

SEM Diaries - 30

Mineralogy Rocks!

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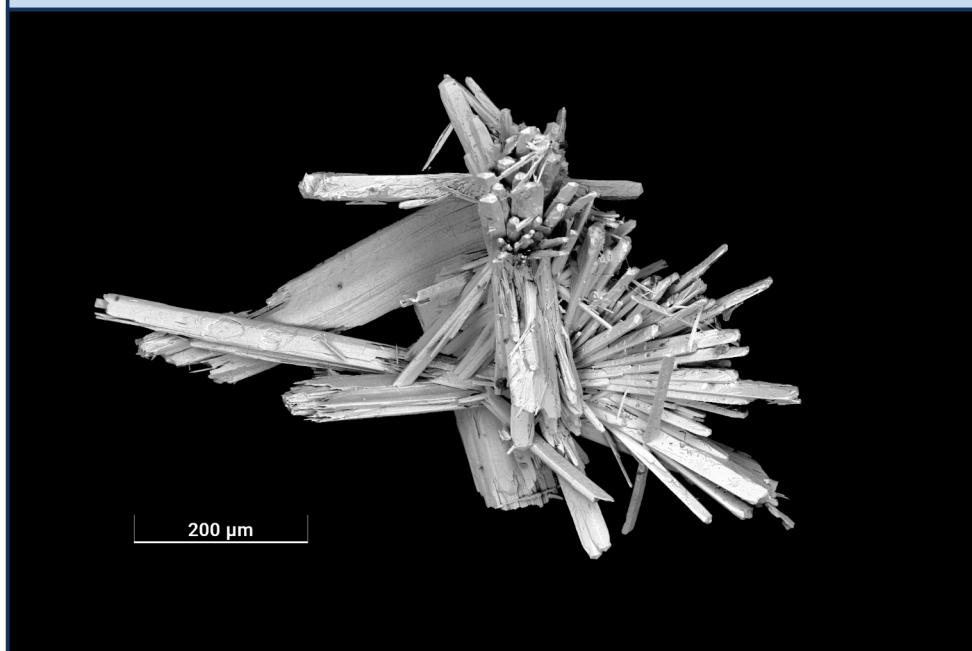


Fig. 1: Backscattered electron image of antimony oxide

Yes, I know it is an awful pun, but the title this time does sum up my somewhat upbeat feelings regarding my SEM at the moment - or at least the anticipation of receiving a new toy to try out!

Recently I was asked by a PMS member, who happens to be a mineralogist, whether my SEM has “EDS”. The answer is, currently, no! However, the question resurrected the thought that had been at the back of my mind for quite a while, that perhaps I ought to look into obtaining this facility.

OK, so what is “EDS”. Well the acronym stands for “Energy Dispersive Spectroscopy” and it is a technique for

determining the chemical composition of a material - but perhaps before I attempt to explain EDS, we should revise what we know about the interaction between an electron beam and the surface (and near surface) of a specimen.

This is normally illustrated by means of the “classic” onion diagram (Figure 2), which can, in turn be broken down into three or four individual parts. The ones we shall concentrate on now are backscattered electrons and X-rays.

Backscattered electrons (BSEs) are electrons that have originated in the electron beam and have penetrated the surface of the specimen. Once they have penetrated they undergo elastic and

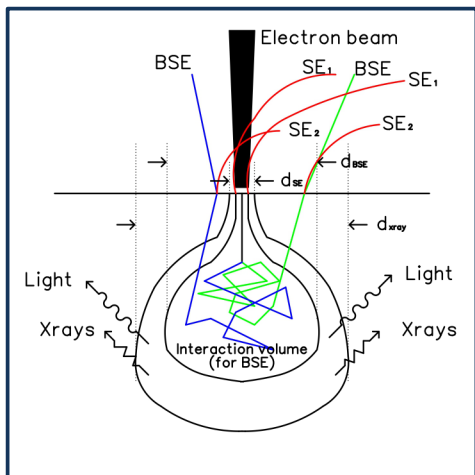


Fig. 2: The "Onion" Diagram

inelastic scattering within the atomic structure of the specimen. Eventually, they will be either absorbed within the specimen or ejected through its surface. All this happens in a volume within the specimen, known as the interaction volume, illustrated in Figure 2. This shows the paths of two BSEs (one in blue and one in green) being scattered around in the volume before leaving the surface once more.

