THE EXTRACTION OF ORGANIC COMPOUNDS FROM SULPHATE MINERALS FOR ASTROBIOLOGICAL EXPLORATION, S. A. Bowden, J. Parnell and J. Cooper. 1 Dept. Geology and Petroleum Geology, University of Aberdeen, AB24 3UE, U.K., (s.a.bowden@abdn.ac.uk), 2Dept Electronics and Electrical Engineering, University of Glasgow, GL12 8LT, U.K.

**Sulphates on Mars:** Sulphates were estimated to constitute 10% of the Pathfinder and Viking Lander sites [1] and up to 30% at the MER-B landing site [2]. This is significant in the context of astrobiological exploration as aqueous environments rich in sulphates could have been a habitat suitable for phototrophic life on Early (3.45 Ga) Earth [3] and sulphates are known to provide a habitat for phototrophic life in a cold, desiccating environment in the Canadian Arctic [4]. The former represent conditions similar to those that may have existed on Mars in the past and the latter conditions similar to those existing on the surface of Mars today.

**Evaporites on Earth:** Evaporite deposits on Earth comprise sulphates, carbonates and halides and have been shown to preserve biomarker information from the environment of their deposition for millions of years, although in lesser quantities than facies-equivalent mudstones [5]. More recently fossil lipids present in stalagmites have been used to study past climates [6]. The lipids in the stalagmites are thought to have been derived from primary producers at the surface and transported by groundwater prior to incorporation within a carbonate mineral matrix.

We are developing a lab-on-a-chip surface-enhanced-resonance-raman-scattering system [7] to analyse evaporite minerals for key organic molecules of astrobiological interest. This has necessitated the production of evaporite minerals that contain suitable target analytes for both proof of concept purposes and to provide a reference material for testing extraction and sample handling protocols.

**Precipitation of model evaporite minerals.** In order to precipitate organic bearing evaporites, solutions of dissolved evaporite mineral and solutions containing a model organic compound (anthracene, aspirin and stearic acid) are mixed and evaporated under standard conditions. The solid mineral phase is collected after all of the water has evaporated.

**Analysis:** Samples of the model evaporite mineral had their surface exhaustively cleaned and were then extracted using micro/mini liquid-liquid extraction: samples were dissolved in pre-extracted deionised water and then extracted three times with DCM. Samples of gypsum (CaSO₄·2H₂O) were dissolved in pre-extracted 20% HCl (aq) and then extracted three times with DCM. Soil samples from Devon Island were Soxhlet extracted and an aliquot of the product separated using a packed silica column into aliphatic, aromatic and polar products. Products were analysed by GC-MS in SIM mode and quantified by GC-FID.

**Model crystals:** The graph in Fig. 1 is a plot of anthracene yield against crystal size (halite). Two important features are: 1) yields per gram of mineral are much lower than the concentration per gram of mineral in the starting solution and 2) the yields for small volumes of mineral are very chaotic. This generally accords with the observation that the concentration of organics in evaporite minerals is low [5], and with most organics being absorbed onto particulate matter in the parent solution which is included within the mineral phase as it precipitates.

![Fig. 1. Yield of anthracene obtained from the liquid-liquid extraction of model crystals of halite precipitated in the laboratory. The starting concentration per g of halite was 5%.
](image)

Broader ranges of organic compound types are now being incorporated in epsomite (MgSO₄·7H₂O), and the effects of varying the concentration in the parent solution are also being investigated. The results obtained so far (Fig. 2) suggest that low rates of incorporation into evaporite mineral phases are probably a common feature for all types of organic compound. Additionally, it appears that there could be a limit on the absolute quantities that are incorporated into evaporite minerals and that organic compounds with functional groups are possibly better incorporated than pure hydrocarbon compounds. The presence of greater quantities of functionalized compounds in mineral matrices matches observations of real systems [8], although the main cause for this in most natural situations is probably the creation of greater quantities of functionalised organic compounds by living organ-
isms. This data suggests that preservation within a mineral matrix could enhance a naturally pre-existing bias.

Fig. 2. Yield of organic compound vs concentration of organic compound in parent solution for various types of simple organic molecule.

**Application to geological samples:** A variation of the mini/micro extraction method used to analyse the model crystals is being applied to investigating the weathering of a biological signal on Devon Island in the Canadian Arctic. In this setting hydrothermal fluids in an impact crater precipitated gypsum which has been colonized by cyanobacteria [4]. Figure 3 shows some of the results obtained so far in which samples from a sulphate deposit that has been colonized by cyanobacteria yielded alkylcyclohexanes with carbon numbers inherited from the alkylresorcinol biological precursors (principally C$_{21}$ and C$_{23}$ [9]). The distribution of carbon numbers for the alkylcyclohexanes in a sample of soil adjacent to colonized sulphate deposit is broader, probably representing inputs from a wider range of sources as well as the diagenetic alteration of the biological precursors. Less than 500 mg of gypsum (CaSO$_4$·2H$_2$O) were extracted to produce the results in Fig. 3. Much of the soil is rich in sulphate minerals, and in the future we will analyse the organic compounds that have been incorporated within these sulphates.

**Application to the development of microfluidic extraction system:** We are using the model sulphate crystals in the development of a microfluidic extraction system that will replace the current bench-top mini/micro extraction method. Among the variables we will consider are the fractionation and concentration of organic compounds that are present, the solvents used during liquid-liquid extraction and how to handle insoluble material present in the sample.

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