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**Cold Curation of Pristine Astromaterials:
Insights from the Tagish Lake Meteorite**

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To be submitted to:

Meteoritics and Planetary Sciences

Revised version of: November 12, 2015

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Abstract

The curation and handling of volatile-bearing astromaterials is of prime importance in current and future plans for sample return missions to targets containing organic compounds, ices, or other volatile components. We report on the specific curation constraints required for the preservation of the Tagish Lake meteorite, a C2 ungrouped chondrite that contains significant concentrations of organic matter, including compounds of prebiotic interest or volatile in character, and which was recovered from a frozen lake surface a few days after its fall. Here we review the circumstances of the meteorite's handling, its complement of intrinsic and contaminant organic compounds, and an unusual reaction between some of the specimens and the Al foil in which they were enclosed. From our results we derive the requirements for curation of the meteorite, and describe a specialized facility that enables its curation and handling. The Subzero Facility for Curation of Astromaterials consists of a purified Ar glove box enclosed within a freezer chamber, and enables investigations relevant to curation of samples at or below -10 °C. We provide several recommendations based on insights obtained from the commissioning and initial use of the facility that are relevant to collection of freshly fallen meteorites, curation of volatile-bearing meteorites and other astromaterials, and planning and implementation of curation plans for future sample return missions to volatile-bearing targets.

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1. Introduction

Extraterrestrial samples, including meteorites, lunar samples, solar wind, cometary dust, asteroidal regolith and interplanetary dust, provide a unique record of the conditions that prevailed during the formation of our solar system, and the geologic processes that have affected many of the planetary bodies within it. As noted by Allen et al. (2011), the majority of extraterrestrial samples formed in environments “strikingly different” from those found at the surface of the Earth. Furthermore, the relative scarcity of these materials makes it particularly pressing that they be preserved as close as possible to their original, natural states. The discovery of indigenous organic species within carbonaceous chondrites has generated widespread excitement because the complex organic materials delivered by carbonaceous chondrites may have played an important role in the delivery of prebiotic compounds to the early Earth (Chyba and Sagan, 1992). Tracking down the sources of the organic species within meteorites and developing a better appreciation of the chemical evolution of these species over the last ca. 4.5 billion years continue to be priorities for the meteoritical community (e.g., Botta and Bada, 2002)

In contrast to meteorites, which represent the random samples of their parent bodies, samples returned by dedicated missions are judiciously targeted from planetary bodies with documentation of the location and context from which the sample is collected. To protect the research value of the returned samples, maintenance of the pristine state of the samples during the initial sampling, the return cruise, the landing and, ultimately, the manipulation of the samples within analytical laboratories are essential. A critical facet of the planning and execution of sample return involves curation (Allen et al., 2011). However, terrestrial contamination continues to bedevil research on the indigenous organic compounds in astromaterials, in spite of the great advances made in the field of curation over the last forty years. This is because

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3 contamination by terrestrial organics begins the moment the samples are brought into the return
4 spacecraft. Such contamination can continue to accumulate throughout the cruise phase of the
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6 journey home, and then the risk of contamination rises appreciably as soon as the incoming
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8 extraterrestrial material is exposed to our biosphere, which is rife with both biotic and abiotic
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10 organic species. Protocols have been established which aim to both reduce the contaminant load
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12 and characterize it, e.g., through witness plates (Allen et al., 2011; Calaway et al., 2014;
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14 Sandford et al., 2010). However, much remains to be learned, especially as planetary exploration
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16 increasingly includes sample return, from increasingly challenging targets (e.g., Allen et al.,
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18 2011; Chesley et al., 2014; Tsuda et al., 2013).
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25 Modern curation facilities have as their primary goal the isolation of astromaterials from
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27 the terrestrial environment (Allen et al., 2011), especially sources of organic contaminants
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29 (Calaway et al., 2014). All modern curation facilities include a HEPA (High Efficiency
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31 Particulate Air) filtration system, which keeps the facility free from airborne contaminants.
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33 Specialized handling practices to limit the transfer of human-derived organics to the samples are
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35 utilized. Cleaning procedures and methods for identifying and monitoring contaminants are
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37 followed (e.g., Calaway et al., 2014). However, the manner in which astromaterials can be
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39 compromised extends well beyond simple sorption of non-indigenous materials on exposed
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41 surfaces or mixture with airborne dust. Oxidation and hydrolysis are extreme forms of invasive
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43 contamination as both processes permanently chemically alter the intrinsic compounds and
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45 minerals in the sample; for this reason, inert atmospheres are utilized in curation to limit reaction
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47 of the indigenous organics and minerals with atmospheric water and molecular oxygen gas. In
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49 addition, there is a real danger that volatile organic species ~~known from~~within carbonaceous
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51 chondrites, such as formaldehyde, acetaldehyde, C₁-C₂ monocarboxylic acids, C₁-C₃-amines,
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etc., will be partially or completely lost, especially if the temperature of the sample rises much above 0 °C. Thus the emphasis is on studies of curation methods that will maintain samples at subzero temperature from collection through to ultimate storage in a cold facility (Allen et al., 2011; Neal, 2000). Classical surface contamination, by contrast, occurs via physisorption, which leaves the mineral surface and the binding molecule intact (Rimola et al., 2010). In fact, the bonding between the physisorbed species and the surface is so tenuous, that even the relatively weak, through-space attractions developed between added solvent molecules and the sorbed organics ~~are~~is sufficient to dislodge the organic compounds from the mineral surface (Oura et al., 2003). Exposure to terrestrial water sources can also lead to the loss of water-soluble-species within the samples through the process of percolation. Clearly, the best option for storage, namely that which halts oxidation and hydrolysis while drastically limiting the loss of volatile organics and any water-soluble species, would be one that is both cold and inert. Recognizing this need, cold curation methods utilizing a -35 °C freezer and -35 °C cold plate in a glove box were tested by the curation group at the NASA Johnson Space Center (Fletcher et al., 2008a). Unfortunately, the cold plate results in a strong thermal gradient and a potential cold trap for contaminants, precluding its effective use in cold curation (Fletcher et al., 2008b).

The fireball produced by the entry of the Tagish lake meteorite was widely observed across northwestern Canada and parts of Alaska at 16:43 UT on January 18, 2000 (Brown et al., 2000). Several pieces of the meteorite were found on the frozen surface of Taku Arm of Tagish Lake on January 25 and 26 by a local resident, who collected some 45 stones without direct hand contact using a clean plastic bag (Hildebrand et al., 2006). The specimens were kept below 0 °C after collection and subsequent transfer to research institutions; some specimens were repackaged in Al foil while others were transferred to Teflon containers. A further 5-10 kg of

material were collected in the spring, just prior to breakup of the lake ice; these specimens were found embedded within the lake ice as a result of freeze-thaw cycling (Hildebrand et al., 2006). Having been exposed to liquid water, this suite of Tagish Lake specimens is typically referred to as “non-pristine” or “degraded”. Studies of the Tagish Lake meteorite demonstrate that it is an ungrouped Type 2 carbonaceous chondrite with affinities to CI and CM chondrites (Zolensky et al., 2002). Tagish Lake is among the most enriched in carbon of all chondrites, containing up to ~6 wt% total C, of which approximately half is organic (Grady et al., 2002). The soluble organic component, while relatively small (~2 % of ~~organic~~~~total~~ C), contains several classes of compounds of prebiotic interest (Glavin et al., 2012; Hilts et al., 2014; Pizzarello et al., 2001). Systematic study of different lithologies within Tagish Lake demonstrate variation in organic matter characteristics that correlate with mineralogy and petrology (Blinova et al., 2014); these variations are thought to represent a record of the effect of parent body alteration on the structure and composition of the organic matter (Herd et al., 2011).

The study of meteorites and other extraterrestrial materials here on Earth has greatly aided the development of the protocols and science parameters for sample return missions (McSween, 1996). The circumstances of the collection of the pristine Tagish Lake meteorite, which have demonstrably aided in preserving indigenous volatile organic compounds (Hilts et al., 2014), at the same time require stringent curation conditions in order to continue to preserve volatile species, minimize terrestrial contamination, and prevent against oxidation and hydrolysis. In this paper, we first review the characteristics of those organic compounds in Tagish Lake which place the greatest requirements on the conditions of curation, as well as the known terrestrial contaminants in this meteorite. Secondly, we describe a unique facility for the curation of pristine extraterrestrial materials and the tests carried out during its commissioning;

while originally designed for the manipulation and characterization of the Tagish Lake meteorite, the facility also represents a test bed for the development of sample handling facilities for sample return from organic- and/or volatile-rich targets. Lastly, we investigate the potential cause of an apparent reaction between the Tagish Lake meteorite and Al foil, and provide some recommendations on collection methods and protocols for fresh meteorite falls.

2. Handling of the Tagish Lake meteorite prior to acquisition

The pristine specimens of Tagish Lake were purchased from the finder by a consortium of institutions in 2006, namely, the University of Alberta and the Royal Ontario Museum (ROM), with funding from Heritage Canada, Natural Resources Canada and the Canadian Space Agency. Two batches of specimens were acquired: those that had been sent to NASA ~~Johnson Space Center~~ (JSC) for classification and study, and those that remained with the finder (Herd and Herd, 2007). The specimens at NASA JSC were documented by R. K. Herd on August 25, 2000 where they were photographed and weighed in a nitrogen cabinet in the Meteorite Processing Lab; in this process they were exposed to room temperature for less than a minute, and otherwise stored in a laboratory freezer in air (Herd, 2000). Furthermore, these specimens were transferred from the plastic bags in which they were collected to Teflon™ bags within screwtop Teflon™ jars. Subsequent to purchase, one of us (CDKH) retrieved the Tagish Lake specimens from NASA JSC; specimens were removed from their containers within a walk-in freezer at NASA JSC for brief documentation, returned to their containers and then packaged within an expanded polystyrene container (Styrofoam™ from ThermoSafe, Inc.), along with a datalogger (Hobo, Inc.). The Styrofoam container was sealed with packing tape and placed into a cooler (Coleman, Inc.) in which -18 °C freezer gel packs (Fisher, Inc.) and a block of dry ice had been placed. The cooler was transported by commercial airline after the dry ice was

disposed of; due to its scientific value, the cooler of meteorites rode in the cabin of the aircraft, not the hold. Once in Edmonton, the Styrofoam container was placed in a cooler containing dry ice and transported by vehicle to the University of Alberta, at which point the Styrofoam container was opened and the meteorite specimens transferred to a Forma model 3670 single chamber laboratory freezer (Thermo Electron, Inc.) set to -30°C , where they remain to the present day. Data obtained from the datalogger demonstrate that the temperature of these specimens never exceeded -7°C between the time of placement within the transport container and transfer to the storage freezer. This storage freezer remains the primary storage facility for the Tagish Lake specimens at the University of Alberta; the freezer is connected to an uninterruptable power supply (UPS) and emergency backup power, securely located, and monitored for both security and temperature. In the case of power loss to the storage freezer, protocols state that the specimens be removed from the storage freezer and placed in a temporary storage cooler filled with -18°C freezer gel packs; longer cooling would be maintained through the use of dry ice, readily available on the University campus.

