**RATIONALE AND PRELIMINARY DESIGN OF AN ICY MINERALOGY PACKAGE FOR DEPLOYMENT AT THE SURFACE OF TITAN.** A. D. Fortes[1], I. G. Wood[1], and D. P. Dobson[1]. [1]Center for Planetary Sciences, Department of Earth Science, University College London, Gower Street, London WC1E 6BT, United Kingdon (e-mail: andrew.fortes@ucl.ac.uk).

**Introduction:** Understanding the geology of Titan's crust, and its interaction with the atmosphere, requires determination of the chemistry and *mineralogy* of surface materials which can only be achieved unambiguously using X-ray diffraction (XRD). Here we describe an icy mineralogy package (IMP) consisting of a miniaturised XRD designed primarily with Titan (and the TandEM proposal [1]) in mind although it is not predicated upon an *a priori* knowledge of surface mineralogy and consequently is applicable with little modification to any solar system body (rocky or icy).

The strength of XRD over more traditional *in situ* techniques (e.g, near-IR spectroscopy) is the capability to 'fingerprint' any crystalline compound present in the sample (down to order 1 wt % abundances) and also to quantify phase proportions to ~ 0.5 wt % accuracy [2], even in complex multiphase mixtures using the Rietveld method [3]. IR spectroscopy often requires photometric modelling, with some awareness of grain sizes and/or subtraction of atmospheric absorption. This ambiguity is exemplified by the case of Europa [4], the surface of which may comprise a mixture of hydrated substances whose near-IR spectra differ only very slightly in the shape of their $H_2O$ absorption bands. Titan's atmospheric $CH_4$ restricts remote spectroscopic analysis of the surface to a few narrow near-IR windows, although the surface spectrum acquired by the Huygens probe is remarkable for its lack of informative absorption bands in the 0.7–1.6 μm range [5].
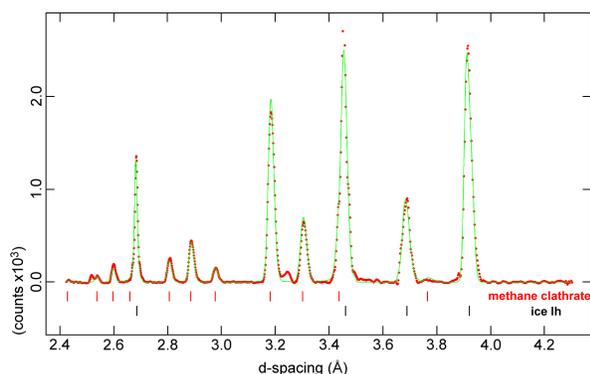
Figure 1.



Figure 1 above is an XRD pattern collected from a 42:58 mixture of ice and methane clathrate synthesised in our laboratory; red points are the data and the green line represents a fitted structural model; the expected positions of Bragg reflections for each phase are shown with labelled tick marks. This illustrates the ease with which water ice and methane clathrate may be distinguished (even with the naked eye in this case), although these have very similar near-IR reflectance spectra [6].

**Titan's surface composition:** Some of the first-order questions regarding Titan are, (1) what is the nature and origin of the bright (highland?) terrain; (2) what is the nature and origin of the dark (sedimentary basin?) terrain; (3) what is the chemical composition and physical structure of the interior; and (4) how have each of these evolved in time (as a result of outgassing and/or atmospheric interactions)? These questions can be answered by characterizing the mineralogy of deposits associated with a range of geological features on Titan's surface, a strategy best addressed from a mobile science platform such as a balloon [1], from which it should be possible to sample regolith from bright and dark terrain locations, from crater ejecta blankets (sampling the upper few kilometers of crust, including readily XRD-identifiable high-pressure polymorphs), from cryovolcanic flows or ash blankets (sampling deeper crustal melting or subsurface oceanic liquid), from aeolian, fluvial, peri-lacustrine and post-lacustrine environments (sampling atmospheric organic detritus).