The higher the atomic number of the material, the smaller the interaction volume, and the more BSEs are ejected from the specimen. For low atomic number materials, such as carbon, almost all the BSEs are absorbed within the volume of the specimen. Figure 3 is a simple illustration of this. It shows the output from my BSED when viewing polished specimens of six different materials with widely spaced atomic numbers. Because these are polished flat there is no topographic information to convey, so the effect is purely down to atomic number (other than minor imperfections arising from the polishing of the gold sample). No SEM settings were changed in between imaging each sample, other than moving the stage.

My Backscattered Electron Detector (BSED) is made up of four independently wired quadrants of photo-diodes, located directly underneath the pole piece of the SEM. The outputs from the quadrants

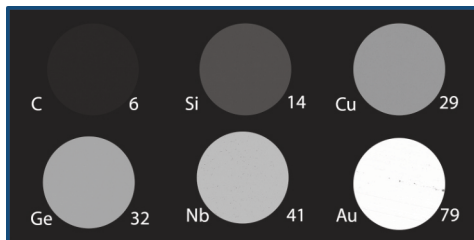


Fig. 3: Output from the BSED for materials of six different atomic numbers. (Carbon, Silicon, Copper, Germanium, Niobium and Gold)

can be added or subtracted in any combination. If they are simply added together they are said to be in "COMPO" mode - short for "Composition". As this implies, it is intended to provide an idea of the chemical composition of the specimen. Connecting one adjacent pair together and subtracting the output from that of the other adjacent pair gives the "TOPO" mode, which is short for "Topographic" and designed to give a realisation of the shape of the specimen.

There is further mode, called "Color", which adds false colour information, a different colour for each channel. When the channels are added together the colours are combined depending on the contribution from each channel for a particular location on the scanned object. I am not sure if this has any scientific use, but it does give "pretty" pictures. (This mode is not to be confused with colour mapping using EDS, where the colours have very specific meanings.)

Figure 4 illustrates the effect of these three different modes, when imaging the polished face of a sample of chromite (Cr_2FeO_4). The top image (COMPO) shows good contrast, suggesting the diagonal feature is made up of material of lower atomic number than its surroundings. The centre image (TOPO) exhibits lower contrast, and a gradation in brightness from right to left. This brightness differential helps to emphasise any shape information. It is clear that although the surface was polished it nonetheless has some lack of flatness.

The bottom image (Color) is included to show the effect of that mode. I shall make no attempt at interpreting it, though!

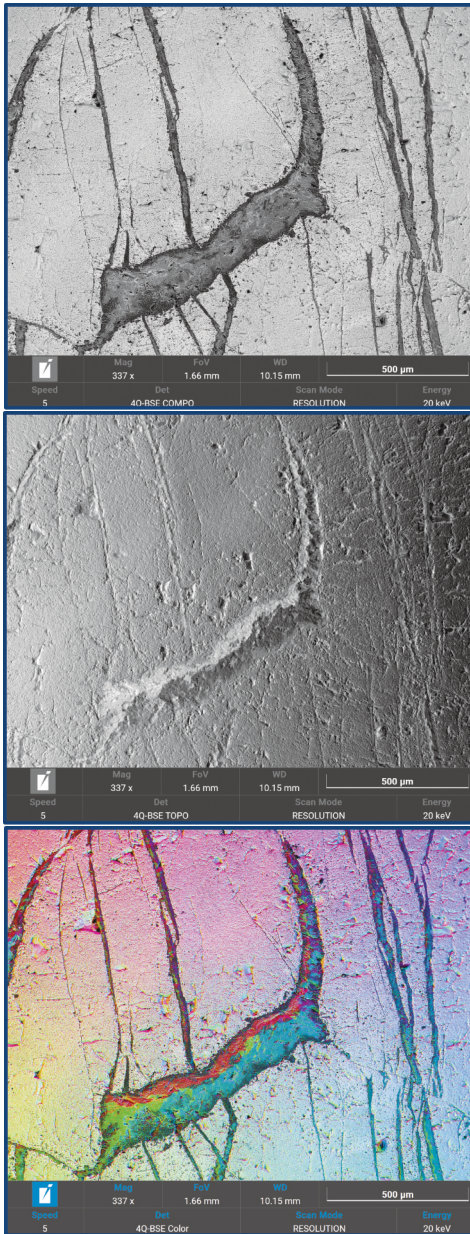


Fig. 4: Illustrating the same part of a polished surface of chromite, imaged using (top to bottom) COMPO, TOPO and Color modes.