Those meteorite specimens that had remained with the finder were documented by R. K. Herd on August 12 and 13, 2000 where they were photographed and weighed at low (unspecified) ambient temperature on Al foil (Herd, 2000). During this process the specimens were briefly exposed to moisture in the air before being wrapped in clean Al foil and placed in clean ZiplocTM bags. Subsequent to purchase, these specimens were packaged up by the finder and placed in a Styrofoam container with freezer gel packs and a datalogger (Hobo, Inc.) which had been supplied to him by the University of Alberta. The finder then drove these specimens to Edmonton over a ~ 2 day period. Data obtained from the datalogger demonstrated that the temperature of these specimens never exceeded 0°C between the placement within the transport

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3 container and transfer to the storage freezer at the University of Alberta. The total weight of
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5 pristine Tagish Lake specimens purchased was 843.5 g. Of this, 200 g were transferred to the
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7 ROM, where all but one specimen (P-2; Hildebrand et al. 2006) are stored in a research-grade
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9 freezer at – 80 °C (Sanyo, Inc.; Nicklin, pers. comm. 2015). Specimen P-2 is the only pristine
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11 specimen that has~~ed~~ been thawed; it is stored in a humidity- and temperature-monitored
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13 environment at room temperature.
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17 Subsequent to acquisition, the meteorite specimens (with the exception of specimen P-2)
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19 were carefully photographed and weighed in a standard walk-in freezer at the University of
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21 Alberta. Air was not filtered, although the circulation fan in the freezer was turned off, in order
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23 to minimize lofting of dust. Clean Al foil was laid down on work surfaces and polyvinyl gloves
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25 and clean tools were used for sample contact. At that time it was observed that some meteorite
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27 specimens had small (< 0.5 cm) spots on their exterior surfaces to which Al foil was adhered
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29 (Figure 1). The foil adhered to these specimens, as well as that in which they were wrapped, was
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31 found to be extremely brittle, and to be associated with a white to colorless, opalescent material
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33 (Figure 1b). The observation of this brittle foil and associated material suggested a reaction
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35 between the foil and compounds or mineral phases within the meteorite. All reacted foil was
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37 retained; some specimens were re-wrapped in fresh foil, although all specimens were ultimately
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39 transferred to their own Teflon screw-top jars. As Al foil is often used as a collection medium for
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41 fresh meteorite falls, this reaction is of interest for collection and curation of freshly fallen
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43 meteorites; as such, the nature of the reaction, as well as Al foil as a source of potential organic
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45 contamination, are investigated further as part of our study.
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54 **3. Contaminant organic compounds in the Tagish Lake meteorite**
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The range of different classes of indigenous organic compounds found in the Tagish Lake stones is quite large. Pizzarello et al. (2001) observed aromatic hydrocarbons, such as substituted benzenes and naphthalenes, as well as long chain aliphatic hydrocarbons in the benzene-methanol extracts of their pristine Tagish Lake sample. Of the four lithologies investigated by Hilts et al. (2014), the DCM extract for specimen 11v – consisting of disaggregated material collected along with stones from the lake surface – displayed the greatest variety of reduced organics. Like Pizzarello et al. (2001), they found long chain hydrocarbons, alkyl benzenes and low molar mass PAHs. In addition, they identified several terrestrial contaminants, the most abundant of which is 9-octadecenamide, or oleamide, whose source was found to be the Ziploc™ bag in which the sample was collected (Hilts et al., 2014). The concentration of oleamide was estimated to be ~10 ppm, based on a comparison of the oleamide signal in 11v to the peak area for the signal in a 100 ppm solution of authentic oleamide. The compound limonene was detected in all four specimens, ranging in concentration from 5 ppm (specimen 11h) to <0.1 ppm (specimen 5b) (Hilts et al., 2014). The δD value obtained for the limonene in 11v (3.5 ppm) and 11i (2.5 ppm), viz. -170 ± 30 ‰, suggests a terrestrial origin for this compound (Hilts et al., 2014). Limonene, which is used a solvent in cleaning solutions and is found in the rinds of citrus fruits, may have been inadvertently transferred to the exteriors of the four specimens during collection or subsequent curation and handling. Hilts et al. (2014) concluded that the disaggregated sample 11v experienced the greatest amount of contamination, both in terms of the number of different contaminants and the concentrations of the contaminants, as a result of its large surface area. They speculated that many of the reduced compounds, namely *n*-alkanes, were also likely terrestrial; by extension, *n*-alkanes in samples

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3 11i and 11h are also likely terrestrial. Here we examine those results in more detail to identify
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5 additional contaminants in the meteorite.
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8 Seven additional terrestrial contaminants are identifiable in the DCM extract for Tagish
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10 Lake specimen 11v: three phthalate esters, decanal, diethylene glycol benzoate, 2-
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12 phenoxyethanol and n-hexadecanoic acid (also known as palmitic acid). Phthalic acid esters,
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14 more commonly known as phthalates, are ubiquitous environmental contaminants, typically
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16 introduced to samples such as these via the containers in which they are stored or through contact
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18 with tainted solvents (e.g., Elsila et al., 2005). Terrestrial phthalate esters were also found in the
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20 DCM extracts of 5b and 11i, but not in 11h (Hilts et al., 2014). Decanal, which is found in citrus
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22 fruits (Qiao et al., 2008), is an ingredient in the manufacture of flavours and fragrances, and so is
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24 almost certainly a terrestrial contaminant. Diethylene glycol benzoate is a common plasticizer,
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26 and thus clearly not indigenous. The compound 2-phenoxyethanol, a preservative used in
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28 cosmetics, probably has a prosaic terrestrial origin as well.
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34 It is our assertion that the n-hexadecanoic (palmitic) acid observed in the 11v DCM
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36 leachate by Hilts et al. (2014) is also a terrestrial contaminant. As with most of the contaminants
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38 seen in 11v, this fatty acid was not observed in any of the other three lithologies. Despite the
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40 presence of a highly polar carboxylate group, the compound is moderately soluble in weakly
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42 polar solvents such as DCM owing to its 15 carbon unit-long, non-polar, hydrocarbon tail
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44 (Foreman and Brown, 1944). Brocks et al. (2008) found n-hexadecanoic acid in 1:1 (v/v) DCM-
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46 methanol extracts of the interiors of Proterozoic rock samples, along with steric acid (another
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48 commonly encountered fatty acid contaminant), di(2-ethylhexyl)phthalate and cholesterol. Based
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50 upon the very low extract/blank ratios for these four compounds, combined with the fact that all
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52 four were observed in the 1:1 (v/v) DCM methanol extract performed on the exterior of these
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3 samples, they concluded that these four compounds were modern contaminants, sourced from the
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5 polyethylene sampling bags into which the rock samples were placed during collection and by
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7 inadvertent contact of the analyst's fingers with the analytical equipment (Brocks et al., 2008).
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10 This conclusion is quite plausible in light of the fact that phthalates are pervasively found in
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12 procedural blanks and n-hexadecanoic acid and cholesterol are readily transferred from human
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14 skin to laboratory glassware (Grenacher and Guerin, 1994).
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17 In another study involving carbonaceous chondrites, a range of linear carboxylic acids
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19 from C₅ to C₁₈ were released, as their methyl esters, by the tetramethylammonium hydroxide
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21 pyrolysis of Murchison and Orgueil IOM (Remusat et al., 2005). The strong preference for even
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23 over odd acids, and the predominance of the C₁₆ and C₁₈ acids, viz. n-hexadecanoic and n-
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25 octadecanoic acid, led the authors to conclude that the acids were produced via biosynthetic
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27 pathways, and thus the n-hexadecanoic and n-octadecanoic acids were terrestrial contaminants.
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29 More recently, Martins et al. (2008) discovered n-hexadecanoic acid in a derivatized extract of a
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31 sample of the Murchison meteorite; the same compound was also detected in a soil extract
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33 analyzed by the group. This finding, along with the high carbon number for hexadecanoic acid
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35 being inconsistent with extraterrestrial monocarboxylic acids (e.g., Naraoka et al., 1999), led the
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37 authors to conclude that the n-hexadecanoic acid in the Murchison meteorite was, in fact,
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39 terrestrial contamination.
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45 As in specimen 11v, the dominant species in the DCM extracts for specimens 11h and 11i
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47 are various branched and linear long-chain alkanes along with some alkyl benzenes and the PAH
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49 naphthalene. A phthalate ester was observed in the DCM extract for 11i, while 11h appeared to
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51 have avoided phthalate contamination (Hilts et al., 2014). The DCM extract for specimen 5b is
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53 quite distinct from the other three samples in that it contains almost exclusively alkyl-substituted
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naphthalenes/benzenes and PAHs, which are closely related aromatic compounds. The only obvious terrestrial contaminants in this specimen are a pair of phthalate esters.

Terrestrial contamination is clearly visible in the water extract for Tagish Lake specimen 11v (Hilts et al., 2014). The compounds 2-methoxyethanol, 2-chloroethanol, 2-(2-chloroethoxy)ethanol and ~~butyrolactone~~butyrolactone are almost certainly products of our modern industrial society: 2-methoxyethanol is a widely used industrial solvent and as a jet fuel de-icer; 2-(2-chloroethoxy)ethanol is used in the pharmaceutical industry as an intermediate; while 2-chloroethanol is employed as a polymerizing agent, a herbicide and an insecticide (Rédei, 2008). ~~Butyrolactone~~Butyrolactone is used as a cleaning agent, a paint remover and as a solvent in the manufacture of polymers and agrochemicals (Zeikus et al., 1999). Notably, the aqueous extract of specimen 11i experienced a level of contamination comparable to that found for 11v. Four of the contaminants, viz. 2-methoxyethanol, 2-chloroethanol, 2-(2-chloroethoxy)ethanol and ~~butyrolactone~~butyrolactone, were identical to the ones observed in the 11v water extract, while the fifth contaminant, 2-(2-ethoxyethoxy)ethanol, known under its trade name as carbitol, is a widely used industrial solvent (Cragg, 2012). The water extract for specimen 11h, which is relatively clean, is contaminated only by a small quantity of phthalate. Lastly, the water extract for 5b seems to be free of any obvious terrestrial contamination.

4. Intrinsic organic compounds in the Tagish Lake meteorite

Indigenous, water-soluble polar compounds in the Tagish Lake meteorite include monocarboxylic acids (Hilts et al., 2014; Pizzarello et al., 2001), dicarboxylic acids (Pizzarello and Huang, 2002; Pizzarello et al., 2001) and amino acids (Glavin et al., 2012; Herd et al., 2011; Hilts et al., 2014). Appreciable quantities of dicarboximides (5.5 ppm) and pyridine carboxylic

acids (7.5 ppm) were also discovered (Pizzarello et al., 2001). There exists significant variability in the complement of indigenous organic compounds between Tagish Lake specimens; for example, Pizzarello et al. (2001) observed linear monocarboxylic acids from C₁-C₉ (i.e. ~~form~~ formic to nonanoic acid), but only in trace amounts beyond C₂; furthermore, only sub ppm quantities of amino acids, amines and amides were detected in the water extract for this sample. By comparison, sStudies of Tagish Lake specimens 5b, 11h and 11i demonstrate significant variability, e.g., in total amino acid abundances: 40 ppb for 11i, 740 ppb for 5b and 5400 ppb for 11h (Glavin et al., 2012) and in total monocarboxylic acids: 359 ppm (11i), 533 ppm (5b), ~~5656~~ ppm (11h) and 387 ppm (11v), including 1-15 ppm C₃ to C₉ (Hilts et al., 2014). Unless otherwise demonstrably affected by terrestrial leaching and/or contamination (as is the case for degraded specimens; Kminek et al., 2002), these variations are attributable to parent body processes (Herd et al., 2011): For example, the low abundance of amino acids in 11i, which is comparable to the total amino acid abundance reported by Pizzarello et al. (2001) for their pristine Tagish Lake sample, is likely the result of the high degree of parent body aqueous alteration reflected by this specimen (Hilts et al., 2014). Amino acid concentrations for less-altered lithologies (e.g., represented by specimens 5b and 11h) are, in fact, more consistent with typical values for aqueously altered CI, CM and CR(1) chondrites (Glavin et al., 2010), and their C isotopic compositions are consistent with extraterrestrial values (Glavin et al., 2012).

Pizzarello et al. (2001) found that mono- and dicarboxylic acids were the most abundant water-soluble compounds in the Tagish Lake meteorite. Forty-four indigenous dicarboxylic acids were found, with succinic, glutaric and adipic acid being present in substantially higher concentrations than the other diacids (Pizzarello and Huang, 2002). The results of Hilts et al. (2014) corroborate and extend that work for monocarboxylic acids; however, no dicarboxylic

acids were detected in their study even though detectable quantities of these acids should be present. The discrepancy may be attributable to difference in the methodology: Pizzarello et al. (2001) analyzed the mono- and dicarboxylic acids (as well as the pyridine carboxylic acids) by GC-MS as their isopropyl esters, whereas Hilts et al. (2014) chose to use the relatively new approach of linking Solid Phase Micro-Extraction (SPME) with GC-MS to analyze for indigenous carboxylic acids and other highly polar species (Huang et al., 2005). Optimal separation of the monocarboxylic acids in the water extracts was achieved by Hilts et al. (2014) by extraction with a Carbowax-Polyethylene glycol (PEG) SPME fiber, followed by separation on a Nukol column. The SPME-GC(Nukol)-MS methodology offers the special advantage that it allows for the direct determination of monocarboxylic acids and other organic compounds with highly polar groups, thereby eliminating the need for a derivatization step (Christie, 1993). The diesters detected by Pizzarello et al. (2001) have a much higher volatility and thus are readily separated on a standard GC column (Pietrogrande et al., 2010). Unmodified dicarboxylic acids, by virtue of their high polarity, cannot be separated on standard polysiloxane columns. We surmise that Hilts et al. (2014) were unable to directly determine dicarboxylic acids using the SPME-GC(Nukol)-MS methodology that had worked so effectively with monocarboxylic acid mixtures because the unmodified diacids had become chelated to OH groups on the surface of the PEG SPME fiber. This unusually strong bonding mode could pin the diacids on the surface and stop them from being ~~flushed off~~ rapidly desorbed by the high temperatures in the GC injection port. We tested this hypothesis by preparing a suite of standard mixtures of carboxylic acids in water and analyzing them by SPME(PEG)-GC(Nukol)-MS; results confirm that dicarboxylic acids are not detected using this method (see Appendix). It appears that the determination of dicarboxylic acids ~~still~~ requires that they be converted to a more volatile form

through some type of derivatization, or awaits the development of an SPME fiber that is tailored to these specific compounds.

