DEVELOPING AN EFFICIENT COORDINATED ORGANIC ANALYSIS FOR RETURNED SAMPLES.
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Introduction: Measuring the abundances, distributions, enantiomeric ratios, and isotopic compositions of soluble organic compounds in extraterrestrial materials is a vitally important step towards understanding their chemical history and the potential exogenous delivery of prebiotic organics to the Earth. Analysis of soluble organic compounds requires sample preparation, including multiple extraction, purification, and concentration steps, which are essential but also place the sample at risk of contamination, alteration, and loss. Although many such methods have been reported in studies of meteorites and other returned samples [e.g., 1-13], there are few rigorous analyses of the trade-offs and consequences of the methods, making it difficult for researchers to make informed choices on how to handle precious and limited samples.

The variations inherent in different preparative methods, and the lack of information on the biases inherent in these methods, complicates interpretation of the resulting data, especially if comparing results from different procedures. For example, Figure 1 shows data from three different analyses of the monocarboxylic acid content in two carbonaceous meteorites. The comparison of carboxylic acid data resulting from the analysis Murchison and Graves Nunataks 92552 aqueous extracts that were prepared using substantially different methods (solid-phase micro-extraction for Murchison [1] vs. vacuum cryogenic transfer with dichloromethane extraction for GRA 95229 [2]) indicates that the Murchison extract has a higher abundance of these compounds. However, the opposite conclusion is drawn when examining extracts from these meteorites after preparing both samples in an identical fashion using a third technique [3].

The limited availability and the value of returned samples, such as the asteroidal material that will be returned by the Hayabusa2 and OSIRIS-REx missions, requires an optimized extraction protocol suitable for targeting a wide variety of organic compound classes during the preparation of modestly-sized (∼1 g) samples. Creating an efficient sample allocation and analysis plan demands an understanding of which analyses can be carried out on sequential extracts from a single sample, and which analyses must be performed in parallel on separate sample aliquots. The effects of choices that enhance analysis of one compound class at the expense of others must be well understood. In our current work, we aim to evaluate and optimize sample preparation methods to create a coordinated approach that (1) enables analysis of multiple soluble organic compound classes present in extraterrestrial materials, (2) maximizes efficiency of sample use, (3) allows for meaningful comparison of this data with previous measurements, and (4) parameterizes losses and changes in the organic complement as a result of sample processing.

Analytical Work: We are examining the effects of preparative methods on six key compound classes: amino acids, amines, carboxylic acids, aldehydes, ketones, and hydroxy acids (Figure 2). In addition, we will evaluate (but not optimize) the ability to analyze hydrocarbons, nitrogen heterocycles, and insoluble organic matter from the water-insoluble portion of samples.

The analytical protocol typically implemented begins with extraction, followed by an optional hydrolysis step and then purification. Figure 3 presents a flowchart of preparation steps leading to various

**Figure 1.** Very different conclusions are reached about relative abundances of compounds in two meteorites when they are analyzed using different preparative techniques (left, Murchison [13] and Graves Nunataks (GRA) 95229 [8]) vs. identical techniques (right, [14]).

**Figure 2.** Our work focuses on six structurally related compound classes.

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\begin{align*}
\text{NH}_2 & \quad \text{OH} \\
\text{H} & \quad \text{amino acid} \\
\text{NH}_2 & \quad \text{amine} \\
\text{O} & \quad \text{carboxylic acid} \\
\text{O} & \quad \text{ketone} \\
\text{OH} & \quad \text{aldehyde} \\
\text{OH} & \quad \text{hydroxy acid}
\end{align*}
\]
sample fractions that can be analyzed for specific compound classes. Our evaluation of protocol steps begins with the final and most complicated step: optimizing purification procedures. Purification protocols involve a combination of steps such as ion exchange or vacuum distillation to separate organic compounds, as well as dry-down steps to concentrate analytes of interest. Our work tests the recovery and fractionation of these methods. Once purification methods have been optimized, we will examine the effects of variables such as pH, temperature, and time on hydrolysis and extraction, using both standards and homogenized Murchison meteorite powder. The residue remaining after extraction will be analyzed for N-heterocycles, hydrocarbons, and insoluble organic matter in order to quantify the effects of serial analyses on these compound classes.

We will use the results of these analyses to produce a roadmap that details and assesses trade-offs and decision points to be considered in future analyses of soluble organic compounds in returned samples. Another important outcome of this study is to understand how the new optimized extraction methods compare to previous methods. This will help put previously published data into the appropriate context and therefore allow better comparisons to be made between meteorites.

### References: