation and analyses were performed at the University of Arizona in the Nine Circles cosmochemistry laboratory.

Methods: *ICP-MS.* Pulverized material from each meteorite sample (~50 mg) was digested in a mixture of concentrated HNO_3 and HF. The solution was dried down and then brought back to the solution with 5% HNO_3. The solutions yielded approximately 100 μg/ml of total dissolved solids. An analytical blank solution was prepared using the same procedure. A Finnigan Element2 HR-ICP-MS (E2) was used for analysis. Solution standards consisted of known amounts of the analyzed elements, were prepared using multi-element standard solutions. Sample concentrations were determined by first subtracting blank signal intensities from those obtained from the sample and standard solutions. A calibration curve was obtained by performing a linear least-squares regression for each element using the blank-subtracted counts and the known concentrations in each standard solution.

LA-ICP-MS. The sample pellets were prepared from pulverized EOC material with the use of a simple "bolt-nut-bolt" configuration. A CETAC Nd:YAG LXS-213 laser coupled with the E2 was used for analysis. The laser was operated in a 6-spot rastering mode. During the analytical runs, the laser beam was focused onto the sample surface with 150 μm-diameter spot, the laser was operated at 50% energy, 20 Hz frequency, and 300 shots per a spot with the He flow rate of ~700 mL/min. Repeated analyses of the reference materials ensured that all results are consistent and comparable. The measurements were based on integrated multi-element time-resolved signals. Each EOC sample pellet was analyzed with respect to each mentioned above RM.

Results: The results of the analytical runs are summarized in Figure 1, which shows relation between the data obtained with the use of the ICP-MS and LA-ICP-MS techniques. We analyzed concentrations of 34 trace elements (Sc, Ti, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Sn, REE, Hf, Ta, W, Pb, Th, and U) in each sample.

Reference concentrations of trace elements in EOC samples were determined in solution using the ICP-MS method by analyzing three solutions for each sample. The results were then averaged. All results obtained by the ICP-MS are consistent with known composition of EOCs [3].

Cross analyses of laser ablation reference materials. Determination of composition of the RM using other reference material as analytical standards showed that in spite of different trace element concentration in different individual RM, the applied LA technique provides high quality results for most elements.

Analytical results for EOC pellets. Analyses of meteorite compositions using the NIST-610 and NIST-612 glasses as RM showed that resultant compositions of the samples differ strongly from the reference concentrations obtained with the use of the ICP-MS technique. Results closer to the reference concentrations were obtained for such elements as Ti, Co, Ni, Sr, Y, Zr, and some of the REE, whereas such elements as Cr, Zn, and Pb showed concentrations 10 and more times higher than in reference solutions. Compositions obtained with the use of basalt glasses BCR-2G, BHVO-2G and BIR-1G are not very different from those obtained with the use of the NIST glasses for most trace elements. However the results obtained with the use of BHVO-2G and especially BIR-1G are much closer to reference values than those obtained with respect to the BCR-2G RM. Unlike the case of the glass RM, compositions calculated with respect to Allende CV3 meteorite material are very close to the results obtained by the ICP-MS. Only such elements as Sc, Cr, V, Zn, W, Pb and some MREE display deviation up to 3 times from the reference concentrations.

Discussion: It seems that during the LA runs, we encountered what is known as a "matrix effect". The laser beam hitting the surface of the pellets creates big holes in the analyzing material. Such holes are incomparable in size with those forming during the laser beam interaction with the surface of the glass RM. Formation of big holes in pellets suggests delivery of much higher amount of material to the ICP-MS analyzer than in the case of the glass. That creates inconsistencies between the calculated and real composition of the samples. As it was shown by the analyses of the pellets of EOC material with respect to different RM, the only way to reliably use sample pellets is to analyze them along with the RM prepared by the same method and from the material compositionally similar to the analyzing meteorite (Allende meteorite in our case). Ideally, an appropriate RM should be analyzed after each analytical run of the studying sample. We intend to continue our search for a fully appropriated RM to analyzed meteorite sample pellets with the use of the LA-ICP-MS technique.

Acknowledgements: Authors are very grateful to M. and K. Killgore who provided us with meteorite samples. This study was supported by the OSIRIS-REx program.

References: [1] Clark BE et al. (2011) *Icarus* 216, 462-475 [2] Ehrenfreud P and Charnley SB (2000) *Annu. Rev. Asron. Astrophys.* 38, 427-483, [3] Friedrich JM et al. (2003) *GCA* 67, 2467-2479, [4] Anders E and Grevesse N (1989) *GCA* 53, 197-214.

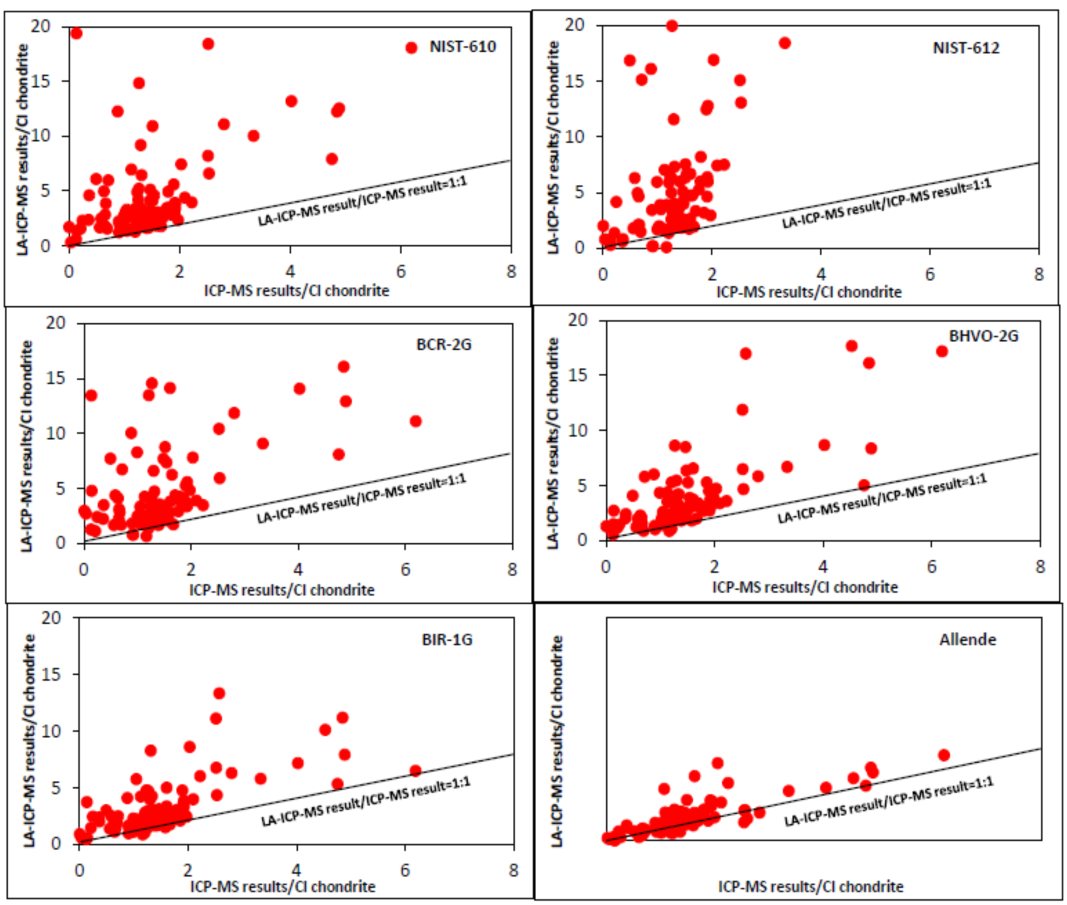

Fig. 1. A comparison between the results obtained by the LA-ICP-MS and ICP-MS methods. Different RM were used for the LA-ICP-MS analyses. Red dots, concentrations of individual trace elements normalized to CI chondrite [4].