The most abundant monocarboxylic acid in the Tagish Lake meteorite is formic acid (Hilts et al., 2014). This result is in contrast to all previous studies on monocarboxylic acids in which it was found that the formic acid abundance was the lowest or amongst the lowest of the monocarboxylic acids observed in the extract (Naraoka et al., 1999; Shimoyama et al., 1989; Yuen et al., 1984). The total abundances determined for the linear monocarboxylic acids from C₁ to C₁₀, viz. 11h (656 ppm), 5b (533 ppm), 11v (387 ppm) and 11i (359 ppm) in the pristine Tagish Lake specimens (Hilts et al., 2014), are well above those reported by Pizzarello et al. (2001) and, in fact, even exceed the total monocarboxylic acid abundances for the Murchison meteorite, which is accepted as one of the most monocarboxylic acid-enriched meteorites known (Botta and Bada, 2002). Contamination by terrestrial monocarboxylic acids has been largely avoided in the pristine Tagish Lake specimens, as evidenced by the presence of highly branched isomers and isotopically heavy δD values (Hilts et al., 2014). ~~Although the high abundances of the monocarboxylic acids in the pristine Tagish Lake specimens may reflect a unique style or mode of organic synthesis and/or parent body modification, -can be attributed to~~ the low temperature storage and handling protocols, ~~which~~ have almost certainly helped to retain the most volatile, low molecular weight acids.

5. Curation considerations and description of the facility

The successes and challenges encountered during the curation and handling of astromaterials in terrestrial facilities over the past >50 years have been used to inform sampling strategies and the subsequent storage and manipulation protocols for invaluable pristine samples

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returned to the Earth. While keeping samples completely contamination-free is next to impossible, there are certain protocols which, if followed, tend to keep contamination at manageable levels. For sample return missions, in particular, any successful analysis of the indigenous material must include an assessment of what possible contaminants might ultimately accumulate on and in the samples during the sequence of steps from sample acquisition through to the final testing in the laboratory. Much has been learned from the study of the organic contamination within and on the surfaces of sample return capsules, such as Hayabusa (e.g., Kitajima et al., 2015) and Stardust (Sandford et al., 2010). Witness plates, kept close to the samples during various stages, from spacecraft to curation facility, are commonly used to record accumulated contaminants, providing a record of the intrinsic organic content released by the spacecraft’s sampling system and associated hardware, and enabling tracking of contaminant introduction and an assessment of cleanliness of the system (e.g., Sandford et al., 2010). Understanding how and when potential contaminants are introduced is a perennial concern for sample return mission planners and curators, especially when it comes to organic compounds; testing is necessary for everything from airborne organics in the atmospheres in which the samples are stored, to adsorbed species on the surfaces of anything that would come into direct contact with the samples (storage media, handling tools and analytical devices), even after these surfaces have been sanitized as the act of cleaning itself has the potential to taint the surface with a different contaminant.

The Subzero Curation Facility for Astromaterials at the University of Alberta is designed with the aforementioned considerations in mind, within the limitations of funding available. At the heart of the facility is an Ar gas glove box (MBraun, Inc.), housed within a controlled environment chamber capable of maintaining temperatures between -30 and -10 °C (Figs. 2, 3).

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3 The glove box – modeled after similar glove boxes at NASA Johnson Space Center and other
4 curation facilities – consists of a single user station, 120 cm wide by 78 cm deep by 90 cm high,
5 made of brushed 304 stainless steel with radius corners, with a polycarbonate window with
6 chemical and scratch resistant coating (Fig. 2c). Integrated into the window is a binocular
7 microscope (Leica, Inc.), fitted with a camera adapter (Fig. 2c, 3a). An adjustable stage sits
8 beneath the microscope, within the glove box (Figure 3a). Exchange of materials and samples
9 into and out of the glove box is provided by either of two cylindrical, brushed 304 stainless steel
10 antechambers (Figure 3b): one 39 cm diameter and 60 cm deep for larger objects; the other 15
11 cm diameter and 40 cm deep. Each antechamber can be evacuated and refilled with glove box
12 atmosphere. ~~Sliding~~ trays in each antechamber provide access to materials; the sliding
13 mechanism uses ball bearings lubricated with vacuum grease. On the right side of the main box
14 is a secondary, storage box made of the same materials as the main box and measuring 46 cm
15 wide by 78 cm deep by 60 cm high (Figure 2c); separated from the main box by a sealable door,
16 this box allows for temporary storage of samples while experiments (e.g., involving solvents) are
17 being carried out in the main box. Illumination within the boxes is provided by two LED light
18 strips – one along the top of the outside of the main box, and the other through a ‘skylight’ in the
19 top of the secondary box. Illumination of specimens on the microscope stage is provided by a
20 fiber optic spot light (Schott, Inc.).

21
22 The atmosphere within the glove box is maintained using an MB 20 G gas purifier
23 (MBraun, Inc.); once charged with high-purity oxygen-free (99.998%) argon, the system
24 continuously recirculates the argon through a purification system, which removes airborne
25 contaminants and maintains O₂ and H₂O to < 1 ppm. HEPA filters on gas inlets also reduce any
26 particulate matter that may be otherwise be circulated into the glove box. An activated carbon
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filter unit on the gas outlet for the main glove box removes any volatile organic compounds that might contaminate the materials used within the purifier; this feature also allows for organic solvents (e.g., chlorinated solvents such as DCM) to be used within the glove box, either for cleaning purposes or to carry out organic extractions on samples within a purified inert atmosphere at low temperature. Nearly all tubing used is 304 stainless steel; VitonTM type B O-rings are used to minimize volatile compounds, similar to NASA ~~JSC Johnson Space Center~~ recommendations (Calaway et al. 2014). Atmospheric purity is displayed on both the touchpad controls associated with the purification system (Figure 3c) and on a standalone digital readout on top of the glove box. In practice, the system is able to consistently maintain purity levels of < 0.1 ppm (i.e., below detection) for O₂ and H₂O. The purification system is re-usable; once levels approach a few to ~20 ppm O₂ (or moisture), the purifier can be regenerated using an Ar/6.7%H₂ mixture through an automated process that takes approximately 16 hours.

Where the facility differs significantly from similar facilities elsewhere, and from previous cold curation testbeds (e.g., Fletcher et al., 2008a; Fletcher et al., 2008b) is the enclosure of the glove box within a low-temperature environmental chamber (Fig. 2b; Model C811 from Convion, Inc.). The chamber has interior dimensions of 216 cm (7' 1") wide by 303 cm (9' 11") deep by 206 cm (6' 9") high, giving it a volumetric capacity of 15.74 m³ (556 ft³). The chamber floor is made of 10 cm (4") thick insulated galvanized steel, while the interior walls are enamel baked on smooth 24 ga. galvanized steel, with 4" foamed-in-place CFC-free polyurethane insulation. The chamber is similar to that used for plant growth studies (a specialty of Convion, Inc.); as such, it can provide closely-controlled temperature, to within 1 °C within a predefined range of -10 °C to -30 °C. The chiller unit goes through two defrost cycles per day, during which the temperature increase does not exceed 4 °C. A secondary thermocouple is

connected to the University's Control Centre, providing remote notification of laboratory personnel in the case of a shutdown and "unplanned warmup". (Such an event does not affect the Tagish Lake meteorite specimens, which are kept in the storage facility, described in Section 2; costs to place the environmental chamber on emergency power backup are prohibitive.) The door on the chamber is 86.4 cm (34") wide by 198 cm (78") high and includes a 35.5 cm (14") square viewing window with light cover (Figure 2d). Fluorescent lighting suitable for low-temperature operation provides lighting within the chamber.

The enclosure of the glove box within the freezer required modification of the glove box purification system by the supplier (MBraun, Inc.); specifically, the purifier and associated touchpad controls are remotely located outside the freezer chamber itself. Gas and electrical connections are made through sealed ports within the chamber walls. The primary reason for the remote location of the purification system is that it is required to operate at temperatures of at least 10 °C. The main consequence of this requirement is that the return gas from the freezer must be warmed up before passing into the purifier. The gas must also then be chilled before returning into the glove box, as the rate of flow (~50 cfm) is too rapid to sufficiently cool the gas to the ambient freezer chamber temperature. To accomplish this, gas flowing into the freezer is chilled using a heat exchanger connected to a 50/50 glycol/water mixture chiller unit (Julabo, Inc.); a second, identical heat exchanger unit warms the gas flowing into the purifier (Fig. 2c). In practice, this setup succeeds in maintaining a minimum 10 °C on the purifier inlet; however, the temperature within the glove box is typically 3-5 °C above the ambient temperature of the freezer chamber (the actual offset depends on the freezer chamber setpoint; e.g., glove box T = -16 °C when freezer T = -20 °C; glove box T = -12 °C when freezer T = -15 °C).

A Class 1000 clean room (Lasco Services, Inc.) serves as a room temperature anteroom to the freezer chamber (Fig. 2a). This anteroom was established to provide a source of clean air for the -20 °C chamber, since HEPA filtering of the freezer chamber air was not practicable. The anteroom also provides improved storage for the University of Alberta Meteorite Collection. Specimens housed in this facility are each double-bagged in standard polyethylene reclosable bags (Shippers Supply, Inc.), and sit in plastic boxes with friction-fit lids (Cargille, Inc.). Cushioning for the specimens is provided by a double-layer of Volara™, a curation-grade, closed-cell foam (Sekisui Voltek, Inc.). Specimens sit within stainless-steel trays lined with a layer of Volara™ within stainless-steel geological specimen cabinets (Lane, Inc.).

The main goal of our study is to test for sources of contaminants from the atmospheres and materials with which specimens may come into contact. These include the atmospheres in the clean room, freezer chamber and Ar glove box; the Volara™ foam and other storage media; interior surfaces of the glove box; and the glove box gloves themselves.

6. Methods

6.1 General

Descriptions of the processes carried out in the commissioning of the Curation Facility are provided in this section. During general operation of the facility, all users are required to wear cleanroom frocks (reuseable polyester from Superior Uniform Group) overtop of clothing, Tyvek boot covers (DuPont, Inc.), and powder-free nitrile gloves for routine access, as well as access to the University of Alberta Meteorite Collection. For work within the freezer, additional insulating layers are worn beneath the cleanroom frocks, and insulating gloves are worn beneath Co-Polymer gloves (G5 from Kimtech, Inc.). In all cases where samples are either examined or

processed within the freezer or within the glove box, Co-Polymer gloves are worn; in this way, the same gloves are always in contact with the specimens. After every procedure in which samples are handled and/or processed, all materials with which samples may have come into contact are retained and stored, thus providing a record of potential contaminant sources.

6.2 Glove box interior

Subsequent to installation and prior to cleaning, and with the glove box operating at room temperature, glove box interior surfaces (back and floor) were each swabbed with DCM-soaked sterile cotton tipped swabs (Puritan, Inc.) in a randomized 4x4 matrix. The sample swabs were further extracted with DCM and analyzed for volatile organic compounds by GC-MS (Section 6.8).

6.3 Cleaning protocols

At the start of commissioning, all parts of the facility were cleaned in order to remove any potential contaminants remaining from their manufacture. The interior surfaces of the glove box were comprehensively cleaned with ultrapure water and HPLC-grade dichloromethane (DCM), using clean room wipes (Contec, Inc.) and a reach tool, with the chamber at room temperature. Exterior glove box surfaces, including the frame, as well as the interior walls of the freezer chamber, were wiped with isopropyl alcohol on clean room wipes, with the chamber at room temperature; this step was carried out in response to the detection of high particle counts in the freezer chamber (see Section 6.6). After installation the floors and walls of the anteroom were cleaned with ultrapure water followed by HPLC-grade DCM, using clean room wipes. Specimen cabinet interior and exterior surfaces, and all sides of the specimen drawers were cleaned with distilled water and HPLC-grade DCM before installation within the anteroom. As DCM is a solvent for VolaraTM, only distilled water was used in its cleaning.

6.4 Glove box atmosphere

Sampling of volatile compounds in the glove box atmosphere was carried out in order to test for compounds that were either inadvertently introduced into the atmosphere, or degassed from plastics within the glove box system, and to test the ability of the purification system to remove these types of contaminants. This sampling was done in two ways: solid phase microextraction (SPME) fibers and activated silica gel. In the first instance, a Carbowax-Polyethylene Glycol (PEG) SPME fiber (Sigma-Aldrich, Inc.) was exposed within the glove box for 28 days, while the system was set to room temperature, and then removed for analysis by GC-MS (Section 6.8). A second SPME fiber was subsequently exposed to the box atmosphere for 54 days at the standard operating temperature of -16 °C (-20 °C freezer temperature), and then removed for GC-MS analysis, under the same analytical conditions.

Continued monitoring of the atmosphere within the glove box was carried out over the following 357 days using activated silica gel, both to test whether there were any volatile compounds not captured by the SPME fibers, as well as to monitor for any adventitious organics accidentally brought into the box during regular operations. In each case, the silica gel (63-200 mesh, 60 Å pore size; Selecto Scientific, Inc.) was combusted in a 450 °C furnace for 8 hours to remove any potential organic compounds absorbed on the silica gel surfaces. After cooling, the silica gel was fully activated via exposure to 110°C for over 12 hours. The first silica gel sample was kept in the glove box (set at -16 °C) for 100 days, and a second sample for 257 days, before being removed and extracted. In both cases the mass of the silica gel was ~9.5 g, and approximately 20 mL of HPLC-grade DCM were passed through the silica gel to extract any compounds captured by the gel. The eluent was concentrated to ~1 ml through evaporation with a stream of dinitrogen gas in a separate lab at room temperature. A procedural blank was also

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3 prepared from a 10 g sample of activated silica gel that was not exposed within the glove box.

