

MAXIMIZING MISSION RETURN SAMPLE SCIENCE THROUGH INTEGRATED INORGANIC AND ORGANIC ANALYSES. S. DiCarlo^{1,2}, A.M. Gargano^{1,3,4}, R.M.G Armytage⁵, W. Buckley⁵, J.B. Setera⁶, E. Berger³, J.I. Simon³. ¹Lunar and Planetary Institute (USRA), Houston, TX, 77058, ²Carleton College, 300 N College St. Northfield MN, 55057 (dicarlos@carleton.edu), ³ARES, NASA JSC 2101 E NASA Pkwy, Houston, TX 77058, ⁴Center for Stable Isotopes, University of New Mexico, Albuquerque, 87131, ⁵Amentum at NASA JSC, Houston, TX, 77058, ⁶University of Texas at El Paso/Amentum-JETS II, NASA JSC, Houston, TX 77058.

Introduction: We are entering a new era in space research as NASA missions target returning with extraterrestrial samples, such as OSIRIS-REx, Artemis, and the anticipated return of the samples collected by the Mars 2020 Perseverance Rover. With this increase in extra-terrestrial samples often collected under mass-limiting conditions, we need sample handling and processing procedures that maximize analytical capabilities on limited material. In this study, we worked on developing a procedural workflow that could combine inorganic trace element analysis with analysis of organic molecules in order to maximize scientific return from returned samples. We also investigated the effects halogen extraction using pyrohydrolysis has on trace element composition. This project used the Center for Isotope Cosmochemistry and Geochronology (CICG) and the Soluble Organics in Astromaterials Lab (SOAL) at the NASA Johnson Space Center and the University of New Mexico's Center for Stable Isotopes.

The chosen martian and near-Earth asteroid analogs were used to test the degree that these combined procedures affected trace element abundances in samples. The inorganic (CICG) and organic (SOAL) laboratories had different contamination concerns. The organic laboratory was concerned by plastic and biological particulates contamination, while the inorganic laboratory was concerned with low blank chemistry due to terrestrial particulate contamination.

We identified sampling handling procedures that would potentially be incompatible. The low blank alumina mortar and pestle used to crush the rocks in the CICG was not cleaned in a furnace at 500°C for 18 hours as the SOAL procedure required, and may have contained organics from past samples [1]. The hot water extraction step from the organic procedure would likely strip out many soluble elements, particularly the alkaline and alkali metals, and the halogens, and this would affect the subsequent trace element analysis [1]. The accuracy of the results from the combined procedure was tested using ratios of chemical elements indicative of planet-forming processes (e.g., core formation, silicate differentiation, fluid and volatile involvement) [2].

Samples: A suite of chondritic meteorites Allende (CV3), Murchison (CM2), EET 96029 (CM2), and LAR 12002 (CV3) as well as a diabase (9A-1) and metasediment (4A-1, 4A-2, 4A-3) from the Pilbara

region in Australia were used for analysis. USGS standards BHVO2 (Hawaiian Basalt), SDC-1 (Mica Schist), and AGV-1 (Andesite) were also used.

Chondrites are a type of undifferentiated meteorite that formed from the accretion of early formed solids in the protoplanetary disk 4.57 billion years ago [3]. They have varying proportions of four key constituents: chondrules, refractory inclusions (CAIs), metallic Fe-Ni, and matrix material [4]. Depending on the level of alteration, chondrites preserve a record of the constituents of the early solar system or of the chemical fractionation or mixing processes within the solar nebula and the protoplanetary disk [3].

The Murchison meteorite (CM2) has a fine-grained black matrix with white, irregular, angular, and crystalline clasts that range from 25µm to 100µm (Fig. 1). According to [5], these clasts are likely CAIs. A rim of lighter material encases the spherical clasts in Figure 1, which are likely chondrules[6]. Yellow discoloration on the meteorite indicates iron oxidation, and the vein of lighter material may indicate hydrothermal activity or terrestrial alteration (Fig. 1).

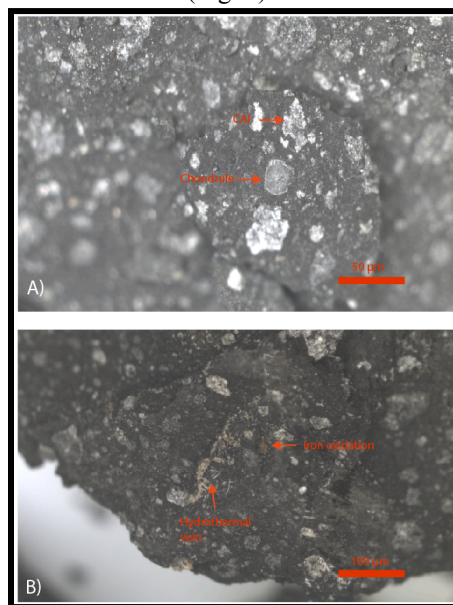


Figure 1: Murchison under a petrographic microscope.

