

3D elemental mapping of materials and structures by laboratory scale spectroscopic X-ray tomography

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Abstract. Using a microfocus X-ray tube and pixelated energy-resolving detector it is possible to measure the X-ray absorption spectrum of a material with high spatial resolution. Given sufficient energy resolution in the detector it is possible to detect and identify absorption edges which are characteristic to individual chemical elements. Using computed tomography the three dimensional (3D) internal elemental chemistry of an object can be reconstructed. The application of spectroscopic X-ray tomography is demonstrated by mapping distribution of heavy elements inside a mineralised ore sample. We correlate and validate this data with high resolution X-ray tomography and energy-dispersive X-ray spectroscopy data.

1. Introduction

X-ray computed tomography (XCT) can reveal the internal three-dimensional (3D) structure of an object, with most notable application to medical imaging. However it finds many more areas of application beyond this, such as in security scanning, industrial inspection, materials science, and archeology [1]. In XCT, the measured contrast is proportional to both density and atomic number variations, with high density regions appearing brighter than low density regions. However it is very difficult to obtain the exact chemical speciation due to the polychromatic nature of the X-ray beam from laboratory X-ray tubes. There are methods, such as dual energy scanning, that can be used to obtain some pseudo chemical sensitivity which are finding increasing application to the medical imaging sector [2]. But still the exact chemical speciation is unavailable. An alternative approach is to use the X-ray fluorescence (XRF) signal emitted from an object. However due to the weak intensity this method is generally limited to very bright synchrotron sources which have a major limitation from a throughput and access point of view [3]. Laboratory-based CT instruments are cheap and widely available, but due to the low intensity of radiation it is very time-consuming to undertake XRF imaging. Over recent years, a range of pixelated spectroscopic X-ray detectors have been actively researched and developed which have the ability to measure X-ray energy of individual photons with positional sensitivity. It is therefore possible use these types of detectors to measure the full attenuation spectrum and map chemical elements based on the K-edge position. Combining this with CT and using a microfocus source it is possible to identify multiple chemical elements simultaneously in 3D without prior knowledge of sample composition and with high spatial resolution [4].



2. Experimental methods

2.1 Equipment We used a microfocus tungsten target X-ray source (spot size $5\mu\text{m}$, 160 kV, 15 μA), and HEXITEC spectroscopic X-ray detector. The detector consists of a 1 mm thick CdTe single crystal ($20 \times 20 \text{ mm}^2$) bump-bonded to a large area ASIC packaged with a high performance data acquisition system. The detector has 80×80 pixels on a $250 \mu\text{m}$ pitch with an energy resolution of 800 eV at 59.5 keV [5,6]. The CT scan was performed using an extended field-of-view by scanning the detector along 5 separate positions in the horizontal direction. Each sub-projection had an exposure time of 45 s (225 s for a full projection) and we performed 120 projections covering 360° (total scan time 7.5 hrs).

2.2 Tomographic reconstruction. An important consideration in spectroscopic XCT is the choice of reconstruction algorithm. Since the signal-to-noise ratio in any one energy channel is low, and with fewer projections (to compensate for longer image exposure times) this can result in poor quality reconstructions. Filtered back-projection type algorithms (such as FDK) produce poor results for sub-optimal scanning conditions (e.g. few projections). Iterative algorithms (such as SIRT) are much better noise tolerant and produce better quality reconstructions (see figure 1). In this work we perform a reconstruction for every energy channel and obtain an absorption spectrum in every voxel (producing a 4D dataset: 3 spatial and 1 spectral). It is therefore important to also consider the spectral quality. As can be seen in figure 1, the reconstructed absorption spectrum is very noisy for the FDK algorithm, with the K-edge almost lost in the noise. However, by using the flexibility of iterative algorithms, whereby the reconstructed image from the previous energy channel can be used as a starting vector for the next reconstruction (so-called channel linked), the quality of the reconstruction is improved both in the spatial and spectral domains. This approach is the algorithm of choice for this work. Due to high volumes of data processing, all reconstructions were performed using GPU accelerated code. We also used a wavelet based Fourier filter applied to the sinogram to suppress ring artefacts.