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5 The blank and the two glove box DCM extracts were analyzed by GC-MS (Section 6.8).

6 7 8 9 *6.5 Gloves*

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Gloves represent a potentially significant source of contaminants, both in the form of volatile organic compounds introduced to the glove box atmosphere via offgassing, and through contact between the gloves and the samples during normal use. Results of studies examining various glove material options in terms of minimizing contamination demonstrate that gloves made of chlorosulfonated polyethylene (Hypalon™ from North Safety, Inc.) – or combinations of Hypalon and other materials such as neoprene or polyurethane – provide the best options based on criteria for offgassing, permeability, particle shedding, cleanability, and flexibility (Calaway et al. 2014). However, we found that the Hypalon gloves supplied with the glove box proved to be unusable as they were insufficiently elastic at normal (subzero) operating temperatures; these were replaced with polyurethane gloves, which retain their elasticity down to -20 °C. Prior to their installation, the polyurethane gloves were cleaned with clean room wipes soaked with 1) ultrapure water and then 2) HPLC-grade DCM. Drippings from the used DCM-soaked wipes were analyzed by GC-MS.

6.6 Freezer chamber and anteroom atmosphere

Initial commissioning of the clean room anteroom demonstrated that it exceeded the Class 1000 specification. Particle counting was carried out subsequently in order to monitor for changes in the clean room atmosphere, especially after installation of specimen cabinets, and after meteorite specimens were stored within the cabinets. A Model HHPC 3+ MET ONE Airborne Particle Counter (HACH, Inc.) was used. Particle counting was also carried out within the freezer chamber, in order to test the ability of the anteroom filtering to clean the freezer

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3 chamber atmosphere. Subsequent to detection of high particle counts in the freezer chamber, we
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5 placed PELCO double-sticky carbon dots (Ted Pella, Inc.) on scanning electron microscope
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7 (SEM) stubs in two areas within the freezer chamber. These were exposed and left in the freezer
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9 chamber for 3 days before being sealed and transferred for SEM analysis. A Zeiss Evo 15 SEM,
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11 operating at 25 kV and a working distance of 8 mm, was used to characterize the larger particles
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13 that were found on the sticky carbon surfaces. As noted above, cleaning of the freezer chamber
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15 surfaces was carried out in order to reduce the number of particles, and particle counting was
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17 repeated.
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22 *6.7 Freezer chamber and anteroom surfaces*
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24 Cotton swabs (Puritan, Inc.) soaked in DCM were used to sample the exterior surfaces of
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26 the glove box, the walls of the freezer chamber, handles of the specimen cabinets and drawers,
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28 and the Volara™ foam in the meteorite storage containers. These swabs were further extracted
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30 using DCM and analyzed by GC-MS.
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34 *6.8 GC-MS analysis*
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36 Gas chromatography separation was performed on an Agilent 6890N using an HP-5MS
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38 (30 m length, 250 µm diameter, and 0.25 µm film thickness) column, located at MacEwan
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40 University. The initial oven temperature was 50 °C and held for one minute after which the
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42 temperature was increased 10 °C/min to a final temperature of 250 °C. The temperature was held
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44 at 250 °C for 20 minutes for a total run time of 41 minutes. Helium was used as the carrier gas at
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46 a constant flow rate of 1.0 mL/min. Liquid samples were injected using pulsed splitless at 275°C,
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48 in which the pulse pressure was 40 psi for 0.20 minutes; after 0.75 minutes a purge flow of 30.0
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50 mL/min was introduced. Injection of SPME adsorbed samples was performed using traditional
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52 splitless injection. Detection was performed with an Agilent 5975C mass selective detector
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(MSD). The following MSD conditions were used for the duration of the run: MS source temperature 230 °C, MS quad temperature 150 °C, low mass 10.0 Da, and high mass 500.0 Da.

6.9 Investigations of aluminum foil as a collection and storage medium

Many practitioners in the field of meteoritics have advised collectors of freshly fallen meteorites to wrap any specimen in clean aluminum foil and make every attempt to avoid direct contact with of the meteoritic material with the skin. This advice will certainly limit the quantities of human-derived biomolecules, such as squalene and cholesterol transferred to the stones, but contamination with these compounds is still possible if the Al foil used to wrap the stones has been manipulated with bare hands. It has been demonstrated that biomolecules on the skin can be readily transferred to laboratory glassware, and thus ultimately introduced into a sample (Grenacher and Guerin, 1994). The GC-MS traces of DCM rinses of glassware briefly touched by human fingers were found to contain appreciable quantities of squalene and cholesterol; smaller quantities of fatty acids and hydrocarbons were also detected (Grenacher and Guerin, 1994). We took foil that had been used to enclose samples 10a and 11i, as well as a clean, 2 x 2 cm sample of Al foil, the same batch which had been used to enclose Tagish Lake specimens at the time of brief documentation in August 2000 (Herd, 2000-unpubl. report). Gloves were used to handle the foil from the specimens, but ungloved hands were used to handle the fresh foil, in order to simulate its potential contamination by finger grease. Approximately 0.5 mL of ultrapure DCM was allowed to travel down and then drip off each sample of Al foil. The drippings were collected and then analyzed by GC-MS.

Brittle Al foil was removed from Tagish Lake specimens 11i and 11s, coated with Cr, and examined using a JEOL 6301F Scanning Electron Microscope (SEM) at the University of Alberta, operating at 20 kV and a working distance of 14 mm; backscattered and secondary

electron images and spectra from energy dispersive spectrometry (EDS) were obtained. To assist in determining its composition and state, the associated opalescent material from specimen 11s was analyzed by a Nicolet Magna 750 FTIR Spectrometer equipped with a Nic-Plan FTIR Microscope, operating in reflectance mode, and by powder X-Ray Diffraction (XRD) using a Rigaku Geigerflex Powder Diffractometer, [both at the University of Alberta](#).

7. Results and Discussion

7.1 Glove box interior and atmosphere

No significant organic contaminants were found on the glove box interior walls, based on the results of the GC-MS analysis of DCM-soaked swabs. In spite of this result, some swabs were visibly dirty, indicating the presence of dusty particles within the glove box, presumably resulting from manufacture and/or installation. The nature of these particles was not explicitly investigated, but the interior of the glove box was thoroughly cleaned as described in Section 6.3.

Results of GC-MS of SPME fibers exposed to the glove box atmosphere are shown in Figure 4. Most of the peaks in both the room temperature and the low temperature traces are column bleed (i.e., cyclic polysiloxanes); however, at room temperature, both styrene and aniline are present. Both of these compounds are common volatiles released from glues, resins and plastics – in this case, from the construction of the box. Notably, both compounds are absent in the low-temperature SPME fiber, attributable to several factors: a decrease in the rate of outgassing of the source materials (glues, resins, plastics) over time; the continuous purging/purification of the glove box atmosphere by the Ar purification system; the low temperature operation of the glove box. It is notable that aniline freezes at $-6.3\text{ }^{\circ}\text{C}$, and thus would not be expected to be present in that atmosphere at standard [glove box](#) operating temperatures ($\leq -10\text{ }^{\circ}\text{C}$).

No detectable compounds were found in the DCM extracts of the silica gel, other than those found within the blank. Any highly volatile organic compounds (i.e., those with normal boiling points well below 100°C, such as formaldehyde (-19 °C) and acetaldehyde (20.2 °C)) that might have sorbed on to the silica gel would have largely been purged from the DCM solution by the dinitrogen evaporation procedure. As a consequence, it is highly likely that such species would not be observed in the GC trace for the extracts of the silica gel. In contrast, we would anticipate much smaller losses for those organics with normal boiling points above 100 °C, such as aniline (184 °C), toluene (110.6 °C) and styrene (145 °C), leading to the appearance of these less volatile species in the GC traces, had they been deposited in detectable quantities. Had highly volatile organics, such as formaldehyde and acetaldehyde, been released into the glove box atmosphere and achieved concentrations at the ppb level or higher during the first 82 days of the commissioning period for the glove box, they would have been detected by the SPME fiber method described above.

7.2 Gloves

Although the polyurethane gloves were found to be sufficiently flexible at low temperature, in practice, they are much more rigid than standard gloves (such as Hypalon) at room temperature. Initial use of the gloves after they have been unused for several hours requires them to be “worked” by repeated flexing by the user, before they can be effectively used for glove box work. The result of this repeated flexing is observed as lighter-colored creases in the gloves; while the use of these gloves has~~ve~~ not resulted in any leaks, we continue to monitor their effectiveness, since the creases are potential points of weakness.

Results of the GC-MS of DCM drippings from the gloves are shown in Figure 5. Not surprisingly, the two dominant species in the rinse were the monomeric species methylene

diphenyl diisocyanate and 1,6-dioxacyclododecane-7,12-dione, from which the polyurethane polymer, the primary component of the gloves, is derived.

7.3 Freezer chamber atmosphere and surfaces

Results of particle counting are given in Table 1. Initial particle counting results indicated a high number of particles in the clean anteroom near the door to the freezer chamber and within the freezer chamber itself (Table 1). Subsequent cleaning of the freezer chamber reduced the particles counts to meet the requirements for a Class 1000 clean room. However, this result demonstrates that the clean room anteroom is insufficient for providing a clean environment within the freezer chamber. Other options, such as standalone HEPA filtration systems, are currently being investigated.

SEM analysis of carbon dots that were left to collect particles in the freezer chamber indicated that the particles were inorganic, composed primarily of Ag, Cu and Si. The largest particles ($> 1\mu\text{m}$) were concentrated towards the outer edges of the carbon dots, indicating that they may have been derived from the tools used to transfer the dots to the sample holder, rather than the freezer atmosphere itself.

7.4 Al foil as a collection medium

The GC-trace of the DCM rinse from the fresh Al foil (Figure 6) contained two peaks, one identified as nonanal and the other as ~~thymidine 5'-monophosphate; the latter peak may alternatively be identified as~~ squalene (Figure A2). ~~If the latter is squalene, it~~ The latter was presumably transferred from human skin through handling. Nonanal, or pelargonaldehyde, a well-known ingredient in perfumes, may have been transferred from human skin along with the squalene. ~~If the correct identification of the second peak is thymidine 5'-monophosphate instead, then that compound may be derived from human skin as well.~~ In contrast, the only peaks

observed in the DCM rinses of the enclosing foil from specimens 10a and 11i (Figure 6) are alkyl diesters, which are ubiquitous industrial solvents. That alkyl diesters are not found on the fresh Al foil suggests that the meteorite specimens were exposed to these contaminants; however, we can rule out contamination of the specimens by contact with human skin. These results confirm that Al foil by itself is not a significant source of contamination, unless it has previously been imbued with contaminants, e.g., by handling without gloves.

Results of analysis of brittle foil and associated material are shown in Figure 7. The white- to colorless, opalescent product of the reaction is present as a layer on the interior of the foil (the side facing the meteorite specimen); in detail, this material shows evidence of desiccation in the form of synuresis cracks (Fig. 7a), suggesting it had been liquid at one time. The foil itself appears to be corroded; some locations preserve what appears to be the incipient reaction proceeding along fractures (Fig. 7b). Notably, more product material is present in association with locations where corrosion has apparently proceeded through the thickness of the foil. EDS analysis of the foil and product show that the product material is oxidized, and contains variable amounts of S and Cl (Fig. 7c-e).

FTIR results of analysis of the opalescent material are shown in Figure 8. The envelope of bands centered at $\sim 1050\text{ cm}^{-1}$ is probably due to the bending vibrations of the hydroxyl groups in $\text{Al}(\text{OH})_3$ (e.g., Klopogge et al., 2002). The large broad absorption between ~~2930~~ 3000 and 3700 cm^{-1} is likely the result of both stretching vibrations for the hydroxyl groups in $\text{Al}(\text{OH})_3$ and the stretching/bending vibrations for water coordinated to the Al^{3+} trication. The bands at ~ 2900 and 2800 cm^{-1} are mostly likely hydroxyl group absorptions as well. We conclude that tThe material is likely the product of desiccation of an aluminous gel; the amorphous nature of the material is indicated by the opalescence observed in visible light (Figure 1), as well as the results from

XRD, which showed diffraction peaks solely from aluminum metal and possibly a hydrous aluminosulfate mineral such as basaluminite ($\text{Al}_4(\text{SO}_4)(\text{OH})_{10} \cdot 4\text{H}_2\text{O}$).