If the material is three-dimensional, rather than polished flat, then confusingly the COMPO mode actually provides better topographical images than TOPO mode. This is illustrated in Figure 1 (frontispiece).

So much for backscattered electrons and how they are suited to mineralogy. Now, what about Energy Dispersive Spectroscopy? This technique makes use of the X-rays that are given off when the electron beam penetrates the specimen.

Many of us will have learnt at school that an atom is made up of a nucleus, surrounded by orbiting electrons. A more detailed description would include the fact that the electrons orbit in a series of shells: K, L, etc and that some of the shells are broken down into sub-shells: $K\alpha$, $K\beta$ etc. When an electron beam interacts with a specimen, a beam electron may eject an electron from one of the inner shells, leaving the atom in an excited state. Very rapidly (within $\sim 1\text{ps}$) an electron from one of the outer shells will move to fill the vacancy in the inner shell, and in the process emit an X-ray. A more detailed description of this process, together with a diagram, can be found in Reference 1.

The characteristics of the X-ray are closely linked to the element from whose atom it originates, so by carrying out a spectral analysis of the X-rays, it is possible to identify the chemical composition of the specimen at a location excited by the electron beam. The software of the EDS system permits the user to select point locations at which the chemical composition of the specimen is to be measured. Alternatively, the beam can be made to scan the entire field of view and build up an element "map" over the entire field. Examples of the spectrum from a point location, and of an element map, are given in SEM Diaries - 31.

As is often the case, the practical results obtained using this method of analysis can be a bit more "nuanced" than the straightforward description above might suggest. For example, the spectral peaks are quite broad, so it is possible that a peak originating from one element can hide that from another of similar energy (per X-ray) but with fewer atoms of that element. Also, it is difficult to resolve peaks of low atomic number elements,

such as beryllium. The technique is now quite well-developed, and within the limitations outlined above it is possible to arrive at an accurate analysis of the composition of a material. This is known as "Quantitative Analysis". This does, however, require careful calibration and good technique, along with a highly polished surface (to about 0.5 μm). A slightly easier process, known as "Semi-Quantitative Analysis" permits one to do away with some of the calibration, but by definition is less accurate. It is also possible to carry out "Qualitative Analysis" which does not presume to provide accurate compositional ratios, but can nonetheless provide information such as "the sample has a large amount of element "a", some element "b" and a trace of element "c".

On the 18th and 19th July I attended a conference at Plymouth University. It was called "SW-EM" and was basically a gathering of users of electron microscopes (both SEM and TEM) in the South-West of England. There were a number of lectures, which were partly about interesting projects being carried out at various universities, but also updates on topics such as engaging with industry as well as outreach to secondary schools (the latter achieved by transporting a desktop SEM to various schools for workshops with children). In addition to the lectures there was a trade show where I was able to catch up with TESCAN and representatives of other suppliers of capital goods and consumables.

I explained my interest in equipping my SEM with EDS to one of the industry representatives there, and he came up with a plan. He would lend me a pre-owned system to try on my SEM for a few months. If I like it I can buy it (or a similar alternative version), if not they would uninstall it and take it away. The hardware they have available is almost unused, though a few years old, so

(hopefully) it would be more affordable than a new system.

You may wonder how dumb I must be to consider spending a five-figure sum on upgrading my SEM, "just because a PMS member would like access to facilities for chemical analysis of mineral samples". Well, those who have stuck with me in reading SEM Diaries over the 7 years or so I have been writing it will realise that my interest in electron microscopy is almost as much about the equipment and how it works as it is about what I am looking at with it. And when I am producing images, my interest is as much about producing pretty pictures as it is about research. Mineralogy and EDS would open up a whole new opportunity to produce pictures of new subject matter in the form of element maps. Anyhow, perhaps it is not healthy to spend all ones time in detailed study of the sexual organs of spiders.

Another aspect of this potential development is the opportunity for collaboration. I have written previously about how much more satisfying it is to work with other people, even if remotely, than just on ones own. I have already established contact with experienced mineralogists, both academics and gifted amateurs, and all are being most helpful and keen to work together. In fact, my name has already been added to the list of authors of one paper on the basis that it uses one of my images!

Anyhow, as someone said at Plymouth:

An SEM without EDS is like a car with only three wheels.

Reference

1. Goldstein, J., Newberry, D., Joy, D. and five others. Scanning Electron Microscopy and X-Ray Microanalysis. Third Edition. Springer 2003. Section 6.2.1