THE *MARS-XRD* INSTRUMENT FOR EXOMARS: COMBINED X-RAY DIFFRACTION AND FLUORESCENCE MEASUREMENTS. K. S. Hill[1], G. M. Hansford, D. Vernon, D. L. Talboys, R. M. Ambrosi, J. C. Bridges and I. B. Hutchinson, Space Research Centre, Dept. of Physics & Astronomy, University of Leicester, Leicester, LE1 7RH, UK, ksh12@le.ac.uk.

Introduction: On Earth, X-ray diffraction is a well-known and tested technique for analyzing the structures of minerals. The X-Ray Diffraction (XRD) instruments are core components of the forthcoming NASA Mars Science Laboratory (MSL) and ESA/NASA ExoMars missions and will provide the first demonstrations of simultaneous XRF/XRD instrument capabilities *in-situ* on an extraterrestrial planetary surface.

MarsXRD is a combined X-ray diffractometer and fluorescence spectrometer selected for the NASA/ESA ExoMars mission to analyse the mineralogy and chemical composition of the Martian rocks and soils. The instrument's targets include a wide variety of hydrated minerals, such as clays [1]. The study of different minerals will be used to better understand the geological evolution of the sites that the ExoMars rover will visit; with its primary mission to investigate the habitability of past, present and future Martian systems.

The University of Leicester team is part of the Italy-UK collaboration that is responsible for building *MarsXRD*. A key area of interest is the effect of the geometry, optimized for XRD, on the quality of the XRF response of the system alongside the ability to resolve the complex mixture of phases present in geological materials. Here we present some initial findings from XRF and XRD tests carried out at the University of Leicester using an Fe-55 source and X-ray sensitive CCD [2], to investigate the ability to identify minerals under *MarsXRD* representative conditions.

The Instrument: The ExoMars X-Ray diffraction instrument incorporates an ^{55}Fe radioisotope source and three fixed-position CCDs, see figure 1, to simultaneously acquire an X-Ray fluorescence spectrum and a diffraction pattern; providing a measurement of both elemental and mineralogical composition [2]. The CCDs cover an angular range from 6^0 to 65^0 enabling the analysis of silicate minerals, from clays or other phyllosilicates characterized by varying d-spacings, to oxides, and carbonates or evaporites.

The XRF/XRD test system consists of a single CCD on a motorized arm, an ^{55}Fe X-ray source, collimator and a sample table which approximately replicate the reflection geometry of the XRD instrument (figures 2, 3). It was used to test 15 geological standard reference materials and 3 Martian analogues. The effect of incidence angle and CCD angles on both the diffraction and fluorescence results were evaluated.

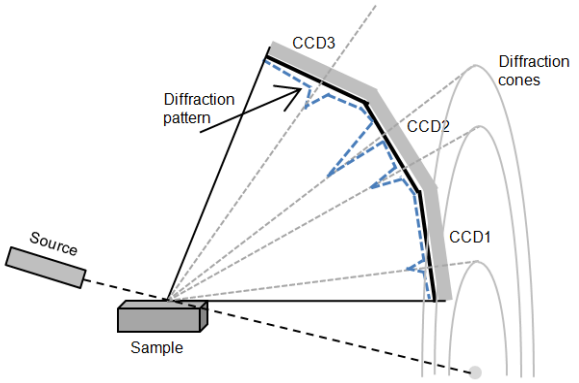

Figure 1 – Mars-XRD measurement concept. CREDIT ESA Mars-XRD Team.

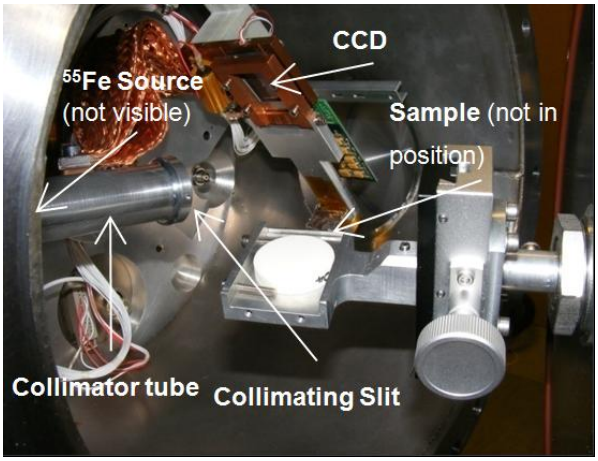

Figure 2 – Experimental set-up of the test facility, Space Research Centre, University of Leicester.

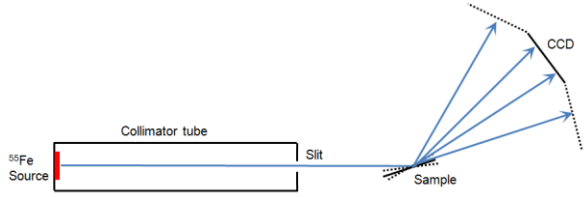

Figure 3 – Schematic diagram of the experimental set-up with both sample and CCD on a rotating axis to replicate incidence/detector angles.