The Al foil appears to have been oxidized from Al^0 to Al^{3+} , ultimately forming $\text{Al}(\text{OH})_3$. The most likely reductant in the meteorite is Fe in the form of Fe^{2+} or Fe^{3+} in magnetite, which is abundant within the matrix of Tagish Lake (Blinova et al., 2014). Alternatively, oxidation of sulfides may have released sulfuric acid which attacked the foil, forming an aluminum hydroxyl sulfate in the process (e.g., Singh, 1985). The hydrous nature of the product material indicates that liquid water was involved in the reaction, possibly as moisture condensed onto the specimens during their documentation August 12-13, 2000, just prior to their being wrapped in Al foil. The presence of S in the material may be indicative of the involvement of sulfuric acid in the reaction, or it may be coincidental: octaatomic S is an abundant component of the soluble organic fraction in Tagish Lake (Hilts et al. 2014), and thus may have been leached from the meteorite into the moisture involved in the reaction. Chlorine may also be coincidental, although the abundance of Cl in some of the product material suggests an external, contaminant source.

7.5 Implications for cold curation

The results of our detailed study of contaminants within the Subzero Curation Facility for Astromaterials provide sufficient baseline information for the commissioning of the facility. Processing of Tagish Lake specimens now occurs on a routine basis. To date, no significant levels of organic contaminants have been observed in any meteorite samples, although the use of witness plates is planned but not yet implemented. In practicality, the facility accomplishes the purpose for which it was built, i.e., to enable the processing of Tagish Lake specimens under clean, cold conditions in an inert atmosphere. The two main limitations encountered thus far in the use of the facility include mitigation of a glove box leak or atmospheric contaminant, and

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3 user comfort. The presence of a leak is a risk for any glove box. Leaks – recorded as increases in
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5 O₂ and/or H₂O on the detector – may result from inadequate seal on the antechamber door, or
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7 failure of O-rings. Atmospheric contamination may occur when volatile compounds are
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9 introduced into the box. An example of this occurred when we transferred vials into the glove
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11 box that had been cleaned with ultrapure water, yet inadequately dried; the small amount of
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13 moisture in the vials froze and then sublimated. The second limitation is user comfort – the low
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15 temperature of the freezer chamber compounds the challenges associated with glove box work.
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17 As with any cold environment work, standard operation involves donning insulated clothing
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19 (under the clean room smocks), working with a partner, and limiting exposure to the cold –
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21 typically 15-20 minutes at a time. The main advantage of the facility is that there is reduced risk
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23 to the specimens once they are transferred into the glove box, allowing for frequent user breaks
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25 (to warm up). However, in the case of a sudden leak or atmospheric contamination event (as in
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27 the example above), rapid mitigation of the problem can be hampered by the cold, especially if
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29 the user has already been working in that environment before the problem is noticed.
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36 Although established for work on Tagish Lake meteorite specimens, lessons learned from
37
38 the commissioning of the Subzero Curation Facility for Astromaterials have implications for
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40 collection media in the event of meteorite falls, and for the design and construction of cryogenic
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42 curation facilities for future sample return, in particular from planetary bodies in which volatile
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44 components (e.g., organic compounds or ices) are expected.
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48 7.5.1. *Implications for collection media-* 49

50 Tagish Lake specimen 11v, collected as a disaggregated sample from the frozen surface
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52 of the lake, contained the highest proportion of contaminants, attributable to its high surface area,
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54 its presumed conditions of handling after collection, and the plastic bag in which it was stored
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(Hilts et al., 2014). Oleamide is a common slip agent used in polymers to counteract friction and make them easier to pry open (Newton, 1993). In this case the extensive and repeated contact of the meteoritic dust with the inner surface of the ZiplocTM bag in which it was stored has resulted in oleamide from the interior of the bag being transferred to a sizable number of fragments that comprise specimen 11v. This is not the first documented occurrence of contamination by plastic bags: Brocks et al. (2008) found a variety of contaminants in the extracts of 26 indigenous hydrocarbon-bearing rock samples from around the world. Manufactured organic compounds derived from polyethylene sample bags, namely C₁₂/C₁₄/C₁₆/C₁₈ fatty acid amides (Grosjean and Logan, 2007) were found exclusively in the extracts of exterior rock sample surfaces. The dominant amide observed in these extracts is none other than oleamide.

The observed degradation of the Al foil in which some of the Tagish Lake specimens were stored is consistent with a reaction between the foil and components within the meteorite. In hindsight, such a result should have been expected as Al is a very powerful reducing agent (e.g., Takacs, 1992), especially when anti-passivating ions such as Cl⁻ are present (Li et al., 2013). In effect, the redox disequilibrium assemblage of minerals and organic matter in Tagish Lake and other carbonaceous chondrites make Al foil an unsuitable material for long-term storage of specimens. Nevertheless, clean, combusted Al foil is a suitable collection medium, as it is itself not a significant source of organic contamination.

7.5.2. *Implications for cryogenic curation facilities:*

Argon was chosen over dinitrogen gas in the Subzero Curation Facility for Astromaterials for two reasons. Firstly, Ar is denser than air, which causes it to mix with air much more slowly than N₂. The greater density of Ar is an asset in those instances where the glove box springs a leak and air gets into the interior of the glove box. Secondly, unlike N₂, argon is utterly inert

under typical laboratory conditions, with the extent of its chemistry being one short-lived, high energy HF adduct formed within a mass spectrometer (Khriachtchev et al., 2000). In fact, studies over the last twenty years that have shown that dinitrogen forms numerous compounds with early transition metals, including most significantly iron (Anderson et al., 2013; Fryzuk, 2003; Hazari, 2010), which runs counter to the view held by many researchers that dinitrogen is unreactive, and thus a suitable “inert gas” for curation of astromaterials. Since many of the same transition metals and their salts are found in meteorites, if the samples are stored and handled under dinitrogen gas, it is possible that unwanted dinitrogen compounds will be formed on their surfaces, especially if the temperature is above 0 °C. This contamination issue is obviated by the use of Ar gas. Perhaps the only disadvantage to the use of purified Ar gas (also relevant to dinitrogen gas) is that it is extremely dry (< 0.1 ppm H₂O), resulting in the sublimation of any indigenous water or other ices over time. Alternatives would be to attempt to match the relative humidity required to preserve indigenous water ice, or to store or process the specimens under ambient air. The decision to store the Tagish Lake specimens under air at low (-30 °C) temperature and to process them under Ar gas is based on practical limitations of the facility, but also reflects an emphasis on preserving and enabling the analysis of intrinsic organic compounds.

The sources of volatile contaminants in clean rooms and glove boxes are reasonably well known, and include filters, sealants, O-rings, paints, adhesives, tiles and packaging material, as well as laboratory consumables, such as garments, gloves, tape, cleaners and reagents (Calaway et al., 2014; Sun et al., 2003). The most problematic organic vapors released by these sources are polymer/plastics additives, such as styrene, phenol, methylstyrene and phthalates, along with amines/ammonia and low boiling hydrocarbons (Sun et al., 2003). Many of these species may continue to be offgassed for several months after installation (Calaway et al., 2014). Our results

of the assessment of volatile compounds in the glove box atmosphere demonstrate that the activity of these species may be reduced by low temperature operation of the glove box, in addition to the typical decrease in volatile species over time as a result of continued offgassing and removal by the purification system.

An additional advantage of low temperature glove boxes for curation of astromaterials is the reduction in reaction rates. An inert atmosphere alone will not completely stop hydrolysis and oxidation from occurring if the sample has been exposed to our atmosphere at any point prior to its storage; molecular oxygen and water molecules on the surfaces and in the interior of the sample will continue to react, even if the sample is immersed in an inert gas. Lowering the temperature as well, however, will drastically slow down the rates of oxidation and hydrolysis and preserve the integrity of the material for longer periods of time.

A cold, inert atmosphere has the added advantage that it will diminish the rate of bacterial and fungal attack on the organics in astromaterials. Several groups have reported unequivocal evidence of fungal and bacterial growth on the surfaces of meteorites that had been exposed to our atmosphere for at least one month, including Tagish Lake (Steele et al., 1999; Toporski and Steele, 2007; Wirick et al., 2004). Bacterial growth in and on carbon-bearing astromaterials is doubly harmful to the study of the organic phases in these materials because the organisms not only remove indigenous compounds through feeding, they fractionate stable isotopes of C and N, and contaminate the remaining material with their waste products and, ultimately when the extraterrestrial “food” runs out, the remnants of their bodies (e.g., Fox, 2002; Steele et al., 2001).

Toporski and Steele (2007) stressed the need for rapid investigation of freshly fallen meteorite or returned samples, as well as the use of appropriate storage conditions within curation and handling facilities to limit bacterial or fungal growth, and hence minimize

contamination with biologically-derived, terrestrial organic molecules. Microbial growth generally terminates below 0 °C due to the lack of liquid water and the decrease in enzymatic activity (Ratkowsky et al., 1982); although desiccated and vitrified organisms as low as -26 °C may survive once warmed up above 0 °C, few organisms can metabolize at temperatures below about -2 °C (Clarke et al., 2013). We maintain that cold temperatures (< -10 °C) can contribute significantly to minimizing contamination by the activity of microorganisms. Furthermore, an anaerobic environment such as that provided by an Ar (or N₂) atmosphere may also inhibit growth of microorganisms, since anaerobic metabolism is much less efficient than aerobic metabolism (e.g., Iuchi and Weiner, 1996).

7.5.3 Summary of recommendations

As a result of our study, we provide the following recommendations for the curation and handling of any astromaterials in which volatiles and/or organic compounds are expected. We note that these recommendations should be considered in addition to existing best practices for astromaterials (e.g., Calaway et al., 2014), within the context of the requirements for the specific type of astromaterial being curated (e.g., Allen et al., 2011). For example, meteorites collected through the U.S. Antarctic Search for Meteorites (ANSMET) program are kept frozen during shipping from Antarctica to NASA JSC, where they are subsequently thawed in a clean (class 1000) continuous-flow N₂ environment (Allen et al., 2011); such conditions will desiccate the samples in order to prevent water-facilitated oxidation of e.g., metal, as intended. This type of processing is perhaps appropriate for the majority of ordinary chondrites – which are volatile-depleted and metal-rich – and considering that many Antarctic meteorites already show some evidence of terrestrial alteration, either the form of oxidation or the formation of evaporite minerals (Hallis, 2013; Jull et al., 1988; Losiak and Velbel, 2011). In this context the purpose of

processing is to halt the progress of terrestrial alteration, although it should be noted that any ices, other volatiles and possibly some portion of the water-soluble organic component will be lost. Our recommendations are most directly relevant to freshly fallen, volatile-bearing meteorites, with the goal of minimizing terrestrial contamination and preserving volatile compounds during collection and long-term curation.

1. Polyethylene plastic bags should be avoided during collection ~~of freshly fallen meteorites~~ (if possible), and for long-term storage of these types of specimens, in favor of combusted glass jars with Teflon-lined caps, or Teflon bags or jars.
2. Al foil which has been combusted ($>450^{\circ}\text{C}$ for 8 hours) to remove organics is a suitable material for collection, but not long-term storage, of these types of specimens.
3. Argon gas should be considered for use in providing an inert atmosphere.
4. Low temperatures ($< -10^{\circ}\text{C}$) should be used to store specimens in order to lower reaction rates, preserve indigenous volatile organic compounds, discourage microbiological activity, and reduce the activity of volatile organic contaminants.
5. Mechanisms to provide clean (Class 1000 or greater) and cold ($< -10^{\circ}\text{C}$) air facilities should be investigated, as such facilities would enable clean, cold processing of samples that do not require an inert atmosphere.

The commissioning of the facility, and ongoing studies involving Tagish Lake and other astromaterials promises to yield key insights into the advantages and limitations of cold curation for future samples returned from volatile-bearing targets.

Acknowledgements

We thank Matt Ross for help with the interpretation of GC-MS data, Graham Pearson for use of the airborne particle counter, Nathan Gerein and George Braybrook for assistance with

SEM data collection, Diane Caird for help with X-Ray Diffraction data collection, and Richard Herd for access to his unpublished report on the Tagish Lake meteorite. [Thorough reviews by Carl Allen, Cari Corrigan and an anonymous reviewer resulted in improvements to the manuscript and were much appreciated.](#) Funding for this study was provided by Natural Sciences and Engineering Research Council (NSERC) Grant 261740 to CDKH, as well as MacEwan University funding to RWH. Funding for construction and commissioning of the Subzero Curation Facility for Astromaterials was provided by the University Research and Strategic Investments Grant Program of Alberta Innovation and Advanced Education (formerly Advanced Education and Technology), the Faculty of Science at the University of Alberta, and NSERC Research Tools and Instruments Grant 360396-08 to CDKH.

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Tables

Table 1. Number of particles measured at various locations within the clean room anteroom and walk-in freezer, using an Airborne Particle Counter.

Particle Size (μm)	Clean Room					Freezer Chamber	
	1	2	3	4	5	Before Cleaning	After Cleaning
						A	A B
≥ 0.3	0	0	0	109	5	12027	7058 7949
≥ 0.5	0	0	0	14	1	951	1094 964
≥ 1.0	0	0	0	3	0	169	362 256

Notes: Values represent averages of up to three 5-minute sampling periods each. Within the clean room (see Figure 2a), locations 1 and 2 are in front of the specimen cabinets, location 3 is in the corner to the left of the freezer door, location 4 is to the right of the freezer door, and location 5 is the in center of the room. Within the freezer, location A is on a stainless steel table near the door (visible in Figure 2b) while location B is in the rear corner of the freezer opposite the door.

