Crystallographic Orientation Information by Soft X-Ray Spectroscopy

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A field emission electron probe microanalyser (FEG-EPMA) equipped with traditional wavelength and energy dispersive spectrometry, together with soft x-ray emission spectroscopy (SXES) and a cathodoluminescence (CL) spectrometer has been used to investigate a geological sample from a Tanzanian deposit containing graphite, quartz and a number of other minerals. One of the aims of this study was to understand the crystallinity of the graphite, as the geology indicated the ore has been subjected to a heating event up to 800°C. At these conditions the carbon should be fully crystalline graphite. Initial Raman analysis had shown a mixture of signals indicating the possibility of different crystallinities of graphite. The SXE spectrometer equipped with a Princeton CCD [1, 2] was used to investigate whether different graphite or carbonaceous forms were present while the CL together with trace Ti analysis, was used to determine the maximum heating temperature using the Tin quartz geothermometry [3]. The sample was mounted in a 25mm round, then mechanically polished with a 1μm final lap and to finish the surface, it was ion beam milled at 2kV, 5°, for 10 minutes using a Technoorg Linda model SEM Prep2. Prior to examination the sample had a 5nm carbon coat applied. Cathodoluminescence maps were spectrally examined and the Ti^{4+} CL peak identified and fitted at each pixel and trace Ti levels measured to calibrate the CL levels as described previously.

For the SXE investigation the mapping was performed at 10kV, 70nA, 600ms dwell with the SXE spectrometer utilising a 200N grating that was configured to show from 1st through to 4th order C Kα reflections. A spectral examination of the C Kα line found that the second order reflection offered the best compromise between resolution and signal-to-noise ratio, Fig. 1. C Kα spectra from across a number of carbon rich grains clearly showed the graphite structure compared to previous spectra [3, 4]. By selecting several energy regions across the C Kα peak and projecting these across the mapped area, Fig. 3, the grains are seen to be composed of graphite with different orientations. Using a scatter plot of the energy regions 260-272eV vs. 280-284eV and selecting the end-member clusters the C Kα spectra are shown in Fig 3. The C Kα is generated by an electron transition from a 2p orbital to an unfilled 1s orbital and theoretical electronic density of states (DOS) calculations by Srbinovsky et al. [5] have shown that the 1s DOS contains no structure while the 2p atomic orbitals do have structure therefore the 2p DOS reflect the shape of the C Kα emission spectra. This study showed that graphite is composed of two distinct spectroscopic forms the $2p_{(x, y)} - 1s$ and the $2p_z - 1s$ (Fig 4.). The theoretical spectral shapes are good agreement with C Kα spectra measured using SXE spectrometer [6].

References:

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[4] M. Terauchi *et al*, Handbook of Soft X-ray Emission Spectra, JEOL Ltd, 2016.
[5] J. Srbinovsky *et al*, Computational and Theoretical Nanoscience **2** (2005), p. 1.
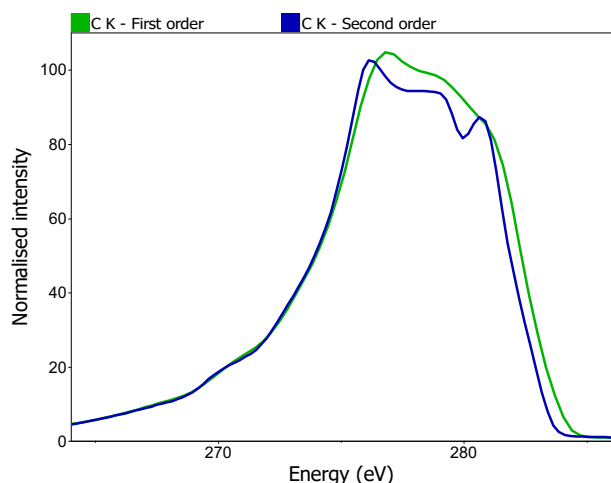[6] The authors acknowledge the support of the ARC, LE130100087.

