

A Study of Sulphate Minerals using a Novel X-Ray Diffraction Technique

S.M.R. Turner, G.M. Hansford, J.C. Bridges, R.M. Ambrosi and D. Vernon.
Space Research Centre, Department of Physics & Astronomy, University of Leicester, Leicester, LE1 7RH, UK,
(gmh14@leicester.ac.uk).

Abstract

Here we present an analysis of sulphate minerals from the Triassic coastline of the South West UK, utilising an Energy Dispersive X-Ray Diffraction (EDXRD) instrument in a novel back-reflection geometry which 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.

1. Introduction

Traditional angle-dispersive X-Ray Diffraction (XRD) utilises the Bragg equation:

$$\lambda = 2d \sin \theta \quad (1)$$

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 d -spacings of a set of crystal planes are characteristic of each mineral phase, allowing XRD to be used for mineral identification, quantification and structural analysis. The EDXRD approach presented here uses a back-reflection geometry where $2\theta \approx 180^\circ$, 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 sample-instrument 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-millimetre 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]. Such a technique

implemented by a lightweight, compact version of the instrument on a robotic arm is 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 rigorous 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 found in Triassic veins from Watchet, Somerset, UK. 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 [4]. The distinction between sulphate minerals such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) 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.

2. Experimental Results

The laboratory facility outlined in [3] was used to carry out experiments on a pressed-powder pellet made from a sulphate sample. Calcium, sulphur and oxygen fluorescence peaks overlapping the diffraction peaks were identified and a process of suppressing these peaks by tuning the source excitation voltage was carried out to reveal the underlying diffraction data. Figure 1 shows sulphur suppression results for one of these pressed powder pellets.

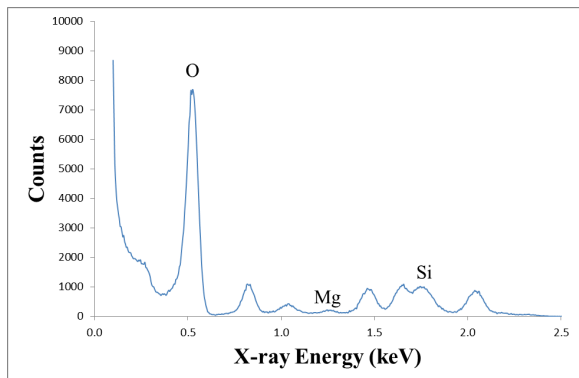


Figure 1: Experimentally acquired spectrum of the sulphate sample. Three peaks can be attributed to fluorescence: O-K, Mg-K and Si-K.

Trace amounts of magnesium and silicon fluorescence were identified in the data shown in figure 1. The Monte Carlo ray tracing program PoDFluX [5] was then used to simulate a diffraction plot of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) using data from [6], with a specified preferred orientation along the (010) plane [7]. Bassanite ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$) was also simulated in PoDFluX using data from [8], with an assumed preferred orientation on the same plane as the gypsum. These plots are shown in Figure 2.

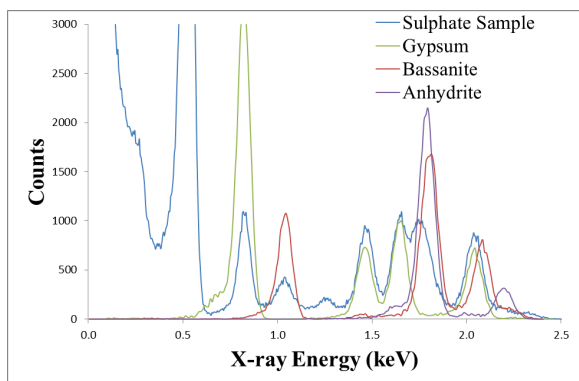


Figure 2: Experimentally acquired spectrum of sulphate sample compared to three Monte Carlo ray tracing simulations produced by PoDFluX.

Figure 2 clearly shows that gypsum fits the data well, explaining four of the five identified diffraction peaks present. Bassanite explains one of the five identified diffraction peaks, which is not explained by gypsum or anhydrite. Gypsum [6] and bassanite [8] were then combined in PoDFluX [5] to produce a 90% gypsum and 10% bassanite diffraction plot, which is shown in figure 3.

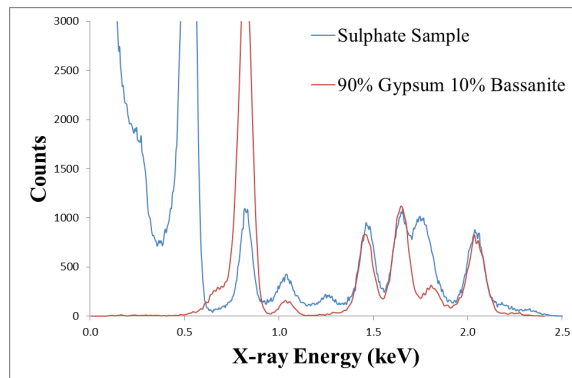


Figure 3: Experimentally acquired spectrum of sulphate sample compared to a Monte Carlo ray tracing simulation of 90% gypsum [6] and 10% bassanite [8] with preferred orientation effects along the (010) plane.

3. Summary and Conclusions

The work presented here demonstrates the capability of a novel EDXRD technique in a back-reflection geometry. Together with PoDFluX [5], this technique has the capability of identifying the mineralogy of samples composed of a mixture of sulphate minerals of varying hydration state, overcoming the effects of XRF peaks which overlap XRD peaks and also preferred orientation. 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., *J. Appl. Cryst.* **44**, 514-525, 2011.
- [2] Hansford, G.M., EPSC Abstract #882, 2012.
- [3] Hansford, G.M., "X-ray diffraction without sample preparation: proof-of-principle experiments", submitted to: *Nuclear Inst. And Methods in Physics Research Section A*, 2013.
- [4] Chevrier, V., Mathé, P. E., *Planet. Space Sci.* **55**, 289-314, 2007.
- [5] Hansford, G.M., *Rev. Sci. Instrum.* **80**, 073903, 2009. doi: 10.1063/1.3160018.
- [6] Boeyens, J. C. A., Ichharam, V. V. H., *Zeitschrift für Kristallographie. New Crystal Structures*, **217**, 9-10, 2002.
- [7] Grattan-Bellew, P.E., *American Mineralogist*, **60**, 1127-1129, 1975.
- [8] Ballirano, P. et al., *European Journal of Mineralogy*, **13**(5), 985-993, 2001.