X-RAY DIFFRACTION ON UNPREPARED ROCK SAMPLES: A STUDY OF SULPHATE MINERALS.

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Introduction: Here we present an analysis of sulphate minerals from the Triassic coastline of the South West UK, utilising an Energy Dispersive X-Ray Diffraction (ED-XRD) instrument in a novel back-reflection geometry that enables analysis of unprepared rock samples. Sulphate minerals are of particular interest in planetary science as they are a product of an aqueous altered environment. This study highlights the potential of a lightweight, compact instrument that could be deployed on the robotic arm of a Mars rover.

Concept: Traditional angle-dispersive X-ray diffraction utilises the Bragg equation:

$$\lambda = 2d\sin\theta$$

where an X-ray beam of a single wavelength λ is diffracted through a range of scattering angles 2θ by a set of crystal planes. The set of d-spacings are characteristic of each mineral phase, allowing XRD to be used for mineral identification, quantification and structural analysis. The ED-XRD approach presented here uses a back-reflection geometry where $2\theta \approx 180°$, and a broadband X-ray source with an energy-resolving detector [1].

Proof-of-principle experiments have shown this new XRD technique to be uniquely insensitive to sample morphology and only intensity dependent with regards to distance [1-3]. In contrast, conventional XRD techniques require that the sample be crushed into a fine powder and be presented to the instrument for analysis with a uniformly flat surface, with sub-mm position accuracy. Therefore the new technique presented here is of particular interest for planetary missions where strict mass, power and volume budgets are imposed on instrumentation [2]. This technique implemented by a lightweight, compact version of the instrument on a robotic arm would be a useful preliminary analysis tool in the context of lander and sample return missions to the Moon, Mars and beyond as it can be used to help select samples for more thorough analysis by more sophisticated instruments within the body of a lander or rover e.g. SAM and CheMin on Mars Science Laboratory.

Here we present results from a study of sulphate minerals. These minerals are of particular interest in planetary science as they can, for instance, form from the evaporation of a body of standing water or groundwater to produce discrete veins [4,5]. The distinction between sulphate minerals such as gypsum ($CaSO_4.2H_2O$) and anhydrite ($CaSO_4$), found in rock veins, is important in order to characterise fluid composition and temperature of ancient aqueous activity. Such analysis would not be feasible with elemental analysis by X-ray Fluorescence (XRF) or an Alpha-Particle X-ray Spectrometer (APXS) alone.

Experimental Results: The laboratory facility outlined in [3] was used to carry out experiments on a pressed-powder pellet made from a sulphate sample and unprepared whole rock samples from Watchet Bay, shown in figure 1. Calcium, sulphur and oxygen fluorescence peaks overlapping the diffraction peaks were identified and a process of suppressing these peaks (except oxygen) by tuning the source excitation voltage was carried out to reveal the underlying diffraction data [6]. Figure 2 shows sulphur suppression results for a pressed powder pellet made from a collected whole rock sample.
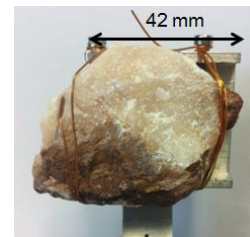

Figure 1. Whole rock sample collected from Watchet Bay sulphate, positioned in sample holder used in the data acquisition.
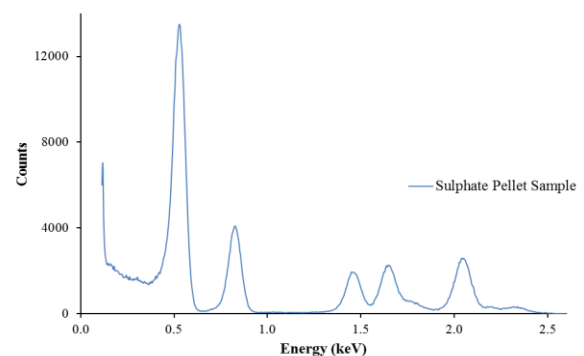

Figure 2. Experimentally acquired spectrum of the sulphate powder pellet sample. One peak can be attributed to fluorescence: O-K at 0.525 keV.