Current models indicate that the crust is composed of water ice and/or methane clathrate structure I [7,8]. It is also possible that mixed structure II clathrates (with methane, ethane and/or nitrogen and noble gases as mixed guest species), occur on Titan [9,10]. Titan's atmosphere protects these surface ices from space radiation that might otherwise act to amorphise the uppermost layers, although the airless Saturnian satellites appear to have mostly crystalline ice at their surfaces [11]. Atmospheric photochemistry yields solid condensates [12] which snow out into the surface; these are probably dominated by unsaturated hydrocarbons such as acetylene (including polyacetylenes) and ethylene, as well as a range of nitriles, the most simple being HCN. Condensation conditions are suitable for the formation of crystalline materials, and the availabe spectroscopic evidence points to crystalline condensates [13,14]. Models of Titan's interior predict that cryolavas will be composed of water ice and ammonia hydrates, perhaps with minor methanol hydrate [15], although alternative models [8] predict that cryolavas may be sulfate- or carbonate-rich brines (solidifying as crystalline salt hydrates). Our laboratory experience shows that brine solutions quenched in liquid $N_2$ always form crystalline hydrates whereas ammonia, methanol, and sulfuric acid solutions form glasses when quenched. These amorphous solids will devitrify, however, on relatively short geological timescales at Titan's surface.

**Instrument design:** Two design concepts are currently under study, which differ in the complexity of the sample handling system, and the range of Bragg angles which may be observed. Both are Guinier cameras [16], one (IMP senior) working in transmission, and the other (IMP junior) working in back-reflection; see figure 2. IMP jnr is intended for deployment on a static surface probe with no sample acquisition capability, collecting a single diffraction pattern through a window in the probe's underside. IMP snr is intended for deployment on a balloon with a sample collection arm able to deliver scoops of surface material to a rotating specimen stage. The latter may therefore be used to analyse many samples at geographically dispersed points.

In each case X-rays are generated by a radioisotope source, $^{55}$Fe for IMP jnr and both $^{55}$Fe and $^{241}$Am for IMP snr, which have half-lives of 997±4 days and 432.2±0.7 years, respectively. The use of radioisotopes for XRD has been described previously [17-21]. From $^{55}$Fe we intend to use the strongest X-ray line at 5.895 keV ($\lambda$ = 2.103 Å) and from $^{241}$Am the L$\beta_1$ line at 17.764 keV ($\lambda$ = 0.699 Å): the collimated beam will be monochromated and focused by a synthetic multilayer optical element (a Göbel mirror). The advantage of using a secondary $^{55}$Fe source is that X-rays of this wavelength will shift all Bragg peaks in the diffraction pattern to larger angles, allowing better resolution of substances with very large unit cells – i.e., Bragg peaks at low $2\theta$ angles (clathrate hydrates, salt hydrates, and sulfuric acid hydrates). Longer wavelength X-rays will be more strongly absorbed along the ray path, but more strongly scattered by the sample than shorter wavelengths. Diffracted X-ray are to be detected using a curved silicon microstrip covering an angular $2\theta$ range of ~60°. The transmission geometry allows us to observe low-angle Bragg peaks which are not detectable in back-reflection. Using $^{55}$Fe, the strong triplet from ice Ih at d-spacings of 3.46, 3.69, and 3.92Å (Fig. 1) occurs at Bragg angles of 31 - 36°; these peaks can just be resolved in back-reflection with a low-angle incident beam (Fig. 2).

**Combined XRF:** X-ray fluorescence (excited by the radioisotope source) will provide accurate elemental abundances and constrain the identification of mineral species from the observed powder XRD data. Carbon, nitrogen and oxygen fluoresce at very low energies, but these emissions can be detected using a lithium drifted silicon detector - Si(Li) - with an ultrathin window.

**Summary:** The proposed IMPs will be able to identify any crystalline substances present on Titan's surface at > 1 wt % levels, and quantify their relative abundance, as well as, in principle, estimate the abundance of any amorphous material. The focusing geometry maximises the flux and resolution obtainable from radioisotope sources and also has the advantage of illuminating a relatively large sample volume (compared to other mini-XRD designs); this improves the measured powder statistics. Most of the mass, and all of the power use is confined to the detector system (which is cooled passively by Titan's atmosphere) and data rates will be very small. The robustness of the technique renders it the method of choice for unambiguous determination of Titan's surface mineralogy.

