

SEM Diaries - 41

It's not all pretty pictures

Jeremy Poole

Stub May 2025 | Posn 07 C Coated | Area 1 | EDS Spot 1

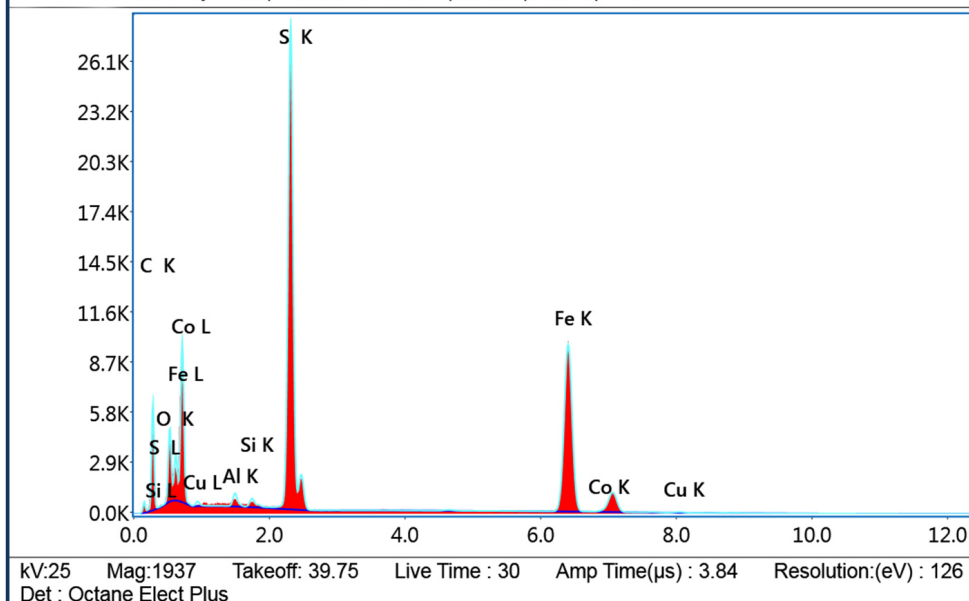


Fig. 1: Graphical output from EDS analysis of a sample of what is thought to be iron pyrites.

As must have become clear to readers of SEM Diaries over the years, the SEM is incredibly versatile. Not only can it provide stunning images with a 3-Dimensional appearance (using the Secondary Electron Detector), and images of polished surfaces showing “Atomic Number Contrast” (using the Back-scattered Electron Detector) but it can also come up with graphs and tables giving a (semi-) quantitative indication of the chemical composition of the specimen. The functionality to provide the chemical composition is provided by the Energy Dispersive Spectroscopy (EDS) detector and processor as described in SEM Diaries-31 (January 2023).

I use the term “semi-quantitative” advisedly. To achieve accuracies (in the

ratio of the elements that make up the specimen) of the order of, say, 1% requires the specimen to be embedded in epoxy and polished to a high degree of flatness (say 1μm) and for the EDS system to be calibrated against physical standards. The system that I use is based on “software” standards, and is less accurate. Furthermore, often the specimen cannot be polished at all, so far from having a flat surface it can be very 3-D in appearance. This will reduce the accuracy of the analysis carried out significantly but can still give an “indication” rather than a “measurement” of the chemical composition.

Over the last year I have been using my EDS system quite a bit in several collaborative projects and I wish I could

say that the results were excellent. In reality I have little experience in interpreting these outputs, and even experts I have consulted do not always have ready answers. This does not mean that my analysis is “wrong” (although I guess it could be) but more that geology and mineralogy are complicated subjects and do not always follow the rules we like to apply to them.

Figure 1 is an example of an EDS spectrum output. Without attempting to explain it in any detail, I can say that on its own it does not convey much information other than indicate which elements have been detected at one particular location on a specimen. The beam diameter at the measurement point is of the order of nano metres in diameter, but as the beam penetrates the specimen the electrons are deflected by multiple collisions with atoms within the specimen, so the actual area that is being measured will be significantly larger (although still very localised).

Within the processor, the measurements are treated to considerable mathematical processing that arrives at an interpretation of which chemical elements are present in the specimen - at that particular spot - and in what ratio. There are two ratios provided: one is in percentage by mass, while the other is in percentage by atoms. These numbers are summarised in a table referred to as the “Quant Results” and can be exported in Excel format.

An example is shown in Table 1. This shows the different elements that were detected under the spot and the ratios of the elements to each other, both by mass and also by atomic proportions. The latter, in the right hand column, are more useful. The sample was a small grain of what was suspected to be iron pyrites, which has the chemical formula FeS_2 or ferrous disulphide. (For the non-chemists among you Fe represents iron and S represents sulphur. Also, the suffix “K” against each element in the left hand column of Table 1 is a reference to the orbit of the displaced electrons that generated the energy signal detected by the EDS system, but need not concern us further.)