Figure 1. C Kα 1st order and 2nd order reflections showing the enhanced resolution of the second order.
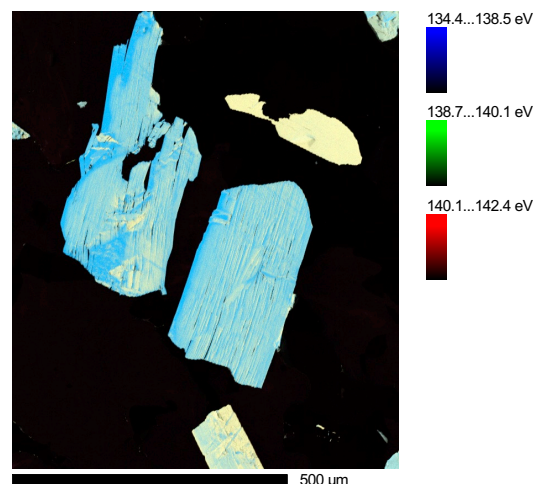

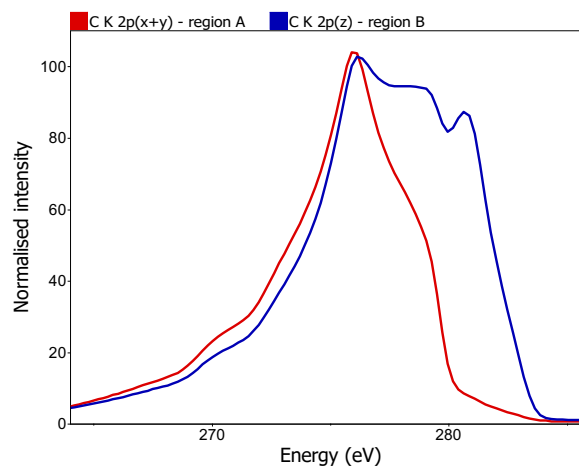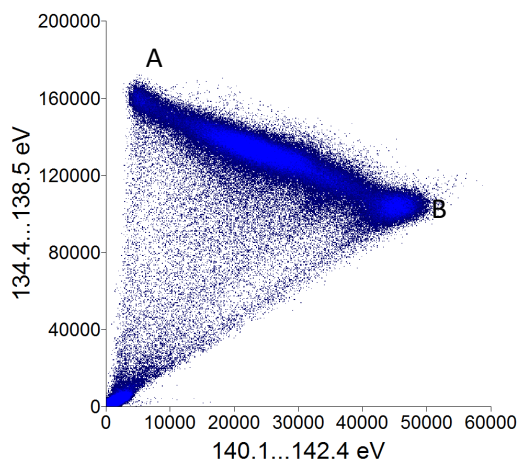**Figure 2.** Map showing three ROI across the 2nd order C Kα.

Figure 3. Scatter plot (left) of pixels from two energy regions measured on graphite. Spectra (right) from end-member clusters associated with Region A giving the C Kα 2*p*(x+y) and Region B gives the C Kα 2*pz*.
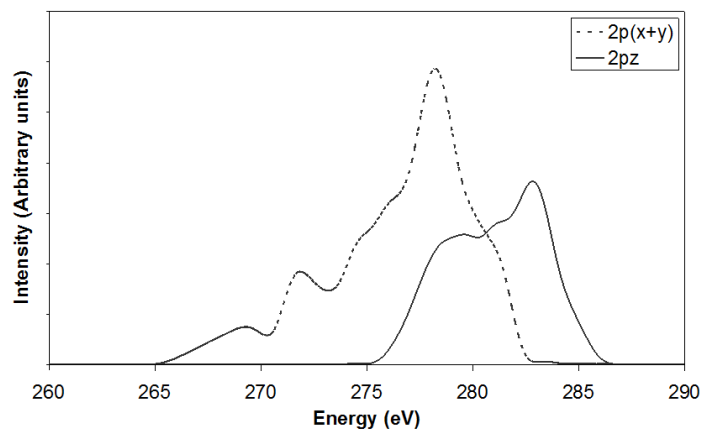

Figure 4. Calculated C Kα DOS for graphite from Srbinovsky et al. [5]. These match the measured spectra given in Figure 3.