PERFECTING THE GAS CHROMATOGRAPHY – MASS SPECTROMETRY (GC-MS) ANALYTICAL PROTOCOL FOR THE IDENTIFICATION OF MARTIAN METEORITE ORGANICS

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Introduction: Martian missions and meteorite analyses indicate that indigenous, organic compounds exist on Mars in the atmosphere, sediments, and rocks [1-3]. Martian meteorites are mainly basaltic in composition, thus our Earth-based analysis of Martian organics is limited to these igneous rocks. However, the Mars Sample Return (MSR) mission will, if successful, provide a wider range of material for ex situ analysis [4] (e.g., sedimentary rocks). It is therefore important to optimize the analytical protocol for identification of organics in Martian material before MSR.

The oldest and most studied Martian meteorite, Allan Hills 84001 (ALH 84001), is an orthopyroxenite which formed ~4 Ga [5]. It is host to carbonate globules (~3.90 Ga) within which macromolecular organic carbon (MMC) can be found associated with magnetite [6]. The textural setting of these organics rules out the possibility for terrestrial contamination, thus making them indigenous to Mars [7]. The formation mechanism of these carbonates has been intensely debated [1,8] but the majority of published literature indicates a hydrothermal origin, possibly via a dissolution-precipitation reaction involving maskelynite and carbonic fluid [9]. Terrestrial analogues containing similar MMC-rich carbonate globules to ALH 84001 are found in the Bockfjorden Volcanic Complex (BVC) in Svalbard [2]. The aim of this research was to analyse the organic composition of these terrestrial analogues in order to: 1) provide a comparison to ALH 84001 and other Martian meteorite MMC, and 2) optimize the methodological protocol of gas chromatography-mass spectrometry (GC-MS) for Martian meteorites.

Geological History of the Analogues: The Svalbard archipelago, Norway, is host to the Bockfjorden Volcanic Complex (BVC) in Northwestern Spitsenberg, within which 3 Quaternary age volcanoes (Sverrefjell, Sigurdfjell and Halvdanpiggen) lie near the N-S trending Breibogen Fault of Devonian age [10]. These volcanoes erupted subglacially approximately 1 Ma and contain equivalent organic carbon abundances to Martian meteorites, have similar basaltic mineralogy, and contain carbonate globules similar to those found in ALH 84001 [11,12] Carbonate globules for the BVC have been attributed to CO^2 rich hydrothermal fluid interaction [11,12]. Investigating the MMC within the carbonate globules of the BVC volcanoes is therefore an important proxy for Martian meteorite organic extraction.

Methods: Three samples were analysed via GC-MS to determine their organic composition: one sample each from BVC volcanoes Sigurdfjell and Sverrefjell, and JSC-1 Martian soil simulant. Samples were crushed using both an agate mortar and pestle and a ball mill (for comparison). Solvent extracts were prepared using the ASE 350 and dichloromethane-methanol (DCM-M). The UoG Agilent GC-MS (GC7890b-MS5977A) was utilized for organic analyses. The powdered sample size was reduced incrementally to test the detection limits of the GC-MS, starting with 1.5g fractions, 0.75g, 0.5g and finally 0.25g. GC-MS is an established technique for Martian mission organic analyses – the Viking landers used GC-MS to identify indigenous chloromethanes and chlorobenzene in the Martian regolith [13,14], and the Sample Analysis at Mars (SAM) suite onboard the Curiosity rover set out to identify as many organic compounds and volatiles as possible in Martian surface material. Eigenbrode et al. [15] report thiophene molecules detected by GC-MS from the SAM suite within in-situ mudstones on Mars' surface. However, igneous Martian meteorites contain low abundances of organics, making GC-MS organic identification challenging.

Implications: Detection of MMC in low abundance material using GC-MS is an important proxy for Martian meteorite analysis and Martian sample return material as small volumes (~0.2g) of material is available for processing. Analysis of terrestrial analogue MMC will provide important insights into Martian MMC and therefore aids in understanding planetary processes. A conclusive protocol will optomise results for future research.

References: [1] McKay D. et al., (1996) *Science*, 273(5277), 924- 930. [2] Steele A. et al., (2012) *Science*, 337(6091), .212-215. [3] Bada, J et al., (1998) *Science*, 279(5349), 362-365. [4] Grady M (2020) *Space Science Reviews*, 216(4). [5] Treiman et al., (2021) *Astrobiology*, 21(8), 940-953. [6] Steele A. et al., (2016) *Meteoritics & Planetary Science*, 51(11), 2203-2225. [7] Mittlefehldt D. W (1994) *Meteoritics*, 29, 214-221. [8] Gleason. J. et al. 1997. *Geochimica et Cosmochimica Acta* 61: 3503–3512. [9] Kring et al., 1998. *Geochimica et Cosmochimica Acta* 62: 2155-2166. [10] Skjelkvåle, B. et al., (1989) *Journal of Volcanology and Geothermal Research*, 37(1),.1-19. [11] Treiman, A., 2012. *Polar Research*, 31(1), p.17320. [12] Steele A., et al., (2007) *Meteoritics & Planetary Science*, 42(9), 1549-156. [13] Freissinet C. et al., (2015) *Journal of Geophysical Research: Planets*, 120(3), 495-514. [14] Heinz, J. and Schulze-Makuch, D. (2020) *Astrobiology*, 20(4), 552-561 [15] Eigenbrode J., et al., (2018) *Science*, 360(6393), 1096-1101.