BUILDING GROUNDWORK RATIONALE FOR LIPID BIOMARKER DETECTION IN EUROPA'S CRYOVOLCANIC DEPOSITS A. Moreras-Marti[1,3] and M. Fox-Powell[2], J. Toney[3], A. C. McAdam,[4] C. A. Knudson[4,5,6], L. J. Lewis[4,5], A. L. Zerkle[1], C. R. Cousins[1] [1]School of Earth and Environmental Sciences, University of St Andrews, Irvine Building, North Street, Fife, UK, KY16 9AL (amm48@st-andrews.ac.uk). [2]AstrobiologyOU, The Open University, Milton Keynes, UK. MK7 6AA. [3]School of Geographical & Earth Sciences, Glasgow University, Gregory Building, Glasgow, UK. 8NN, [4]NASA GSFC, Greenbelt, MD 20771, [5]CRESST II, Greenbelt, MD 20771,[6]University of Maryland, College Park, MD 20742.

Introduction: Throughout this decade, two fly-by missions, NASA's Europa Clipper and ESA's Jupiter Icy moons Explorer (JUICE), will lay reconnaissance groundwork for the future landers that will directly search for evidence of life on Europa's surface [1,2]. Europa's surface material will not only inform about external processes, but also about the potential habitability of its ocean beneath the thick ice shell [3]. Cryovolcanism is a major route by which extrusion of subsurface fluids can occur. Cryovolcanic deposits could therefore preserve biosignatures transported from the ocean to the surface, making them high priority targets for landed missions [4]. Telescopic observations of Europa's surface composition suggest it's made of water ice, with several highly hydrated phases [5-7], dominated by magnesium and sodium-chloride and sulfate salts, although the relative endogenic and exogenic contributions to these phases is an ongoing debate [6-7].

Experimental work shows that microorganisms can be captured by minerals produced through freezing of silica rich hydrothermal fluids, and can then be detected in cryogenic mineral precipitates using spacecraft relevant techniques [8]. Salts themselves can also capture organics within the mineral matrix, either in fluid inclusions or along crystal boundaries [9]. Therefore, there is a need to understand how microbial biomarkers can become captured within Europa-relevant salt phases and ultimately detected using techniques considered for future missions.

The goal of this study is to build a rationale for prioritising cryovolcanic deposits for biosignature and/or indigenous organic detection. Knowing which hydrated cryovolcanic materials to target that best preserve organic molecules will be crucial to future missions confidently detecting, or ruling out, evidence of life. We use natural salts analogous to the non-icy deposits on Europa's surface to achieve this.

Description of analogue site: Axel Heiberg Island (AHI) in the Canadian Arctic, hosts unique hypersaline springs, of which Lost Hammer spring was used for this study [11]. The spring is characterised by highly saline anoxic fluids which upwell from depth, forming extensive deposits of hydrated sodium sulfate and chloride [10,11]. Furthermore, Vis-NIR reflectance analysis from Lost Hammer salts show major absorption features with similar asymmetry and broadening to the NIMS data from europan non-icy material [11].