Methods: A literature review of geochemical reservoirs within [7,8] was conducted to identify useful element ratios that represent signatures of planetary processes. Cr/V was identified as a common indicator of planetary core formation. Rb/Sr, Rb/Zr, and K/Ca were identified as common indicators of

fluid involvement. La/Ho and Ce/Yb were identified as common indicators of silicate differentiation.

Trace Element Analysis Procedure

The Murchison meteorite was crushed by hand using an alumina mortar and pestle. 50 mg of the crushed powder was placed in a Teflon vial, and one drop of water was added (after weighing) to the vial to counteract any static. Three “chips” were extracted from the metasedimentary Pilbara core, and one “chip” was extracted from the diabase Pilbara core. Chips from the same core were not homogenized. 50 mg of each of the terrestrial and the rest of the meteorite samples were similarly placed in 3 mL Teflon vials. Then, the Teflon vials were partially unscrewed in order to allow vaporized acid to enter the vial when heated. 4 mL of 3:1 HF: HNO₃ solution was added to Teflon vessel inserts, and the Teflon vial was placed in the Teflon vessel inserts. The Teflon vessel inserts were encased in Parr digestion vessels and placed inside an oven at 150°C for a minimum of two days. The vials were removed from the Parr digestion vessels, and the contents of the vials were transferred to 15 mL Teflon vials, where 5 mL of 50% HNO₃ was added. The vials were capped and placed on a hotplate at 120°C. After 48 hours, they were, uncapped and dried. Then, 3 mL of HNO₃ (2x distilled) was added to each vial and dried at 85°C. The samples were sonicated and transferred from the Teflon vial to a polypropylene bottle. Samples were diluted 2000-fold with 2% HNO₃. Next, samples were analyzed for inorganic trace elements via an Element XR ICP-MS. Procedural blanks were used to track contamination, and acid blanks were monitored for blank correction. Allende and BHVO-2 were used as calibration standards. Low-, medium-, and high-resolution instrument modes were selected for a suite of elements based on the Center for Isotope Cosmochemistry and Geochronology (CICG) standard operating procedures.

Pyrohydrolysis Procedure

Powdered rock samples were leached overnight at room temperature in DI water [9]. A 250 mL round bottom flask was connected to a quartz tube, and a rock

sample was placed within the tube [9]. The quartz tube was connected to a condensing column [9]. An oxy-propane glass-blowing torch was used to melt the rock sample while water vapor was pushed through the quartz tube [9]. The halogens were partitioned into the water vapor and collected as a solution. The solution was measured for halogens using an Element XR ICP-MS [9]. The residual rock sample in the quartz tube was chipped off, dissolved (see *Trace Element Analysis Procedure*), and measured for trace elements on the Element XR ICP-MS.

Results: Lithophile elements (Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Sc, Ti, V, Y, Zr, Nb, Hf, Ta, Al, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U, P, Cr), siderophile/chalcophile elements (Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb, P) were measured. Samples were normalized to a CI chondrite [10]. The plots in Figure 2 show a clear distinction between terrestrial and meteorite samples, indicating that they are useful ratios for this analysis.

Future Work: The ratios identified will be used to analyze trace elements from the residuals of SOAL’s organic procedure and the halogen extraction to investigate how trace elements are affected by these procedures. The lessons learned from this work will guide future sample handling procedures in coordinated inorganic and organic sample studies.

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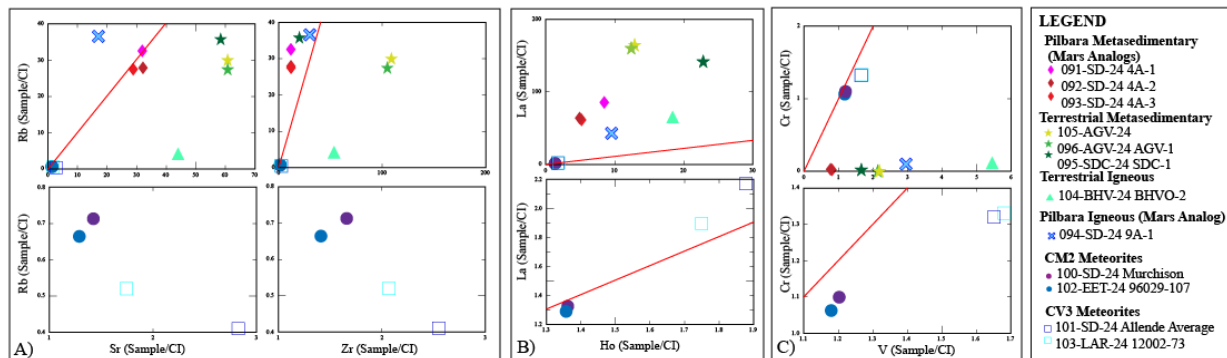


Figure 2: Ratios of elemental abundance in meteorite and terrestrial samples normalized to a CI chondrite [10]. The red line indicates a 1:1 ratio. A) Rb vs Sr and Rb vs. Zr, indicating fluid and volatile mobility. B) La vs. Ho and Ce vs. Yb, indicating silicate differentiation. C) Cr vs. V, indicating core formation.