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SEM-XRF: FULL RANGE EDS DATA ON LARGE AND IRREGULAR SAMPLES

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Micro-X-ray fluorescence spectroscopy [XRF] is a well-known and complementary analytical technique to electron beam energy-dispersive X-ray spectrometry [EDS] for the characterisation of the elemental composition within samples. The XTRACE X-ray source enables the XRF technique to be utilised on a scanning electron microscope [SEM]. Micro-XRF excitation analysis is also a small area (volume) technique ideal for low-kV or beam sensitive samples as there are no charging effects (i.e., minimal sample preparation), the advantages of which include higher sensitivity for the detection of trace elements, higher energy X-ray line excitation (full spectrum range up to 40 keV), as well as information from greater depth within the sample. The availability of modern X-ray polycapillary optics yields an X-rays focus spot size down to 10 µm, all contained in an X-ray source that can be mounted on a SEM port. X-ray energy detection uses the existing EDS detector on the SEM. Accordingly, the SEM system will subsequently have dual source potential, i.e., both an electron and an X-ray source (Fig. 1), which together offers new possibilities for material characterisation. This capability has been termed "*Full Range EDS*" using the new capabilities created with a dual excitation of micro-XRF and electron beam sources combined with an EDS detector. The addition of a micro-XRF source to a conventional EDS set-up creates a dual-beam system, where samples interact with either the electron beam of the SEM or the X-ray photons from the micro-XRF source, or both.

Full Range EDS delivers a wide range of benefits over conventional EDS, allowing users to discover more about their sample. This includes the ability to:

- See high energy transitions, including the ability to detect additional elemental line series that are not seen in conventional EDS, especially above 20 keV.
- Detect and quantify trace elements.
- Analyse beam-sensitive and non-conductive samples.
- Visualize topographic samples at high-resolution.
- Gather elemental maps over large areas at micrometre resolution.
- Detect elements and minerals at and below the sample surface.
- Analyse multi-layered systems.

The SEM user can operate a micro-XRF system using similar parameters as an electron beam system (hereafter referred to as e-beam), yielding data-sets similar to traditional SEM-EDS analysis, whilst obtaining additional information from the X-ray source sample interaction. Electron excitation has a higher excitation efficiency for light elements (e.g., C, O, Na, Mg, Al, Si), and it is possible to perform measurements down to boron (B) and possibly lithium (Li). X-ray excitation efficiency is better for heavy elements (e.g., Cr, Mn, Fe, Co, up to U) and allows the detection of trace concentrations down to 10 or less ppm for a range of elements. The larger information depth of X-ray excitation yields a deeper look inside the sample, allowing the characterisation of relatively thick layers or even of multilayer systems starting from 1 nm and ranging up to 50 µm or more, which is not possible with electron excitation. Micro-XRF works with a fixed X-ray beam, consequently, X-ray elemental distribution maps must be acquired via stage movement. Developments of adding a piezo-based stage (rapid stage) mounted on top of the SEM stage enables high-speed elemental X-ray mapping over large areas (Fig. 2), thus making it

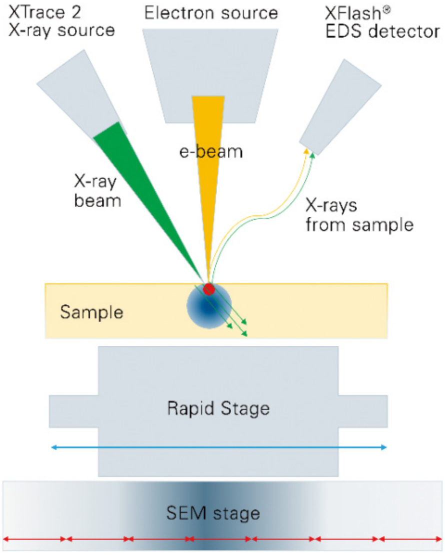

Figure 1. The micro-XRF works with a fixed beam and cannot raster like an e-beam. Therefore, a special stage (rapid stage) has been developed for high-speed element distribution measurements with X-ray excitation. This stage is mounted on top of the existing SEM stage and can be easily removed when it is not required.