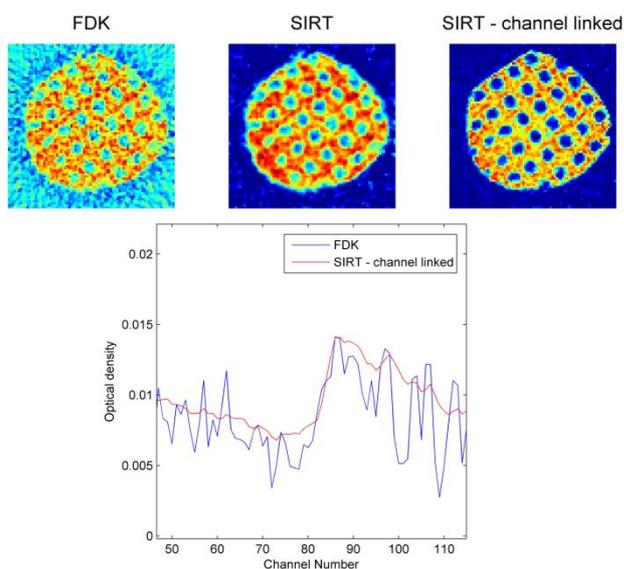


Figure 1. Testing of different reconstruction algorithms used in spectral X-ray tomography. The sample is a lattice carbon structure impregnated with palladium metal (Pd). Reconstructions using filtered back-projection (FDK), simultaneous iterative reconstruction technique (SIRT) and channel-linked SIRT methods are shown. Iterative reconstruction algorithms produce superior images, with the channel-linked method showing the best quality. The plot below shows two voxel spectra covering the Pd K-edge (step change in optical density at channel number 83) from the same voxel inside the sample, reconstructed using FDK and channel-linked SIRT methods, respectively. A clear reduction in spectral noise is evident in the latter case.

2.3 Core sample We scanned a 20 mm diameter core sample from a mineralised gold-bearing ore using spectroscopic X-ray tomography. The sample mostly comprises pyrite (FeS_2) and quartz (SiO_2), with minor amounts of gold (Au), galena (PbS), chalcopyrite (CuFeS_2) and bornite (Cu_3FeS_4). The Au and Pb containing phases both occur as small inclusions of about $100 \mu\text{m}$ diameter. In order to obtain a reference data set, we also scanned this sample using a high resolution X-ray CT system (Zeiss Versa XRM 520). In order to validate this data we also mechanically sliced open the core sample and performed electron probe microscopy and spectroscopy (JEOL JXA-8530F Hyperprobe).

3. Results

Figure 2 shows aligned and correlated spectral XCT and high resolution XCT reconstructions of the core sample. Small high density inclusions are evident which were theorised to be the Au and galena phases. However they were inseparable using classic gray level thresholding techniques largely because of their similar density and x-ray attenuation. In addition, due to potential alloying of gold with silver (Ag) (forming electrum), the gray levels of Au particles was found to vary wildly, making separation and identification almost impossible. However using the spectral XCT data, we can extract individual voxel spectra, where step changes in the optical density correspond to elemental K-edges. Identification of Au and Pb K-edges (at 80.7 keV and 88.0 keV respectively) and subsequent 3D mapping enables us to distinguish and separate these two phases. Unfortunately, the silver (Ag) K-edge was unidentifiable due to very high X-ray attenuation at 25.5 keV in this large sample. Using the two aligned datasets, particle inclusions were identified via spectral XCT, and 3D rendered using the higher resolution data, with blue coloured inclusions corresponding to galena (PbS) and red coloured inclusions corresponding to Au containing material. In this way a more detailed and accurate visualisation of the 3D morphology of the core sample can be obtained.

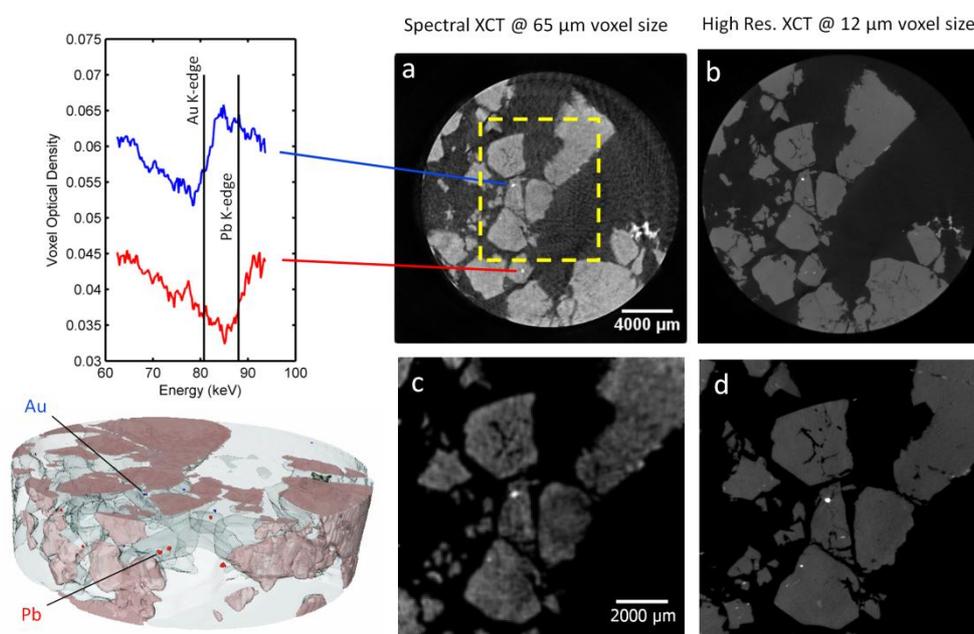


Figure 2. Correlated spectral XCT (65 μm voxel size) and high resolution XCT (12 μm voxel size) datasets. a) Slice through the spectral XCT data showing 2 voxel spectra from different particle inclusions. b) Corresponding slice through the high resolution dataset. c) Spectral XCT data zoomed region (yellow dashed box in (a)). d) High resolution XCT zoomed region. A 3D render of the whole volume with separated Au and Pb phases is shown in the bottom left of the figure.