Data Analysis: We present results from testing the XRF/XRD response from a range of geological standards. To replicate the actual flight device, 3 separate data acquisitions of 6 hour duration were required as this test facility uses one CCD on a rotating axis with a rotating sample to reproduce the angles required. As many minerals have few peaks below 25^0 2θ (this does

not include clays) we acquired data at two higher angles as only non-clay minerals were investigated in this preliminary study. The incidence angles were set to 16° and 23°, and the CCD position was set to capture 2θ = 25-45° and 45-65° respectively.

XRF results: The CCD yields an X-ray spectrum which allows elemental identification and quantification (figure 4). The Quantitative X-Ray Analysis System (QXAS) software package [3] was used to calibrate the fluorescence spectra of the standard reference materials. A matrix correction was established using a subset of reference materials and the assumption that the remaing component of the dark matrix is oxygen. A second subset of reference materials were then used to calibrate the fluorescence intensities, and these steps were then applied to unknown samples. Major rock-forming elements of silicate minerals have been identified such as *Ca*, *K*, and *Ti* which were efficiently fluoresced. Artefacts such as the *Mn-K* peaks (due to simultaneous diffraction) and *Al* (collimator) are products of the current experiment design. Each element peak is resolvable, however light elements (lower *Z*) are increasingly difficult to detect due mainly to lower fluorescence yield and absorption within the sample.

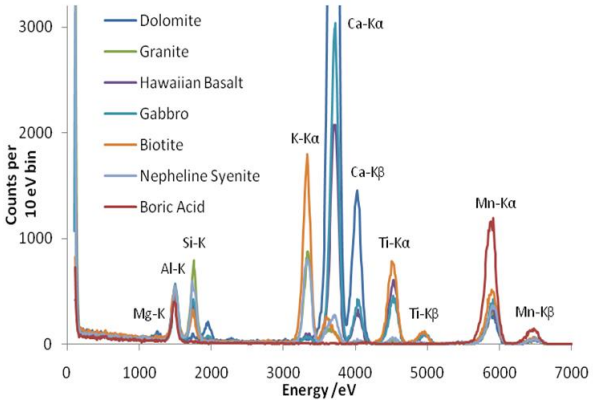

Figure 4 – A selection of Standard Reference Material fluorescence spectra from the highest CCD angle only.

XRD results: The Monte Carlo ray-tracing model, PoDFluX [4], was used to simulate X-ray diffraction and fluorescence and has allowed comparison of the experimental results to modelled diffractograms to derive approximate quantification of the identified phases (figure 5). The geometry of the experimental set-up is known to limited accuracy, typically $\pm 2^0$ in angles and ±2 mm in positions and so PoDFluX was used to infer the errors in the nominal geometry by matching the modelled line intensities and widths with the experiment results. The phases present and their concentrations in the standard samples were identified from the peaks present and checked in PoDFluX until a good agreement between experiment and model was achieved. The XRF spectra are a useful tool to help identify phases present in the standards when not immediately obvious from the diffractogram peaks.

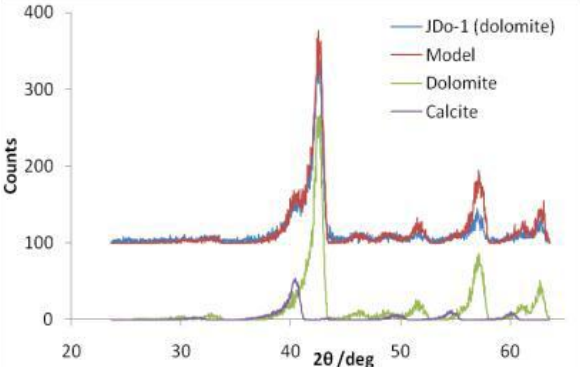

Figure 5 – Dolomite diffractogram (JDo-1, *GSJ*) model matched to experiment indicating the presence of a calcite component in addition to the main dolomite component.

Discussion: By combining XRF and XRD measurements, *MarsXRD* can provide a complete characterization of a rock sample. The XRF results using an XRD-optimized geometry demonstrate the detection of rock forming elements from Na to Ti and aids the identification of phases in the accompanying diffractograms. The PoDFluX model is excellent in aiding understanding and replicating experimental conditions. Comparing the experimental diffractograms to PoDFluX modelled results allows an approximate quantification of different phases identified. This work will be extended to include calibration of the full range of hydrated minerals of interest, including clays, carbonates and sulfates.

References: [1] Mustard J. F. et al. (2008) *Nature*, 454. [2] Marinangeli L. et al. (2007) *LPS XXXIX*, Abstract #1322. [3] QXAS software package, IAEA Physics Section, Seibersdorf Laboratories, Austria. [4] Hansford G. M. et al. (2009) *Rev Sci Instrum.*, *80*, (7):073903.