The Monte Carlo ray tracing program PoDFluX [7] was then used to simulate the expected diffraction peaks of gypsum ($CaSO_4.2H_2O$) using data from [8],

with a specified preferred orientation along the (010) plane [9]. The preferred orientation of the crystallites is caused by the alignment of crystallites when the pellet was pressed. This plot is shown in figure 3 and clearly shows that gypsum fits the data well, explaining all four of the diffraction peaks.
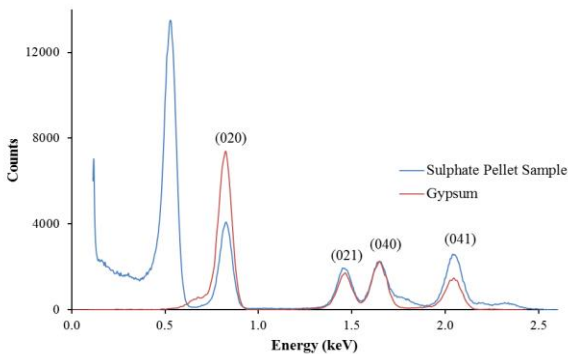

Figure 3. Experimentally acquired spectrum of the sulphate pressed-pellet sample compared to the Monte Carlo ray tracing simulation for gypsum produced by PoDFluX. Miller indices of diffraction peaks are labelled.

Figure 4 shows sulphur-fluorescence suppression results for a whole rock sample from which the pressed powder pellet was made. The experimentally acquired data is compared to a diffraction and fluorescence model of gypsum produced by PoDFluX [7] using data from [8], with a specified preferred orientation effect along the (010) planes due to the natural alignment of the crystallites. Magnesium, aluminium and silicon fluorescence are also included in the model.
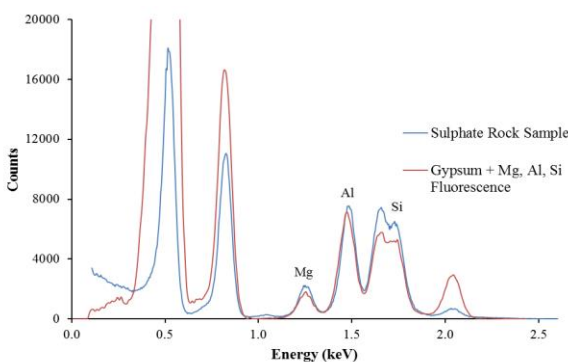

Figure 4. Experimentally acquired spectrum of the sulphate whole rock sample compared to the Monte Carlo ray tracing simulation produced by PoDFluX.

The spectrum in figure 4 shows more peaks than the spectrum in figure 3 due to magnesium, aluminium and silicon fluorescence, but clearly shows that gypsum

fits the data well. The fluorescence of these three elements is due to minor, unidentified minerals.

Using a bespoke back-reflection setup, comprising an annular silicon drift detector centered on the incident X-ray beam, measurements have been taken to further assess the capability of the technique. Figure 5 shows calcium-suppression results for a whole rock sample, which was broken off from the sulphate sample pictured in figure 1. An XRD model of gypsum produced by PoDFluX [7] using data from [8], for diffraction peaks only, is also shown in figure 5 for comparison.
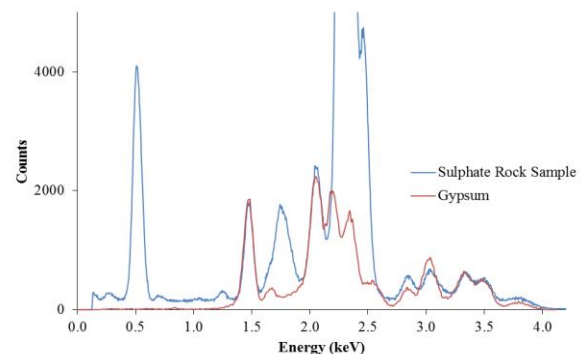

Figure 5. Experimentally acquired spectrum of the sulphate rock sample compared to a PoDFluX simulation of gypsum.

Conclusions: This work demonstrates the capability of a novel ED-XRD technique in a back-reflection geometry. Together with PoDFluX, this technique is capable of identifying sulphate minerals, overcoming the effects of fluorescence peaks that overlap diffraction peaks and also the effects of preferred orientation. Additional sulphate mineral samples and iron-oxide minerals will also be presented. This demonstrates the potential of an instrument based on this technique, and its potential use on the arm of a rover or lander deployed on a planet, such as Mars.

References: [1] Hansford G. M. (2011) *J. Appl. Cryst., 44,* 514-525. [2] Hansford G. M. (2012) EPSC, Abstract #882, 2012. [3] Hansford G. M. (2013) *Nuclear Instruments and Methods in Physics Research A, 728,* 102-106. [4] Bridges J. C. et al. (2014) *JGR: Planets,* 10.1002/2014JE004757. [5] Schwenzer S. P. et al. (2015) 46th LPSC, abstr. #1441, Houston. [6] Hansford G. M. et al. (2014) *J. Appl. Cryst., 47*(5), 1708-1715. [7] Hansford G. M. (2009) *Rev. Sci. Instrum., 80,* 073003. [8] Boeyens J. C. and Ichharam V. V. H. (2002) *Zeitschrift für Kristallographie. New Crystal structures, 217,* 9-10. [9] Grattan-Bellew P. E. (1975) *American Mineralogist, 60,* 1127-1129.