Figure Captions

Figure 1. Examples of Al foil and associated material found with some Tagish Lake specimens.

A) Specimen 11s showing brittle Al foil adhered to its surface. B) Opalescent grains found in close association with brittle foil (also from specimen 11s).

Figure 2. The Cryogenic Curation Facility at the University of Alberta, consisting of a Class 100 room temperature anteroom (A), and a walk-in freezer (B) in which an Ar glove box is housed (C).

Figure 3. Detailed views of selected components in the Cryogenic Curation Facility, including the main glove box chamber (A), sample exchange antechambers (B), the gas purification system and associated heater and chiller units (C), and a viewing window in the freezer door (D).

Figure 4. GC-MS traces for SPME fibers exposed to glove box atmosphere at room temperature (top) and at -20 °C (bottom).

Figure 5. GC-MS trace of DCM rinse of polyurethane gloves, with blank shown for comparison.

Figure 6. GC-MS traces of DCM rinses of fresh Al foil (top), and Al foil from specimens 10a (middle) and 11i (bottom).

Figure 7. Altered Al foil from Tagish Lake specimens. SEM secondary electron images of altered foil in specimen 11i (A) and 11s (B); EDS spectra (C-E) show variation in composition in terms of S and Cl from across all samples analyzed. Cr in the EDS spectra is from the conductive coat applied during sample preparation.

Figure 8. FTIR spectrum of opalescent material associated with altered Al foil, with locations of major absorptions noted.