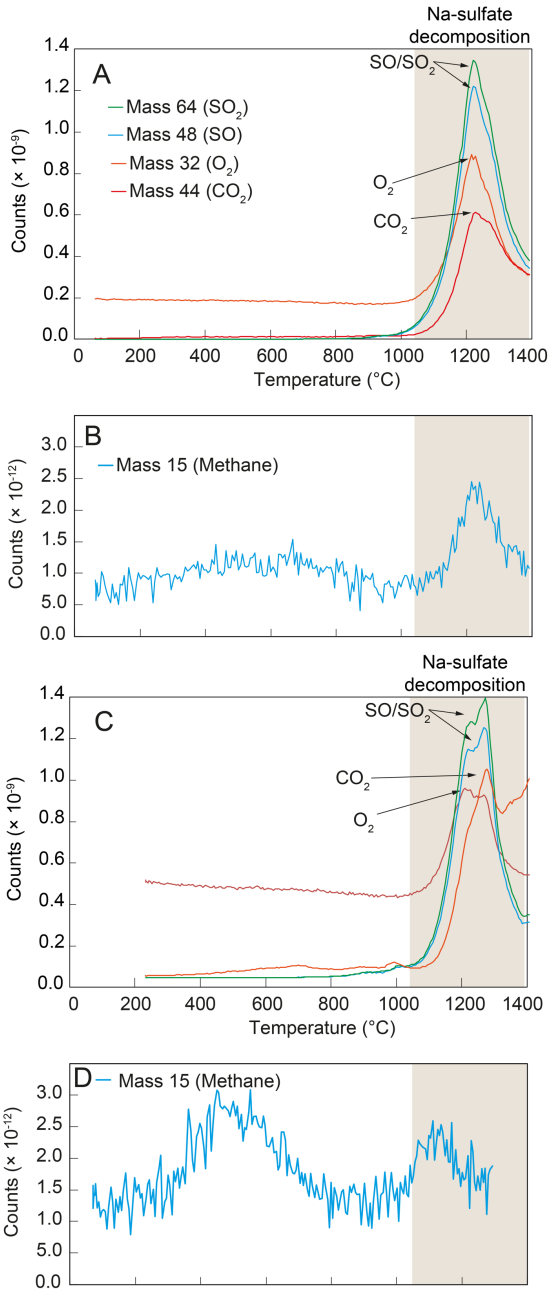

Figure 1. EGA-MS analysis of Lost Hammer salt sample AH_17_143 (A, B) and AH_17_167 (C, D). A and C: O_2/CO_2 and SO/SO_2 evolutions. B and D: Methane evolutions.

These properties make the spring materials suitable analogues for the cryovolcanic non-icy deposits at Europa [11,12]. The pH of the brine from which these salt deposits precipitate ranges from 5.7 to 6, the temperature increases from -3.6 to 1.8 °C and the dissolved oxygen increases from 0.1 to 7.7 ppm [11]. The chloride water concentration is 4000 mM, and sulfate concentrations 60 mM [11]. The indigenous microbial communities comprise halotolerant and sulfur-cycling groups.

Methods: Eighteen samples from the Lost Hammer spring salt deposits were analysed with evolved gas analysis mass spectrometry (EGA-MS). The EGA-MS analyses were performed using a Setaram Labsys Evo Thermogravimeter/Differential Scanning Calorimeter coupled to a Pfieffer OmniStar quadrupole mass spectrometer set up to operate under SAM-like heating and carrier gas flow conditions (~1 mL/min He flow rate and ~25 mbar of He gas pressure in the pyrolysis oven). These results are coupled to lipid biomarker analysis. The total lipid content of the samples was extracted and separated into different compound classes for analysis using silica gel column into four fractions N1 to N4 to yield: aliphatic hydrocarbons; ketone, ester and aromatics; alcohol and polar lipids respectively. Those three fractions were analysed by GC-FID and GC-MS to quantify the various compounds the samples contain.

Preliminary results: EGA-MS data show gas evolution peaks for *m/z* 48 and 64 (SO and SO_2 respectively), and *m/z* 32 and 44 (O_2 and CO_2 respectively) all at about 1200 ºC, the temperature at which the sodium sulfate breaks down. Mass *m/z* 15 was monitored for methane, and gas evolution was also noted at this temperature and lower temperatures (Figure 1). The O_2 likely results from sulfate breakdown, and the CO_2 may result from oxidation of some organic compounds.

The EGA-MS results indicate organics co-evolve with the breakdown of sulfates, suggesting that some sample organics are hosted within the sulfate salts. Evidence of the organics are observed in the EGA data likely oxidized (e.g., to CO_2) by the O_2 evolved at similar temperatures. Organics in the sulfates may indicate co-precipitation with the salts directly from the spring brines during either a primary crystallization, or during a secondary/latter recrystallisation. Sodium sulfates are very soluble and the LH salt deposits could have undergone dissolution and reprecipitation. This also suggests that the presence of organics trapped within Europa-relevant sulfates can be inferred from data obtained by flight-like pyrolysis techniques.

The results from this study will inform the development of *in situ* mission science at Europa by understanding the preservation of lipid biomarkers in materials with similar mineralogy to Europa's surface.

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