SPECTROSCOPIC METHODS FOR ANALYZING ORGANIC COMPOUNDS IN FLUID INCLUSIONS DURING PLANETARY EXPLORATION. A. Mazzini 1, R. Li 2, and J. Parnell 1, 1Department of Geology and Petroleum Geology, University of Aberdeen, Meston Building, King’s College, Aberdeen AB24 3UE, Scotland, UK, 2Open Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China.

Introduction: Fluid inclusions are valuable sources of information on the conditions under which their host minerals were precipitated. In the context of planetary exploration, information about fluid chemistry is particularly important, as it could provide constraints on the suitability of the environment to support of life, and could even contain direct biomolecular signatures of life. Accessing the fluid in inclusions trapped at the surface/near-surface of a planet such as Mars will therefore be an objective of high priority.

In this report we show examples of two case studies using spectroscopic techniques which provide data on organic compounds in fluid inclusions. The techniques used are Raman spectroscopy and Time of Flight-Secondary Ion Mass Spectrometry (TOF-SIMS), both of which are being miniaturized for future space exploration missions. Both of these techniques can provide data on both organic and inorganic compounds in the same analysis, so offer a versatility that is suitable for fluids that are mixed or of uncertain nature. Raman spectroscopy was undertaken to demonstrate the organic content of inclusions entrapped in chemosynthetic carbonate at a modern cold seep site. Cold seeps have been identified as targets for astrobiological exploration [1], so this demonstration is a valuable indicator that we may be able to identify organic fluids within them. TOF-SIMS was undertaken on a sample containing two populations of oil inclusions, to demonstrate that they can be distinguished.

Raman Study: Raman spectroscopy relies on the scattering of monochromatic radiation due to interactions with molecules in solids and fluids. Spectra show shifts in the energy of the scattered radiation to frequencies with a wavelength distribution characteristic for a given compound.

The technique was demonstrated using a sample from the seafloor on the Voring Plateau, offshore Norway. Methane seepages have been recorded on the sea floor, around which there has been precipitation of carbonate crusts containing a shelly community. The carbonates are assumed to be chemosynthetic. Fluid inclusions have been identified in aragonite cements within the crusts. Measurements were made using a Renishaw Raman microscope at Kingston University, under the guidance of Dr. P. Murphy.

Figure 1 shows a Raman spectrum from a 2 micron inclusion, in which two components are evident; the aragonite host, and hydrocarbons within the inclusion. We are unable to resolve the hydrocarbons, suggesting that they are not simply methane. Larger inclusions would allow better resolution.

TOF-SIMS Study: Secondary Ion Mass Spectrometry (SIMS) has been applied to fluid inclusions by several workers [e.g. 2]. However the particular technique of TOF-SIMS has previously found only limited use in geological studies [3]. TOF-SIMS instruments are especially suitable for studies where limited quantity of sample is available, as they allow increased transmission of material and simultaneous detection of all masses leading to very high sensitivity. They also have the advantage of measurement of trace quantities of both organic and inorganic components.

Organic fluid inclusions were examined from the Eocene Shahejie Formation in the Bohai Basin, Eastern China. The organic inclusions are assumed to represent entrapped oil. Two populations of organic inclusions are distinguished in limestone. These are primary (syn-cementation) and secondary (in cross-cutting trails). Microthermometry and fluorescence characteristics [4] show that these two populations have a different composition, and therefore constitute a test for the sensitivity of the TOF-SIMS techniques. A TOF-SIMS 2000 produced by φ Physics Electronics Phi Evans was used to analyse the organic composition of the inclusions, using the methods of Diamond et al [2].

TOF-SIMS Spectra for the organic inclusions are shown in Figure 2. The inorganic fragment ions of both the primary and secondary organic inclusions are mainly Na+(23), Mg2+ (24), Si4+ (27), K+ (39) and Ca2+ (40). Ca2+(40) is the strongest peak, because the host mineral of the organic inclusions is calcite (CaCO3). In the organic fragment ion peaks, the organic structures of the secondary organic inclusion are mainly aliphatic hydrocarbon (with mass number of 29,43,57,71… with formula CnH2n+1), unsaturated olefinic hydrocarbon (with mass number of 41,55,69,83 … with formula CnH2n-1), but relatively little aromatic hydrocarbon (with mass number of 65,77,79…). The inorganic ions of the primary organic inclusion are similar to that of secondary organic inclusions, but we can also detect H2O+(18), and higher Na+(23) and K+(39) contents. This suggests that the primary organic inclusions contain a mixture of organic material with saline water. Compared with secondary organic inclusions, the primary organic inclusion contains proportionally more olefinic hydrocarbon, with lesser quantities of saturated aliphatic hydrocarbon, and negligible aromatic hydrocarbon. The differences in organic compounds indicate that distinct compositions of oil were present during the two stages of fluid entrapment.

Application to Exploration on Mars: The two techniques discussed both have the advantage of being used
without the need for prior extraction or derivatization, and are non-destructive. They are therefore regarded as suitable for in situ analysis on Mars. It has been suggested that TOF-SIMS can detect various biomolecules in fossilized bacterial biofilms, and consequently the technique has been advocated for non-destructive analysis of returned samples [5]. There is also potential to use TOF-SIMS for in situ analyses [6, 7]. The application of Raman spectroscopy to astrobiological exploration is being developed by the identification of organic compounds that might be expected in stressed microbial communities [8], demonstration studies on meteorites [9], and miniaturization for Martian missions [10].

Our specific application of these techniques to fluid inclusions required fine laser focusing to target the inclusions. Although the techniques can be directed by imaging on a scale of microns/tens of microns, we are not yet at the stage where we can apply them to such specific targets during a remotely conducted analysis. It is likely that successful remote targeting of the contents of fluid inclusions will be made by increasing the sensitivity of analysis for a volume of mineral (which incorporates inclusions), rather than reducing the beam size and imaging individual inclusions. This would mean that the chemistry of inclusion fluids would be diluted by the chemistry of the host mineral, but where the objective is to identify organic compounds any ambiguity about precisely where the compounds are located is of secondary importance.