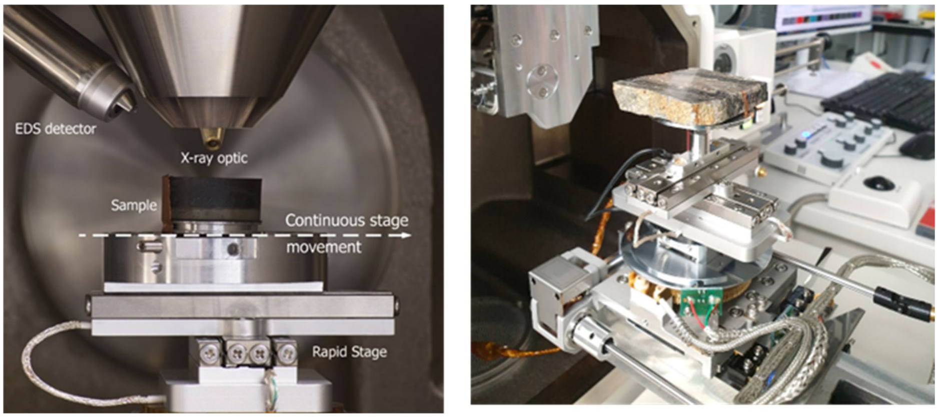

Figure 2. Gold-bearing epithermal sample from Karangahake deposit, New Zealand. The sample is approximately 5 cm in width. The Table (in Fig. 3) shows the relevant minerals and elements of interest. The sample is carbon coated as both X-ray and electron analyses will be performed.

suitable for the analysis of larger samples (i.e., centimetre-scale) that traditionally are not analysed in an SEM. The control of the X-ray source is fully integrated, thus allowing for simultaneous electron and micro-XRF acquisition, incorporating light element spectral data as well as trace element and/or higher energy X-ray data during the sample analysis. Sample preparation requirements are minimal for micro-XRF analysis and thus a wide range of sample types can be analysed (e.g., no carbon coating required; no high-quality polished surface required; low vacuum). Applications include economic geology, petrology, mining, mineral processing, forensics, environmental and archaeology, amongst others.

In this application example relevant to the field of geology, exploration, mining and metallurgy, the objective is to determine elemental and mineralogical information about the sample to aid in understanding the geological processes and potential economic deposit genesis as well as mining, metallurgical and mineral processing considerations. This demonstrates the potential when utilizing the benefits of a combined electron and X-ray excitation system on a SEM. The selected sample is from a gold-bearing epithermal deposit (Karangahake) in New Zealand. Figure 2 is an image of the gold-bearing sample to be analysed. Figure 3 is a mosaic map of the elements of interest and the selected analytical conditions as measured using the micro-XRF source. In addition, in this sample it is possible to detect trace elements such as the K-lines for Se, Ag, Cd, and Sb that are not usually detectable by e-beam EDS analysis as the concentrations are too low and/or the relevant element energy line is too high. This provides an understanding of their distribution and mineralogical and textural relationships.

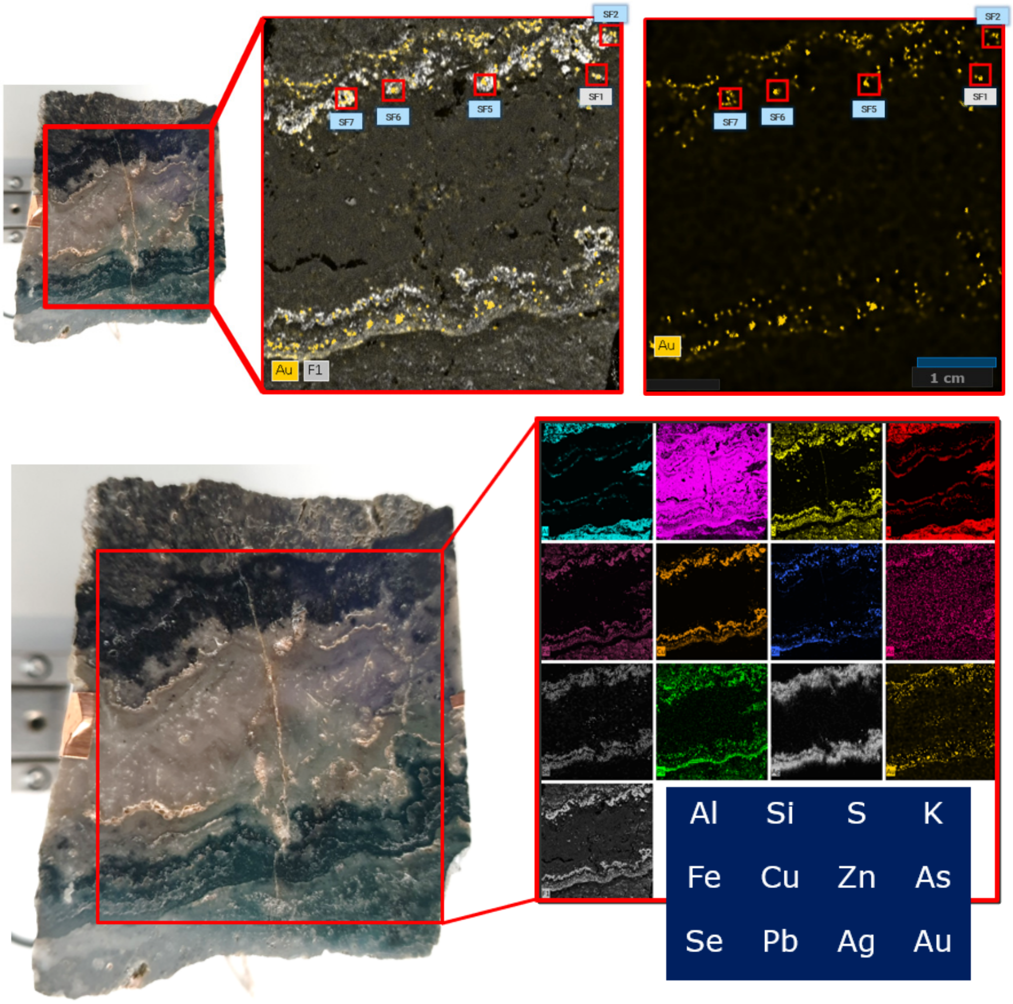

Figure 3. Large area X-ray map (45 mm x 45 mm) of an Au-bearing epithermal sample acquired with XTRACE (analytical parameters: tube voltage: Rh at 50 kV; anode current: 600 µA; pixel spacing: 100 µm; analytical time: 94 mins). Elemental maps as indicated in the blue box at the bottom of image. Note the mineralisation, especially Ag and Ag alone parallel veins. Bottom row is an expanded view of the total X-ray intensity map and Au elemental distribution. Red fields are areas selected for enhanced mapping using the electron beam.

As can be seen in Fig. 3, the micro-XRF hypermaps successfully identify the presence and location of gold (Au) and silver (Ag) bearing grains within the sample. In addition, it is possible to ascertain that these gold grains are primarily native gold or electrum. This large area map was achieved in 94 minutes. Furthermore, there are known peak overlaps for the various gold peaks, and thus an intensity map of a single Au element line might lead to misinterpretation. For example, the Au-Lα-line has an energy of 9.704 keV, which overlaps with Zn-Kβ (9.569 keV) and W-Lβ (9.682 keV), both of which occur in Au-bearing deposits. Thus, to confirm the presence of Au, the information must be correct deconvoluted, and the presence of all the Au element lines should be confirmed.

Now that the presence of gold has been confirmed and the various positions of gold bearing grains identified, it is possible to analyse selected areas using the electron beam to yield higher resolution maps over specific areas (Fig. 4). These follow-up analyses can be achieved by switching to e-beam SEM analyses (which requires sample coating and high vacuum) or selecting specific areas in the sample for further sample preparation prior to analysis. In this case, the former is preferred, and examples of such maps are shown in Fig. 6 and clearly highlight the fine scale relationship between Au and other elements associated with the mineralisation such as Zn, Fe, Cu, and Pb. Thus, in the space of one analytical session, the benefits of *Full Range EDS* using a dual source X-ray and electron SEM system in the analysis of a gold-bearing sample were utilised thus creating an improved workflow.

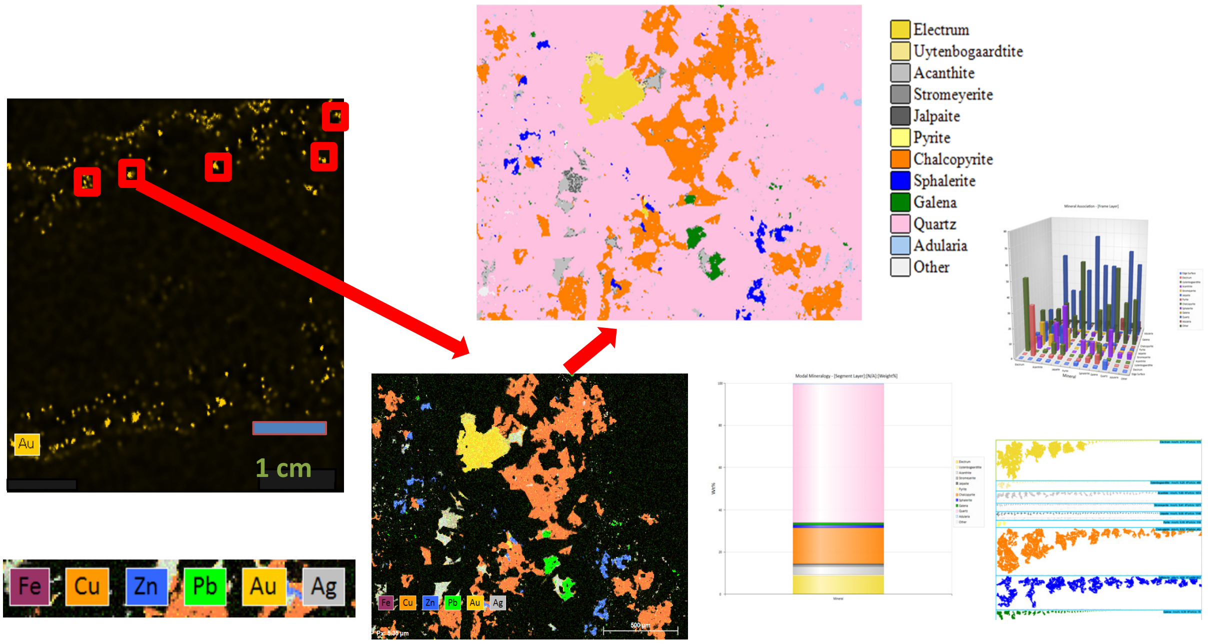

Figure 4. Electron beam analysis of selected areas where gold grains are known to be present resulting in a high resolution (1 µm or less) element intensity maps enabling the identification and relationships between the Au-grains and various sulphides using automated mineralogy (AMICS) software.

However, as may be apparent, such a system can be applied across a wide variety of applications, especially given the increased sample types, minimal sample preparation, and analytical capabilities now possible due to the addition of the X-ray source been incorporated to the SEM. Other examples can apply across a wide-range of applications and include capabilities to display topography (Fig. 5), trace element identification and quantification (Fig 6.), and high-energy X-ray line identification and deconvolution (Fig 7.).

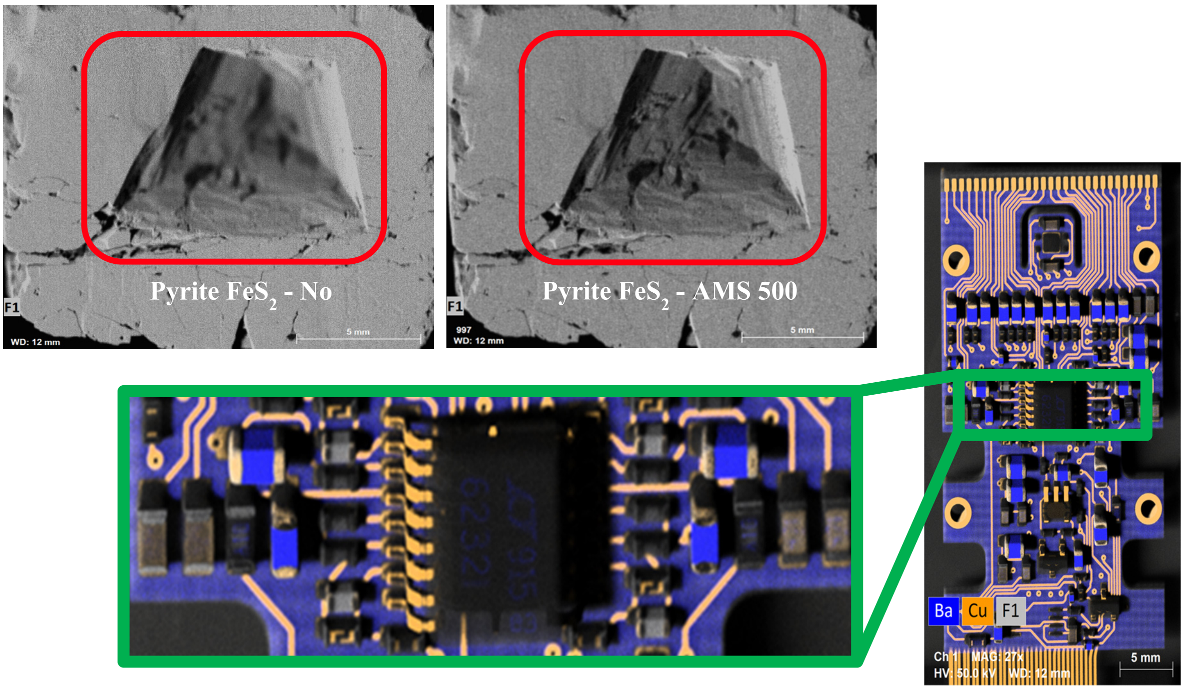

Figure 5. The aperture management system (AMS) used in QUANTAX micro-XRF systems facilitates the high-resolution mapping of samples with 3D features, such as electronic components, at varying working distances, or within samples, such as a pyrite grain (no AMS (left) and with AMS (500 µm) (right)), in this case, to a depth of 2.1 mm.

