

MORE SCIENCE WITH LESS: A WORKFLOW TO MEASURE ISOTOPIC COMPOSITIONS OF 16+ ELEMENTS IN 500 MG OF CHONDRITIC MATERIAL. G.A. Brennecka^{1*}, J. Render¹, Q.R. Shollenberger¹, T.S. Kruijer¹, J. Wimpenny¹, E.A. Worsham¹, L.E. Borg¹, H. C. Connolly Jr^{2,3,4}, D. S. Lauretta³, ¹Lawrence Livermore National Laboratory, 7000 East Ave., Livermore, CA, 94550 USA; ²Department of Geology, Rowan University, Glassboro, NJ, USA; ³Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, USA; ⁴Department of Earth and Planetary Science, American Museum of Natural History, New York, NY, USA. (*brennecka2@llnl.gov)

Introduction: Getting the most information possible out of the material available is a good practice for any science involving physical samples. However, this mantra is acutely important when dealing with material returned from a space mission. As such, the impending return of material by the OSIRIS-REx mission from asteroid Benu [1] necessitates participating laboratories prepare for judicious use of limited material, particularly when destructive analyses are involved.

Cosmolocation and provenance of extraterrestrial material—including the study of Benu’s relationship to known meteorites—can be addressed through quantifying non-mass-dependent isotopic variations. Such variations can be caused by radioactive decay, nucleosynthetic source differences [e.g., 2–4], or secondary neutron reactions [e.g., 5, 6]. However, this type of research typically requires complete dissolution of a significant portion of a bulk sample. Considering that Benu is assumed to be similar in its chemical composition to CI or CM carbonaceous chondrites [e.g., 1, 7], an isotopically representative sample cannot be obtained from only a few milligrams of material. Additionally, hundreds of milligrams of material is often required to achieve the analytical uncertainties necessary to discern small nucleosynthetic differences from trace constituents in carbonaceous material.

Using the expected sample mass available for bulk analyses from Benu [1] and the goal to obtain high-quality data on as many isotope systems as possible, we have devised a chemical separation protocol to purify at least 16 individual elements useful for obtaining radiogenic information, nucleosynthetic composition and/or neutron dosimeter data from ~500 mg of carbonaceous chondrite-like material. Using this chemical procedure, the elements Ti, Cr, Fe, Ni, Sr, Zr, Mo, Ba, Nd, Sm, Gd, Dy, Er, Yb, Hf, and W are purified to mass spectrometry readiness with ample amount to achieve state-of-the-art precision for each given system.

Method: Starting from ~500 mg of dissolved carbonaceous chondrite material, the solution is divided into three primary aliquots, designated A, B, and C, representing 1%, 9%, and 90% of the original solution, respectively. Aliquot A remains unprocessed and is used to measure major and trace element concentrations

of the entire sample. Aliquot B is utilized for isolation of major element isotopic compositions (i.e., Ti, Cr, Fe, and Ni). The largest aliquot, C, is used as the source of the trace element isotopics (i.e., Sr, Zr, Mo, Ba, Nd, Sm, Gd, Dy, Er, Yb, Hf, and W). A simplified flowchart is given in Fig. 1.

Major element isotopics. Aliquot B is first passed through an anion exchange column (AG1-X8) to separate Fe, Ti, Cr, and Ni from the matrix. Subsequently, a column of TODGA resin is used to separate Ti and an aliquot containing Cr and Ni. Each of these four elements targeted in aliquot B are further purified using a combination of anion and/or cation (AG-50W-X8) exchange resins (see Fig. 1 for details).

Trace element isotopics. Like the major elements, aliquot C is passed through an anion exchange resin, separating into aliquots primarily containing 1) Mo; 2) Sr, Ba, and rare earth elements (REEs), and 3) Zr, Hf, and W. The Mo is further purified using TRU resin, whereas a cation column is used to sequester Sr, Ba, and the REEs. The Sr-containing portion is cleaned with Sr Spec resin, and the REEs separated from one another using LN resin or an α -HIBA-based separation procedure. The solution containing Zr, Hf, and W is passed through a series of anion, TODGA, and LN resins to purify each element (see Fig. 1 for details).

Samples: In preparation for sample return by OSIRIS-REx, we are testing our full procedure—from sample dissolution to isotopic measurement—on Benu proxy materials for all 16 listed elements. Approximately 500 mg each of Allende (CV3), Murchison (CM2), Aguas Zarcas (CM2), Tarda (C2-ung.), and Calama 005 (CO3) are being processed to verify blanks, yields, and measurement accuracy. Not only is this good practice on the full procedure prior to arrival and processing of Benu samples, but the data obtained will be a baseline for comparison with similar samples run in parallel with those from Benu. All available elemental and isotopic data from the proxy materials will be presented at the conference.

Discussion: Conducting isotopic measurements of multiple elements (i.e., Ti, Cr, Fe, Ni, Sr, Zr, Mo, Ba, Nd, Sm, Gd, Dy, Er, Yb, Hf, and W) at the requisite precision from a single aliquot will provide cohesive information about Benu’s history. This combined

elemental suite represents a wide range of geochemical behaviors and isotopes formed by various radiogenic or nucleosynthetic processes. Therefore, these elements are integral for Solar System reconstructions, establishing Benu’s relationship to other known samples (if any) and, ultimately, determining where Benu formed in the Solar System.

