

ANALYSES OF MOLECULAR AND COMPOUND SPECIFIC C AND H ISOTOPIC RATIOS OF VOLATILE ALDEHYDES AND KETONES IN MURCHISON USING HEADSPACE SOLID-PHASE MICROEXTRACTION ON-FIBER DERIVATIZATION. M. R. Alexandre¹ (marcelo_alexandre@brown.edu), Y. Huang¹, E. Santos¹, P.P. Heck², H. C. Connolly Jr.^{3,4,5}, D. S. Lauretta⁴. ¹DEEPS, Brown University, Providence, RI 02912, USA; ²Robert A. Pritzker Center for Meteoritics and Polar Studies, Negaunee Integrative Research Center, Field Museum of Natural History, Chicago, IL 60605-2496, USA; ³Department of Geology, Rowan University Glassboro, NJ, USA; ⁴Lunar and Planetary Laboratory, University of Arizona; ⁵Department of Earth and Planetary Science, American Museum of Natural History, New York, NY, USA.

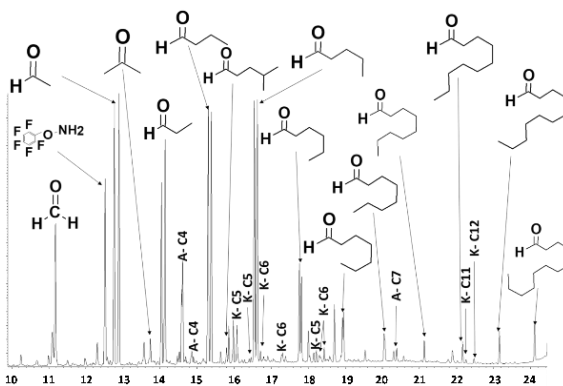
Introduction: For analysis of aldehydes and ketones in Murchison, currently published analytical methods [e.g.1,2] require "one-pot" derivatization into higher-molecular-weight compounds (e.g., aldehydes, ketones, and amines). For example, short-chain ketones and aldehydes can be derivatized using (S,S)-(-)-1,4-dimethoxy-2,3-butanediol (DMB) derivatization, and amines using (S)-(-)-N-(trifluoroacetyl) pyrrolidine-2-carbonyl chloride (TPC) [1,2]. These derivatization methods also permit compound-specific carbon isotopic analyses of ketones, and aldehydes in carbonaceous meteorites. Derivatization methods produce sufficiently high molecular weights of resulting derivatives, which avoids losses during the evaporative concentrating step. In addition, one class of compounds is analyzed each time so that chromatographic coelutions are minimized. If using an optically pure derivatization reagent, quantification of chirality is possible, and separation can be achieved using non-polar gas chromatography (GC) columns.

However, there are a few important caveats when using these derivatization methods. Derivatization reagents are functional group-specific, with volatile compound classes not targeted being lost in subsequent concentrating step. Thus, a pre-assumed fraction of original sample mass or bulk organic extractions must be dedicated solely to the analysis of aldehydes and ketones while other compounds are lost in the analytical procedure, resulting in high sample consumption. For high-value samples such as asteroid Bennu, the one-pot derivatization approach may not be practical. In addition, derivatization reactions in solution may result in the formation of artifacts from reaction by-products and reagent impurities. These artifacts will mix in the parent solution, hence affecting analysis of other compound class not targeted in the derivatization. Artifacts or impurities from derivatization reagents or processes are often low-molecular-weight volatile compounds and can be difficult to differentiate from indigenous compounds or cause chromatographic coelutions and baseline fluctuations. For compound-specific isotopic analyses, any chromatographic coelutions and baseline fluctuations can result in inaccurate isotopic measurements.

An alternative approach to overcoming problems associated with one-pot derivatization is to use solid-phase microextraction (SPME) with or without on-fiber derivatization. The main objectives of this study are to demonstrate the use of SPME on-fiber derivatization to analyze aldehydes and ketones using gas chromatography–mass spectrometry (GC-MS) and gas chromatography–isotope ratio mass spectrometry (GC-IRMS).

Methods and Results: For our analyses, we prepared an interior fragment of Murchison ME2644.26.92 from the Field Museum of Natural History. Our headspace SPME on-fiber derivatization methods for low-molecular-weight carbonyl compounds differ greatly from the conventional one-pot derivatization followed by solvent extraction previously used to characterize these compounds in carbonaceous chondrites [1,2]. The derivatization reagent used for low-molecular-weight aldehydes (and ketones) is 2,3,4,5, 6-(pentafluorobenzyl)-hydroxylamine (PFBHA) [3]. Before sample adsorption, the derivatization reagent is pre-loaded by headspace SPME on to the fiber [4] for 5 minutes. Subsequently, the fiber is exposed to the air space that has equilibrated

Fig. 1. Headspace SPME on-fiber derivatization of



Murchison carbonyls (A=branched aldehydes; K=ketones of variable carbonyl positions and alkyl substitutions) as PFBHA derivatives allows direct GC-MS analyses of these volatile compounds.

with aqueous extracts in a glass vial for 60 minutes at 50°C. Derivatization takes place only on the fiber surface in the headspace of the aqueous extraction solution. Thus, only a fraction of the target compounds that are airborne and to be analyzed by a specific instrument (GC-MS or GC-IRMS) are derivatized, whereas the remaining target compounds in solution stay in their original underivatized forms and do not contact the derivatization reagents. Derivatization reagent is functional group-specific (e.g., PFBHA will react with carbonyls group) and does not affect other compound classes in the vapor phase. Derivatized vapor phase target compounds on the fiber were transferred to GC-MS and subsequently into GC-IRMS for analyses. Our approach, therefore, minimizes any possible cross-contamination of the parent solution and minimizes sample consumption. We have identified at the level of structural composition 14 aldehydes, ranging from formaldehyde (C₁) up to dodecyl aldehyde (C₁₂) (Figure 1). Within the same pool of compounds, we also have identified three aldehydes and eight ketones with unknown structure. However, within more than 50 chromatogram peaks (Figure 1), it is possible that other compounds of interest are present.

Conclusions: Our SPME on-fiber derivatization approach represents a very promising non-invasive analyses of volatile carbonyls in carbonaceous meteorites (and Bennu samples), allowing compound-specific identification of aldehydes and ketones never before reported in Murchison. We will implement this analytical technique as part of the sample analysis phase of the OSIRIS-REx mission [5], focusing on constraining abundances within the returned regolith from asteroid Bennu, and including analyses of compound-specific isotope ratios.

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References: [1] Aponte, J.C. et al. (2014) *GCA* 141, 331-345. [2] Aponte, J.C. et al. (2019) *ACS Earth Space Chem.* 3, 463-472. [3] Bourdin, D. and Desauziers, V. (2014) *Anal. Bioanal. Chem.* 406, 317-328. [4] Parshintsev, J. et al. (2015) *J. Chromat. A* 1376, 46-52. [5] D. S. Lauretta et al. (2021) in *Sample Return Missions*, ed. A Longobardo (Elsevier): 163-194.