X-ray Diffraction without Sample Preparation

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1. Introduction to Back-Reflection X-ray Diffraction

In conventional x-ray diffraction, the well-known Bragg equation:

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

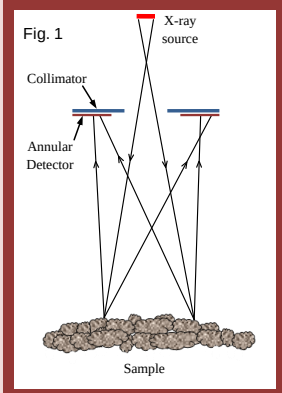
is implemented by fixing the x-ray wavelength λ and scanning the scattering angle θ (angle-dispersive x-ray diffraction, or ADXRD) in order to derive the set of *d*-spacings which are unique to each crystalline phase. Alternatively, θ may be fixed and the x-ray wavelength 'scanned'. In practice, a broadband x-ray source (e.g. an x-ray tube) is used together with an energy-resolving detector, and this method is known as energy-dispersive x-ray diffraction (EDXRD). The Bragg equation can be rewritten in energy terms:

$$Ed \sin\theta = 6.199 \text{ keVÅ}$$

The fixed angle may be freely chosen, and small scattering angles ($\theta < 10°$) are commonly used. Recently, the author has implemented EDXRD at $2\theta \approx 180°$ [ref. 1], a geometry which has received no attention in the scientific literature. This geometry has one unique, highly-advantageous property: *the diffraction pattern is insensitive to sample morphology.* In contrast, conventional techniques require flat, powdered samples positioned with sub-mm accuracy. Furthermore, the intrinsic geometry of the method and the simplicity inherent to EDXRD enables a compact, lightweight design suitable for planetary applications. The technique also shows great promise for a diverse range of commercial applications, such as mining/quarrying, geological prospecting, online industrial quality control, and analysis of valuable specimens in archaeology and art. Some of these applications require a hand-held/portable instrument.

2. Implementation

A schematic layout of a back-reflection instrument is shown in Fig. 1. The closest possible approximation to the $2\theta = 180°$ geometry can be achieved with an annular detector having a central hole for transmission of the excitation beam. The Rococo-2 multi-element silicon drift detector (SDD) from PNDetector GmbH, shown in Fig. 2, is suitable for this purpose, while the requirement of a broadband source is easily satisfied with an x-ray tube. A detailed geometry can be derived on the basis that geometric broadening of diffraction lines is negligible compared to the detector resolution; see ref. 1 for details.



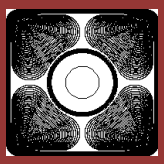
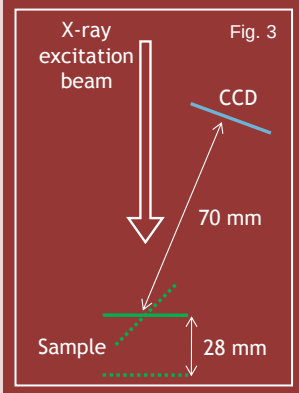
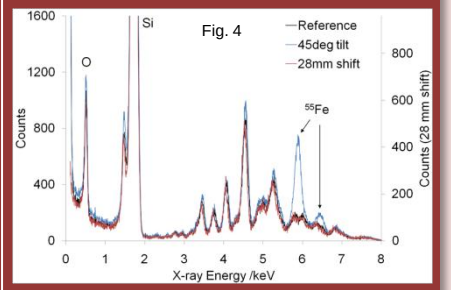


Fig. 2. Rococo-2 SDD

3. Proof-of-Principle Experiments and Suppression of Fluorescence Peaks

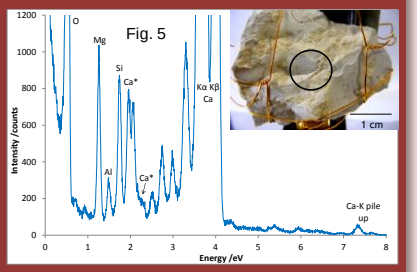
In order to prove the principle of the method, a pressed-powder quartz pellet was mounted in three distinct positions, Fig. 3. The results are shown in Fig. 4 – the very high degree of correspondence between the three spectra demonstrates how insensitive the technique is to the sample position and, by inference, to the sample shape. These gross sample movements are unthinkable in conventional angle-dispersive XRD.

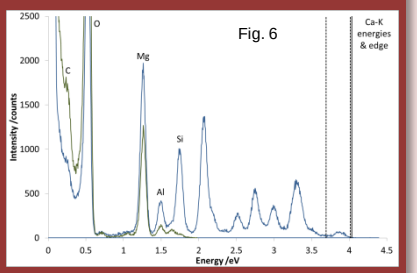


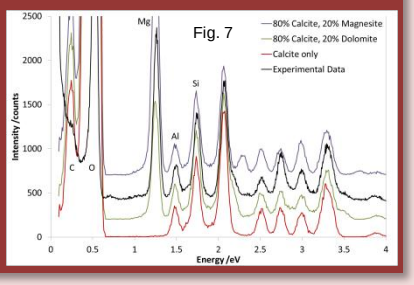


Limestone Example

To show that the method is applicable to unprepared rock samples, a limestone specimen was analysed. The inset to Fig. 5 shows an image of the rock; the circle indicates the size and position of the x-ray excitation beam. In Fig. 5, fluorescence and associated peaks have been labelled, and the spectrum is dominated by very intense Ca-K fluorescence. Other peaks are due to diffraction, and can readily be identified as calcite, $CaCO_3$. Fig. 6 shows the effect of suppressing the Ca-K fluorescence by tuning the x-ray tube source just below the corresponding absorption edge. An additional calcite diffraction peak is revealed and the spectrum is also 'cleaner'. Comparison of the experimental data with simulations [ref. 2], Fig. 7, shows clear identification of dolomite, $CaMg(CO_3)_2$, as the secondary mineral and rules out magnesite, $MgCO_3$.







4. Conclusions

The unique advantage of the back-reflection technique is its insensitivity to the sample morphology, allowing combined XRD and XRF analysis of *unprepared* rock samples. The inherent geometry of the method promotes a compact instrument design which is a big advantage for both planetary and terrestrial applications. Acquisition times are also short, on the timescale of a few minutes to achieve good signal-to-background on the diffraction peaks. The problem of overlap of diffraction and fluorescence peaks has been largely solved by tuning of the excitation voltage in order to suppress fluorescence peaks. The main drawback of the method is that the resolution of diffraction peaks is limited by the detector resolution. Note that this limitation is technological, it is not inherent to the back-reflection method itself. Future work will focus on characterising the technique with a wide range of geological and other sample types.

References:
1. G. M. Hansford, *J. Appl. Cryst.*, **44**, 514 – 525 (2011), doi: 10.1107/S0021889811012696
2. Graeme M. Hansford, *Rev. Sci. Instrum.*, **80**, 073903 (2009), doi: 10.1063/1.3160018.

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