In addition to supporting cosmolocalization research on Benu and its connection to other Solar System materials, some of the isotopic systems mentioned above also double as neutron dosimeters. Specifically, the surface evolution of planetary materials can be examined by the isotopic compositions of elements affected by cosmic-ray irradiation, which leads to secondary neutron capture reactions (Fig. 2).

The isotopes ^{149}Sm , ^{155}Gd , and ^{157}Gd have large thermal neutron capture cross sections, while ^{167}Er and ^{177}Hf have a high probability to capture epithermal neutrons [e.g., 5, 6]. Monte Carlo simulations using the abundances of these isotopes in conjunction with trace element abundances of the bulk sample can be used to determine the neutron fluences, thermal/epithermal neutron ratios, and energy profiles. This will constrain the exposure history of the samples on the surface of the parent body, informing us about the space weathering and resurfacing environment on Benu—an important compliment to Benu’s nucleosynthetic signature and relationship to known meteorites.

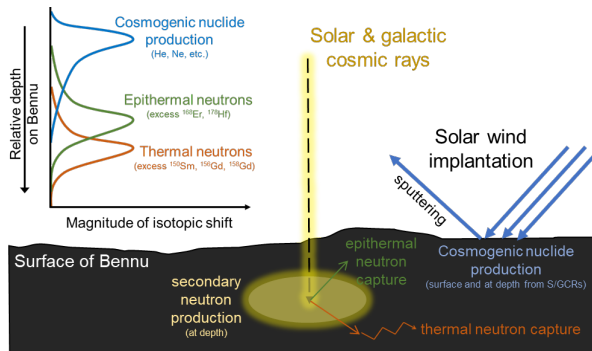


Fig. 2. Space weathering on a planetary body can cause shifts in a variety of isotopic systems; these shifts can be used to understand the weathering and resurfacing history of Benu (modified from [8]).

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References: [1] Laretta D.S. et al. (2022) *Science* 377, 285-291. [2] Warren P.H. (2011) *EPSL* 311, 93-100. [3] Render J. and Brennecka G.A. (2021) *EPSL*, 555, 116705. [4] Render J. et al. (2022) *EPSL*, 595, 117748. [5] Hidaka et al (2020) *ApJ*, 904, 183. [6] Sprung et al. (2010) *EPSL*, 295, 1-11. [7] Hamilton V.E. et al. (2019) *Nat. Astron.* 3, 332–340. [8] Noble S.K. (2004). Brown University Dissertation #3134328.

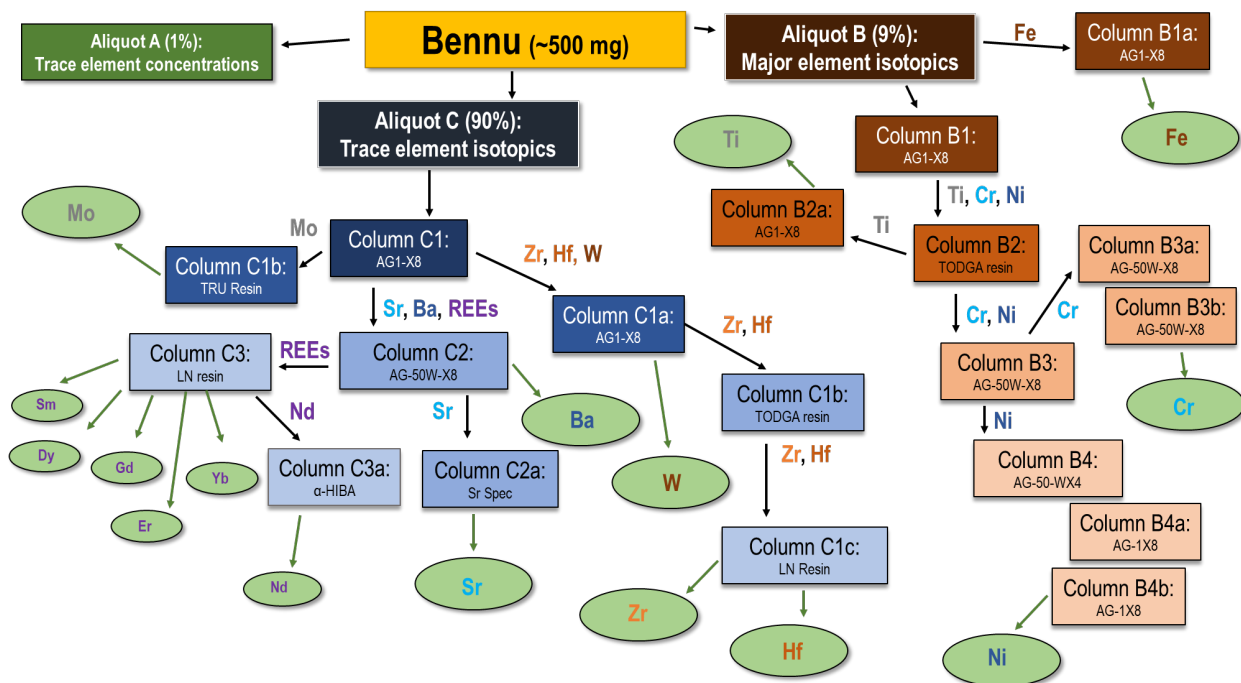


Fig. 1. The generalized flowchart for chemical separation and isotopic measurement of 16 elements from ~500 mg of Benu material. Green shapes represent aliquots ready for mass spectrometry and brown/blue color families indicate progress of the sample from each aliquot.