Figure 1

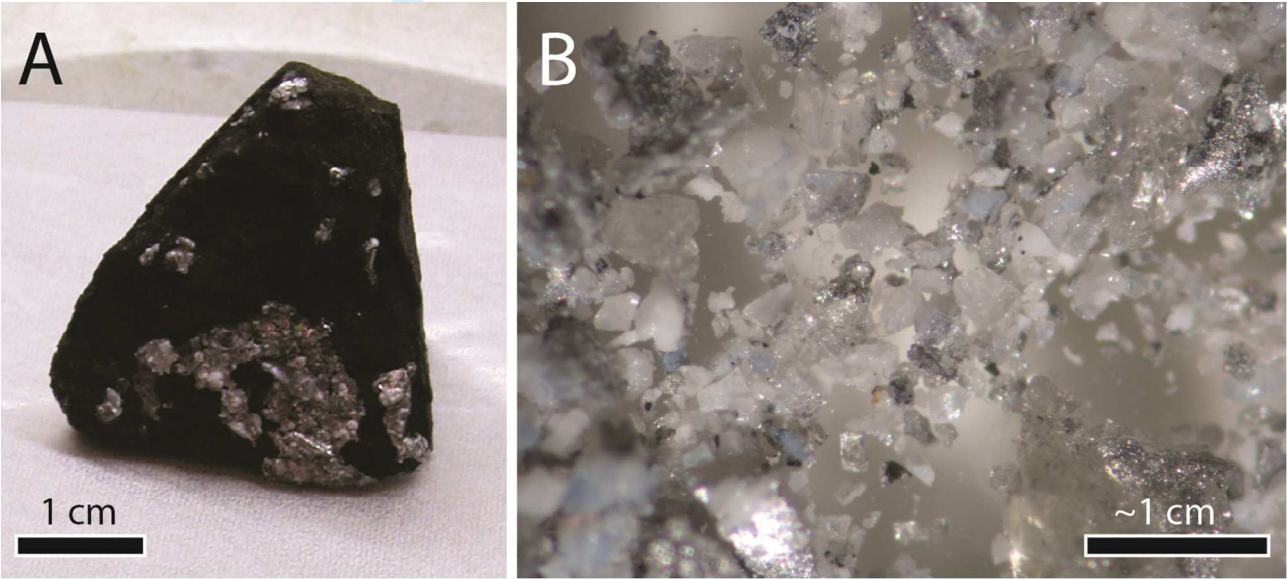


Figure 2

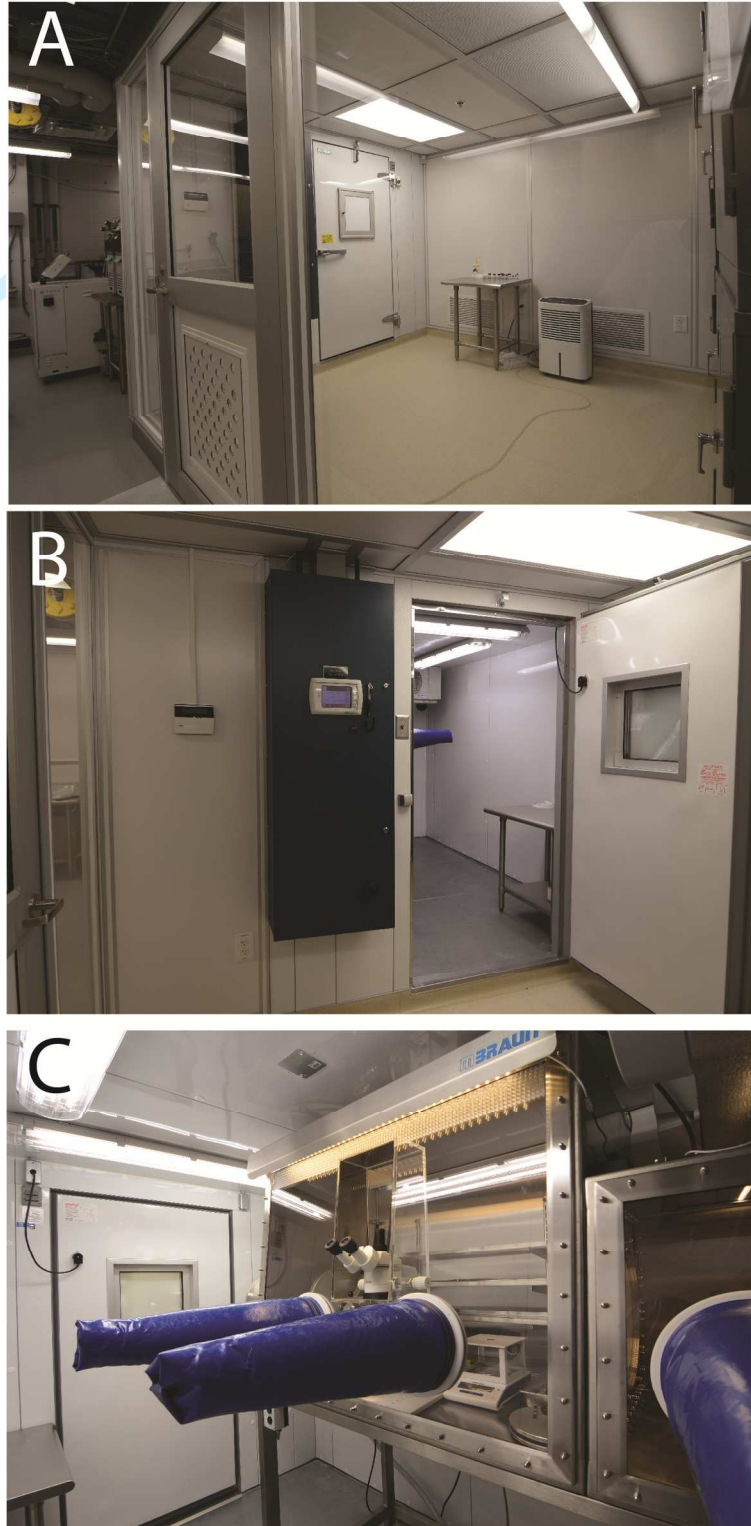


Figure 3

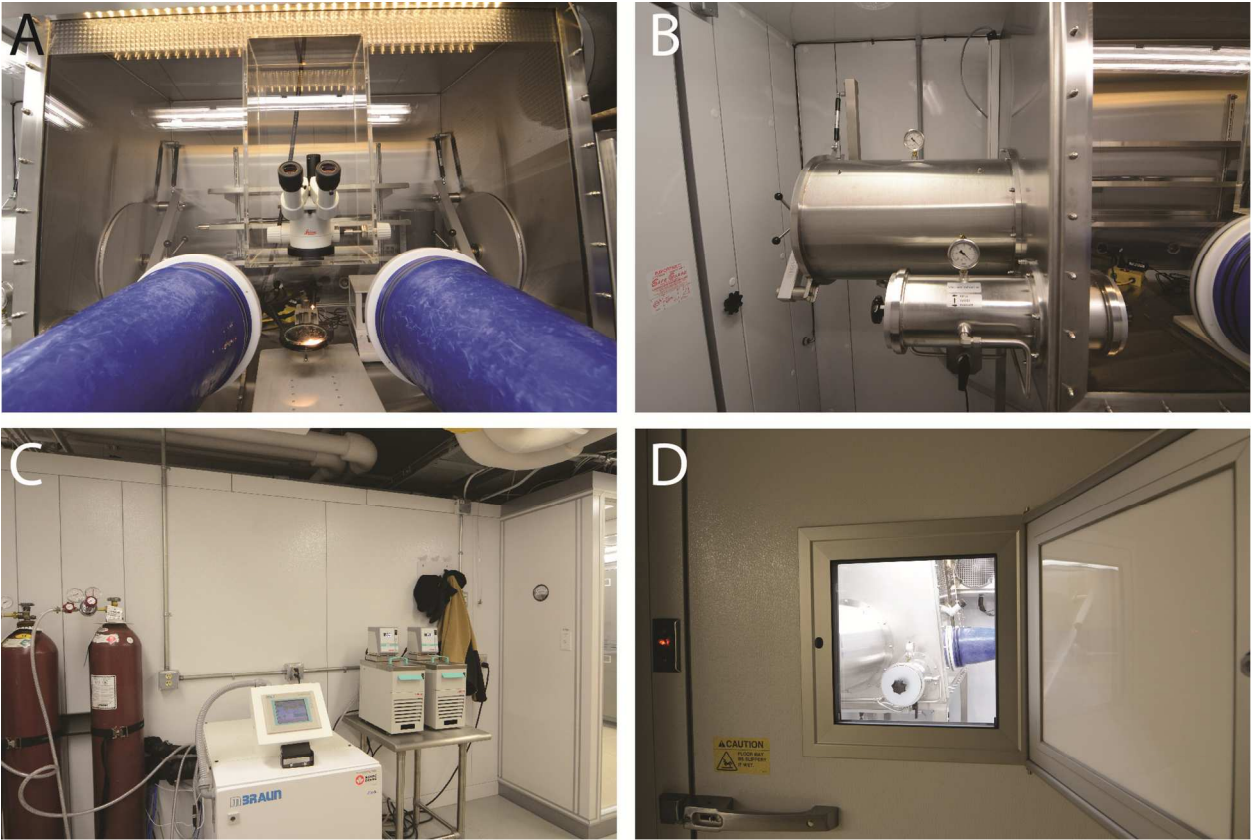


Figure 4

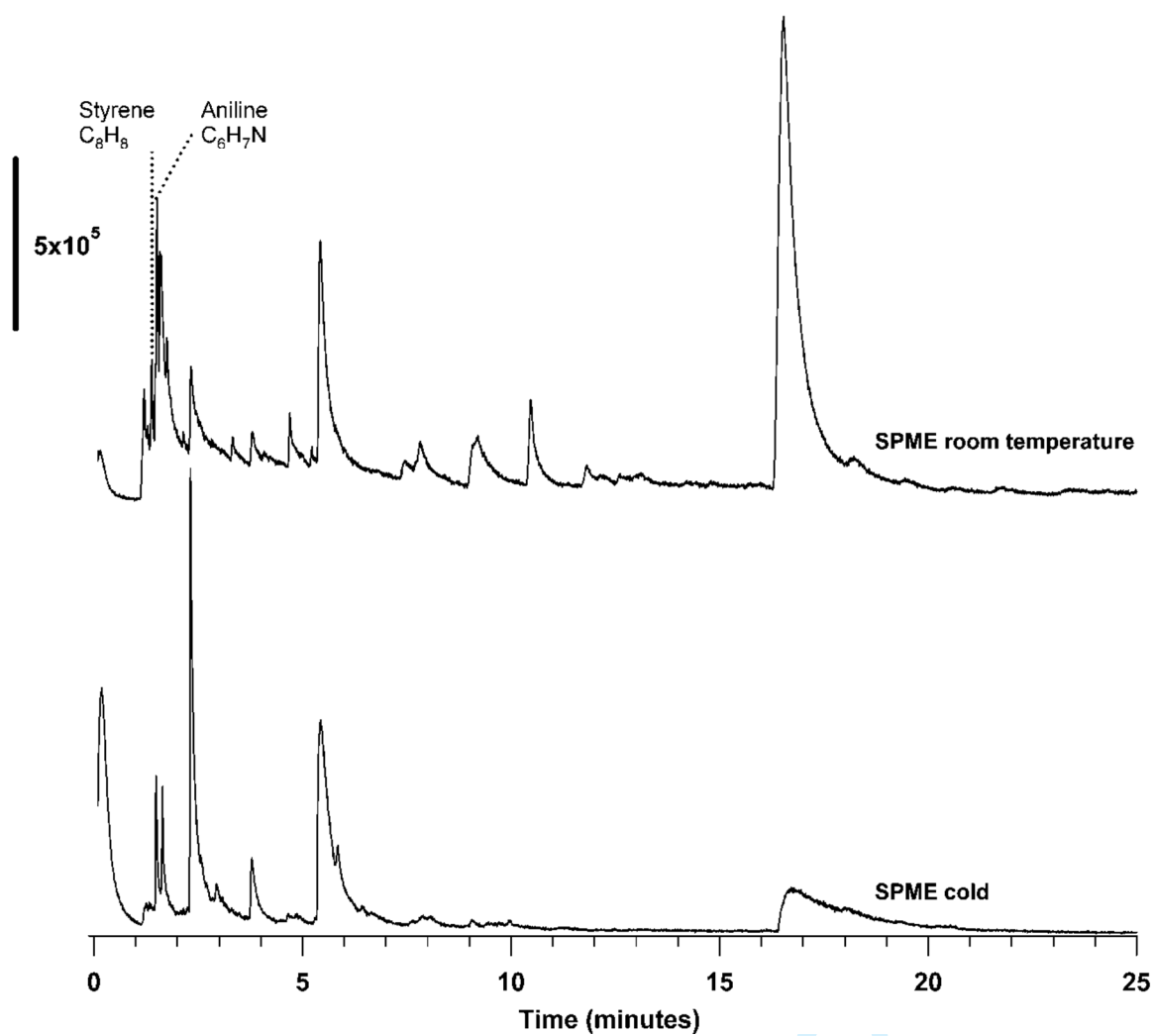


Figure 5

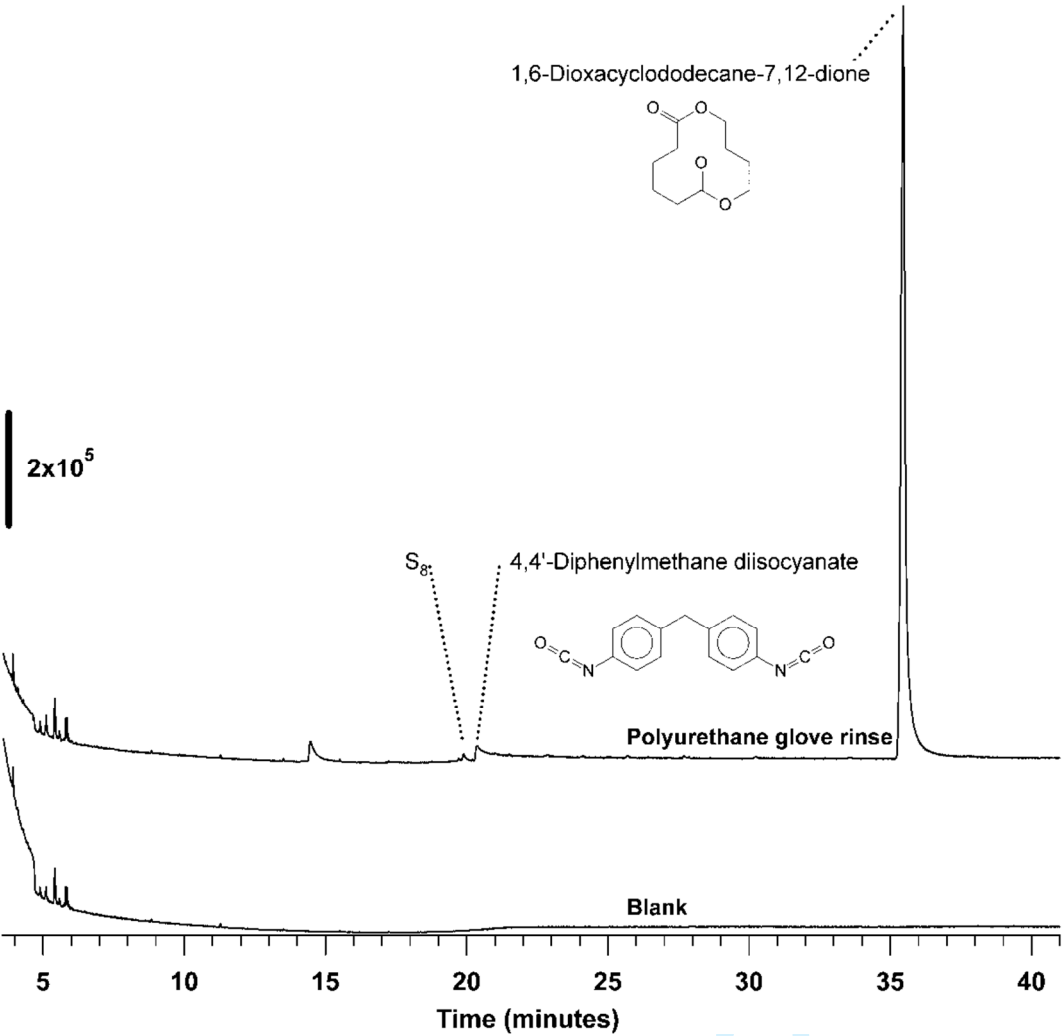


Figure 6

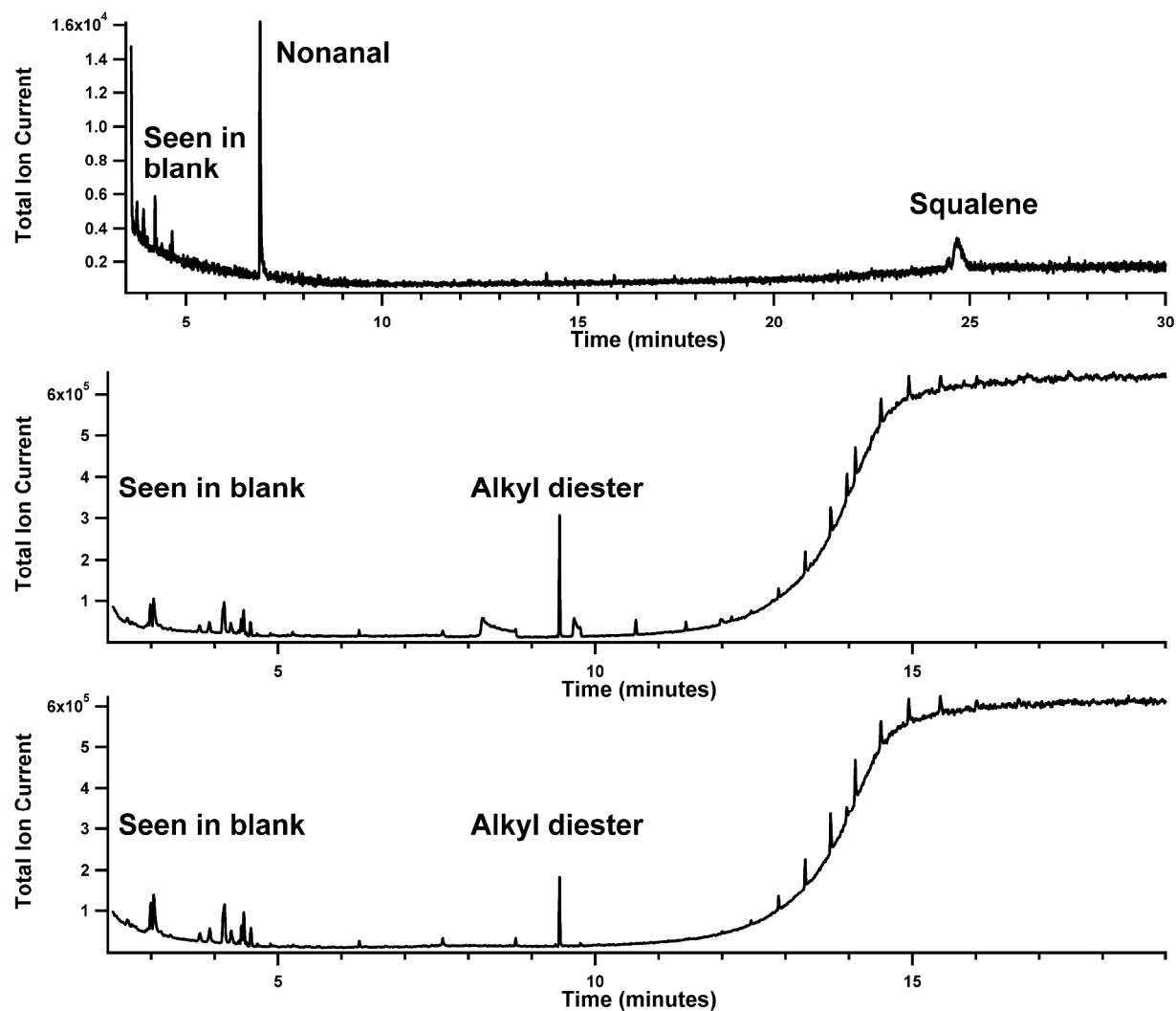


Figure 7

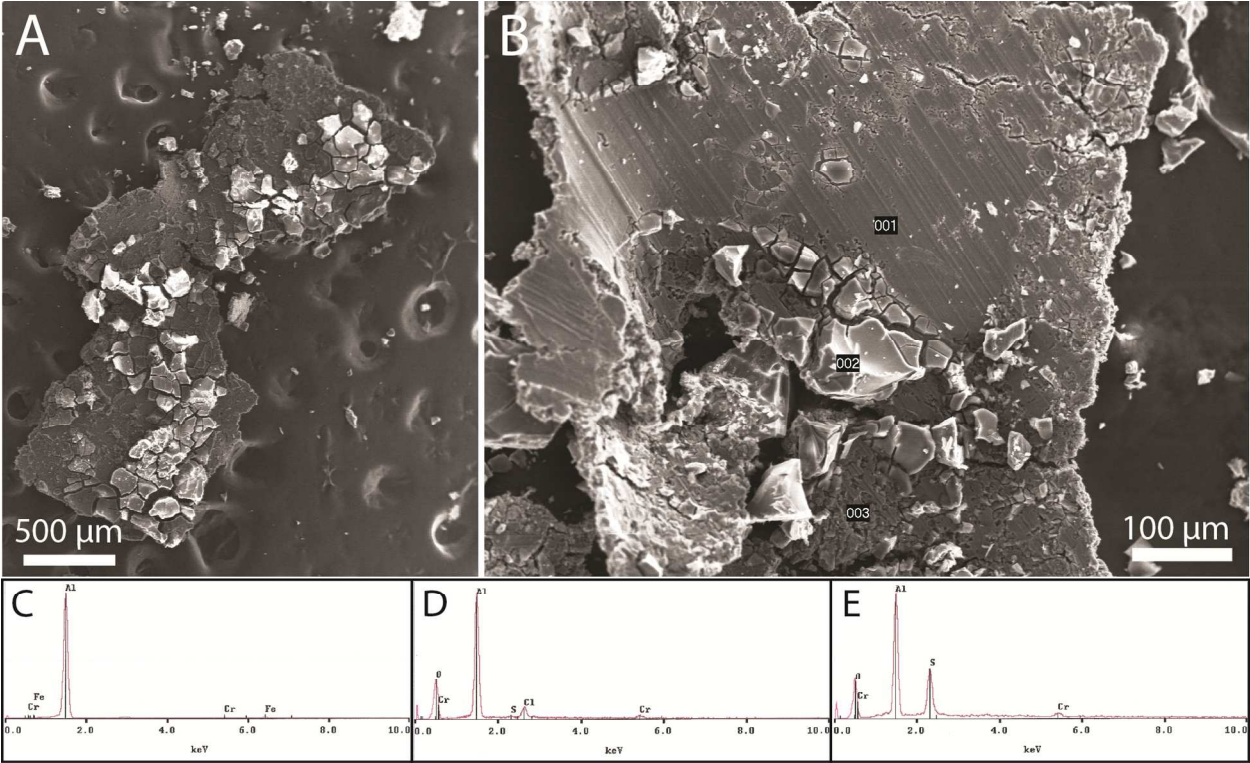
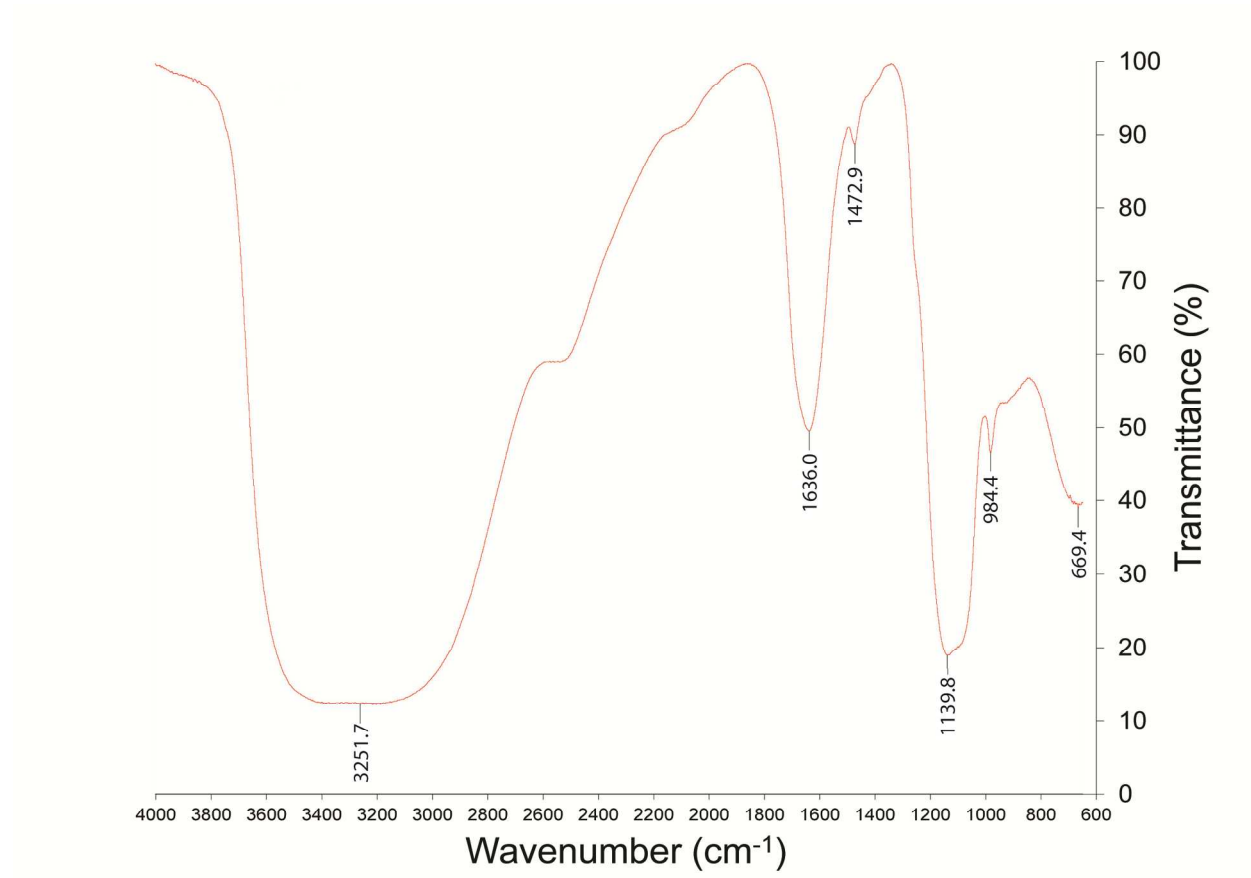