In order to validate the data, we mechanically sectioned the core sample and performed electron probe spectroscopy mapping, which we can correlate to the XCT data, as shown in figure 3. Large area maps covering the entire surface clearly show the locations of pyrite (Fe and S maps) with low concentrations of Cu (chalcopyrite). We only observed very minor concentrations of Au and Pb in this slice. A zoomed in region in the spectral XCT data shows the location of a small inclusion which was found to have a K-edge at 88.0 keV suggesting this feature to contain Pb; the corresponding Pb WDS map confirms this. Only by high resolution electron probe mapping were we able to find concentrations of Au and Ag in very small inclusions, below the resolution of the XCT data. Some of the Au and Ag is co-located confirming the presence of electrum. It should be noted that the electron probe data originates from a very thin slice (~ 2 micron thickness) which can make it very difficult to find and quantify trace concentrations, highlighting the benefits of a 3D method like spectral XCT.

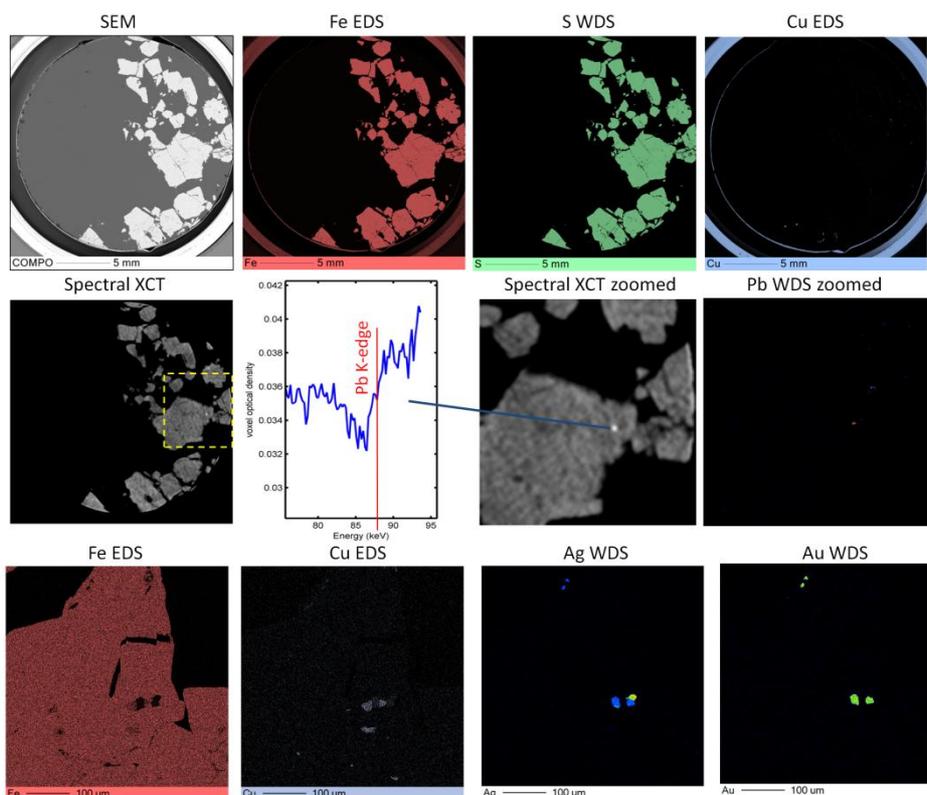


Figure 3. Electron probe microscopy and spectroscopy mapping of a polished section of the core sample. Top row: full area maps of whole section (10 μ m pixel size). Middle row: Correlated spectral XCT slice, with a zoomed region. Bottom row: small area, high resolution mapping (500 nm pixel size) to find small concentrations of Au and Ag. Note that Pb and S were mapped using wavelength dispersive spectroscopy (WDS) since their emission peaks are overlapping.

4. Conclusions

We have shown how laboratory-scale spectroscopic XCT can be used to non-destructively map the distribution of chemical elements in 3D. Elemental sensitivity is obtained by identifying K-edges in the reconstructed voxel attenuation spectra. This data can be combined with high resolution XCT and electron probe spectroscopy data to quantify and validate the results. This enables us to obtain a more accurate representation of an object's 3D chemical structure.

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