Figure 2.



IMP senior

IMP junior
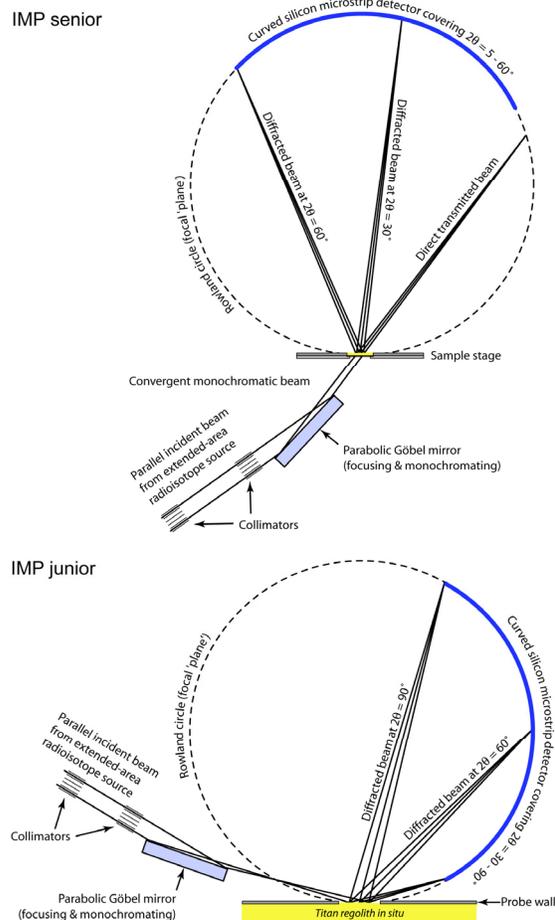
**References:** [1] Coustenis, A., et al. (2008) paper submitted to *Astrophys. Instr. Methods*. [2] Hill, R. J. & C. J. Howard (1987) *J. Appl. Cryst. 20, 467-474.* [3] Rietveld, H. (1969) *J. Appl. Cryst. 2, 65-71.* [4] Carlson, R. W., et al. (2007) *Eos Trans. AGU 88, abstract P51E-02.* [5] Schröder, S. E., & H. U. Keller (2007) *P&SS, doi:10.1016/j.pss.2007.10.011.* [6] Smythe, W. D. (1979) *PhD thesis, UCLA.* [7] Tobie, G., et al., (2006) *Nature 440, 61-64.* [8] Fortes, A. D., et al. (2007) *Icarus 188, 139-153.* [9] Osegovic, J. P., & M. D. Max (2005) *JGR 110, doi:10.1029/2005JE002435.* [10] Thomas, C., et al. (2007) *A&A 474, L17-L20.* [11] Cruickshank, D. P., et al. (2005) *Icarus 175, 268-283.* [12] Lavvas, P. P., et al. (2007) *P&SS, doi:10.1016/j.pss.2007.05.027.* [13] Khanna, R. K. (2005a) *Icarus 177, 116-121.* [14] Khanna, R. K. (2005b) *Icarus 178, 165-170.* [15] Kargel, J. S. (1992) *Icarus 100, 556-574.* [16] Wölfel, E. R. (1983) *J. Appl. Cryst. 16, 341-348.* [17] Bugenis, C., et al. (1968) *Rev. Sci. Instr. 39, 1754.* [18] Gregory, J. C., & T. A. Parnell (1972) *IEEE Trans. Nucl. Sci. NS-19, 224-232.* [19] Lobov, S. I., et al. (1969) *Nature 222, 767.* [20] Preuss, L. E., et al. (1967) *J. Appl. Phys. 38, 3404.* [21] Toothacker, W. S., et al. (1967) *Nature 216, 255.*