Figure 8



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Appendix: Testing the SPME(PEG)-GC(Nukol)-MS method for mono- and dicarboxylic acids

Three standard mixtures of carboxylic acids were prepared: one with only monocarboxylic acids, one with only dicarboxylic acids, and a third with a mixture of both (Table A1). Analyses were carried out in the same manner as outlined in Section 6.8. Figure A1 contains the chromatograms arising from the SPME(PEG)-GC(Nukol)-MS analyses performed upon the three mixtures. These results provide unequivocal support of our hypothesis as no dicarboxylic acids are observed in either the dicarboxylic acids trace or the mono and dicarboxylic acids mixture trace, while all of monocarboxylic acids are seen in the monocarboxylic acid trace and the trace for the mono- and dicarboxylic acids mixture. Thus, it is clear that the high polarity of the dicarboxylic acids and the ability of each dicarboxylic acid molecule to form two strong bonds to polar surfaces, such as the outer layer of PEG, precludes their direct determination using our SPME-GC(Nukol)-MS methodology. It would appear that at least for the present, the determination of dicarboxylic acids still requires that they be converted to a more volatile form through some type of derivatization.

Table A1: Carboxylic acid solutions used in testing the SPME(PEG)-GC(Nukol)-MS method

Compound	Nominal Concentration (ppm), monocarboxylic solution	Nominal Concentration (ppm), dicarboxylic solution	Nominal Concentration (ppm), mixed solution	Chemical Formula
Monocarboxylic Acids				
Acetic acid	25		12.5	C ₂ H ₄ O ₂
Propanoic acid	25		12.5	C ₃ H ₆ O ₂
Isobutyric acid	25		12.5	C ₄ H ₈ O ₂
Buteric acid	25		12.5	C ₄ H ₈ O ₂
Isovaleric acid	25		12.5	C ₅ H ₁₀ O ₂
Valeric acid	25		12.5	C ₅ H ₁₀ O ₂
Isocaproic acid	25		12.5	C ₆ H ₁₂ O ₂
Caproic acid	25		12.5	C ₆ H ₁₂ O ₂
Heptanoic acid	25		12.5	C ₇ H ₁₄ O ₂
Dicarboxylic Acids				
Malonic acid		25	12.5	C ₃ H ₄ O ₄
Succinic acid		25	12.5	C ₄ H ₆ O ₄
Glutaric acid		25	12.5	C ₅ H ₈ O ₄
Adipic acid		25	12.5	C ₆ H ₁₀ O ₄
Pimelic acid		25	12.5	C ₇ H ₁₂ O ₄
Suberic acid		25	12.5	C ₈ H ₁₄ O ₄
Azelaic acid		25	12.5	C ₉ H ₁₆ O ₄
Sebacic acid		25	12.5	C ₁₀ H ₁₈ O ₄

Figure A1.

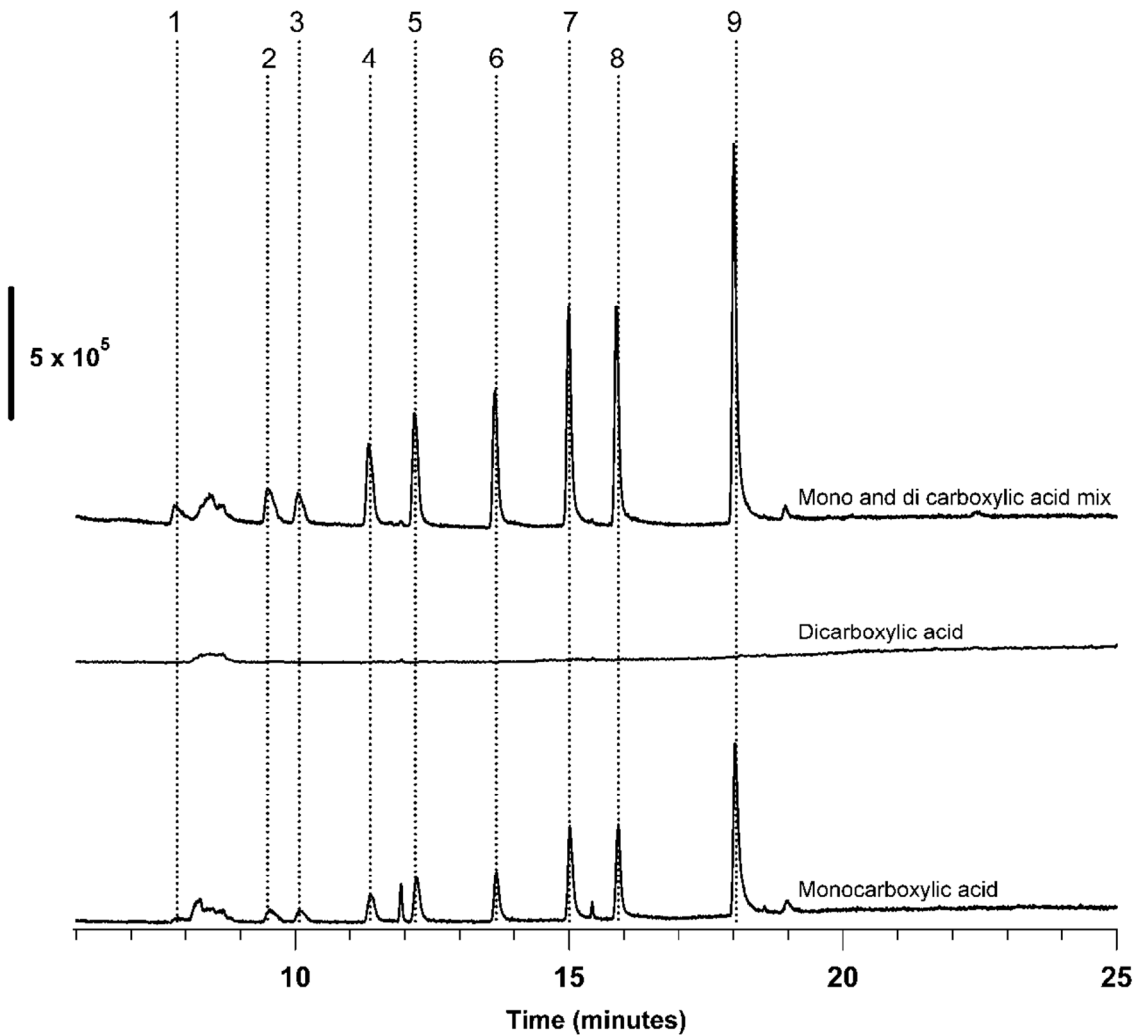
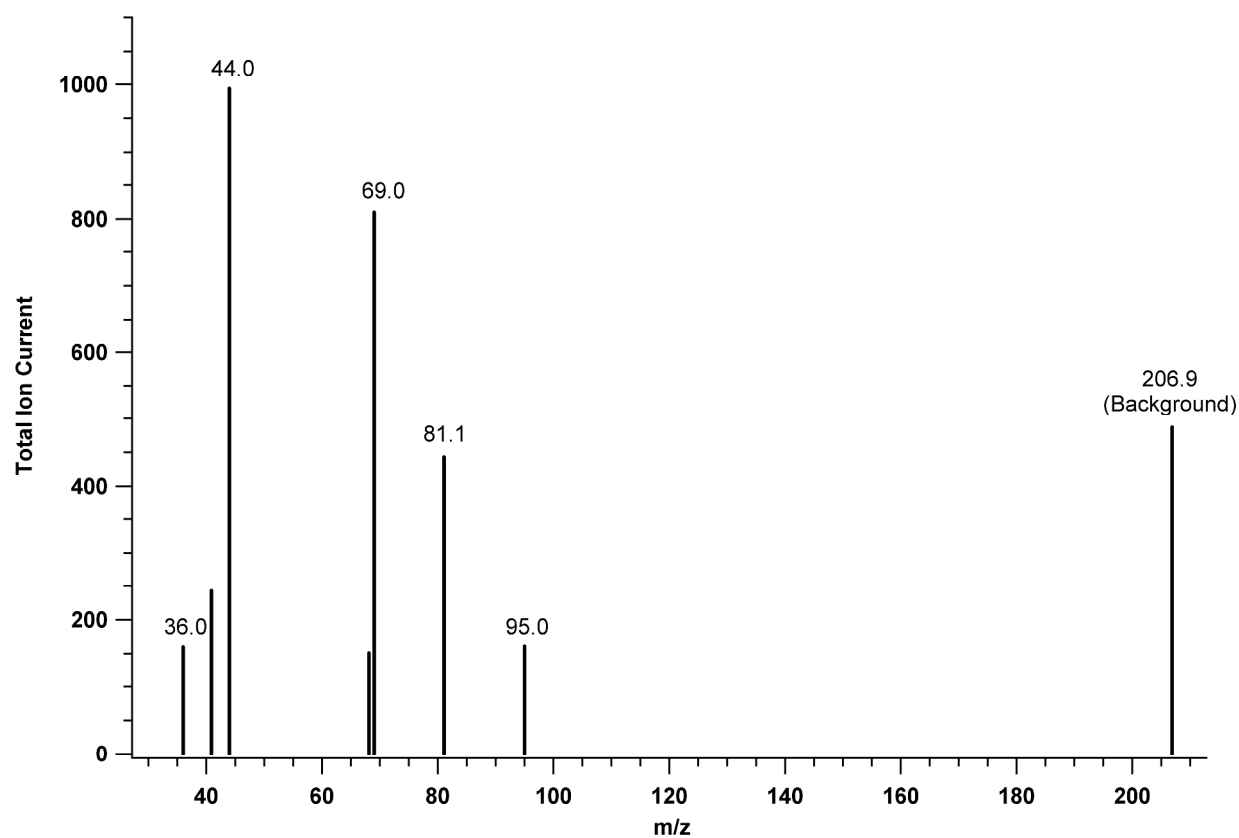


Figure A1. Chromatograms of the three mono- and dicarboxylic acid mixtures tested using the SPME(PEG)-GC(Nukol)-MS method.

Figure A2**Figure A2.** Mass spectrum for squalene identified from rinse of Al foil (Figure 6).