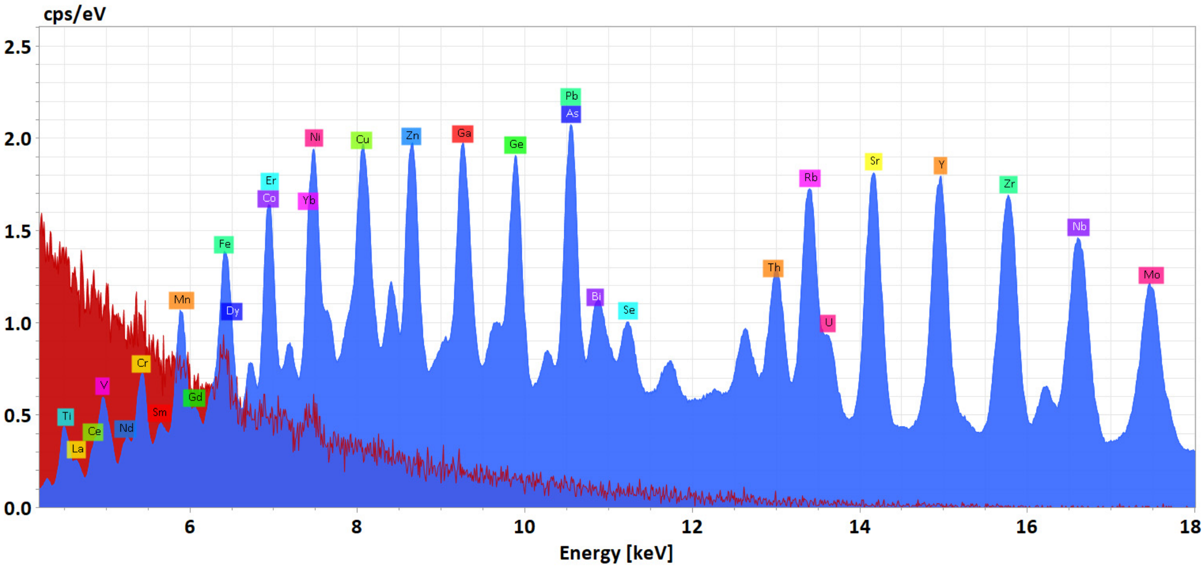

Figure 6. Comparison of spectra collected on the NIST 610 glass using conventional SEM EDS at 30 kV (red) and *Full Range EDS* at 50 kV (blue).

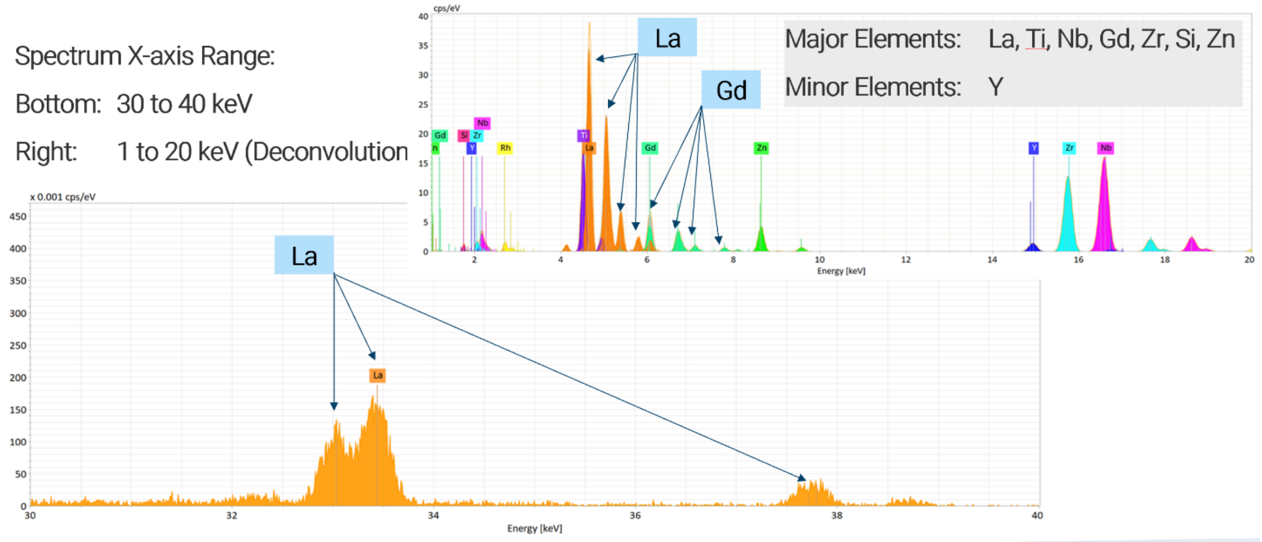

Figure 7. Analysis of high index glass showing the capability of *Full Range EDS* to identify and deconvolute high-energy X-ray lines not normally considered with electron beam excitation.