Now, looking at the atomic % for Iron and Sulphur in the table it would seem that

CREATION DATE	05/08/2025 12:42	
PROJECT	DG STUB MAY 2025	
SPECIMEN	POSN 07 CARBON COATED	
AREA	AREA 1	
SAMPLING REGION	EDS SPOT 1	
KV	25	
LIVE TIME	30 s	
AMP TIME	3.84 μ s	
TAKEOFF ANGLE	39.75 deg	
RESOLUTION	125.9975	
ELEMENT	WEIGHT %	ATOMIC %
C K	41.1	64.3
O K	12.3	14.5
AL K	0.6	0.4
SI K	0.3	0.2
S K	20.9	12.3
FE K	24.3	8.2
CO K	0.2	0.1
CU K	0.2	0.1

Table 1: Chemical analysis of material containing what is thought to be iron pyrites

the ratio is more like two atoms of Fe to three of S, or Fe_2S_3 , which happens to be ferric sulphide! What is more, although the sample is not flattened or polished in any way, the ratio is really accurate - if it were ferric sulphide! Incidentally, for a completely different project with material from the Jurassic Coast (mentioned later) rather than a mine in County Durham, I found similar ratios of Fe to S in a material that resembled iron pyrites. What is going on? And, quite apart from the “wrong” ratio between Fe and S, what is the reason for the high percentages of Carbon and Oxygen?

Given that I am neither a chemist, nor a mineralogist, nor even a geologist, I consulted others who are better qualified. Among my questions was “given how close the ratio of iron to sulphur is to ferric sulphide, are we sure that that is not what we have?”. A case of wanting to believe the simple solution. However, the experts on both projects are convinced the material is iron pyrites and thus have been working out causes for the excess iron. Without going into any detail it

seems that the excess iron could be bound up in oxyhydroxides (including rust). The hydrogen would not be detected by EDS, although as can be seen from Table 1, there is significant oxygen present. The large amount of carbon is not totally unexpected. Iron pyrites is formed by the deposition of iron and sulphur in the pores and cavities of an organism during fossilisation, so it is possible that some of the original organic material might have survived “pyritisation”.

Completing the discussion of Table 1, it is probably fair to suggest that the results for the trace elements (aluminium, silicon, cobalt and copper) could well be totally spurious given the nature of the sample and its preparation, along with the very low values.

For the project on material from the Jurassic Coast mentioned earlier, we were studying tiny fossilised bivalves (shellfish) in a “seam” of iron pyrites. There were also a few bivalves outside this seam.

Figure 2a is a light micrograph of one of the bivalves outside the seam. The shell material can just be made out as a black line, while adjacent to this, on the inside is a layer of iron pyrites. The gold colour of this might help to explain why iron pyrites is known as “fools gold”. Figure 2b is an electron micrograph of the same bivalve, made using the backscattered electron detector, with the brightness of the image at any particular location indicating the atomic number of the predominant element at that spot. The higher the atomic number, the brighter that spot or area. The sample is a section across the material, sawn “flat” but neither polished nor embedded.

For completeness I include Figure 2c, which was imaged using the secondary electron detector.

EDS analysis was done at various spot locations, indicated in Figure 2b.

Area A was rich in Calcium, Carbon and Oxygen, with some Silicon. This suggested that the matrix in which the bivalve is trapped is limestone, with some sandstone.

The arrow at B points to the edge of the shell. This was analysed at higher magnification to ensure that the spot was



Fig. 2a: Small fossilised bivalve shell, in a flattened section of marl material. Scale bar 250 µm. (Light Micrograph)

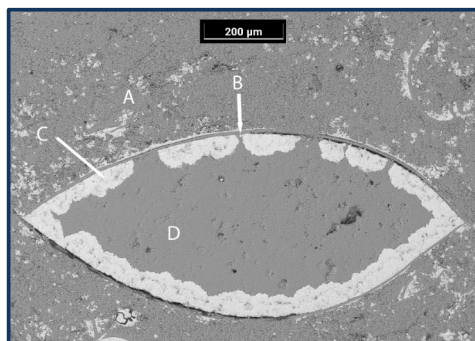


Fig. 2b: Same fossilised bivalve, imaged using the Backscattered Electron Detector

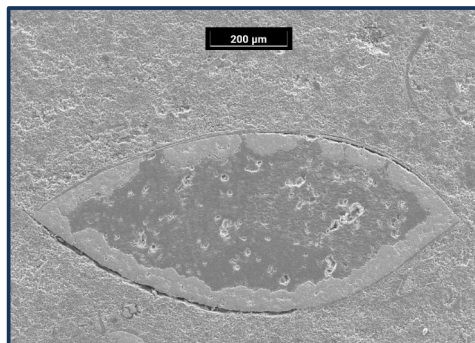


Fig. 2c: Same fossilised bivalve, imaged using the Secondary Electron Detector

located on the shell edge itself. The composition at that location was: Calcium 22%, Carbon 20% and Oxygen 56%. This is a very good match for the presumed shell material of calcium carbonate (CaCO_3).

The arrow at C points to the iron pyrites lining of the shell. The ratio of Iron to Sulphur was found to be 23% to 33%. As for the sample described in Figure 1 and Table 1 this contains more Iron that would be expected from pure iron pyrites, and the reason for the discrepancy would likely be the same as that described for the first sample.

The material inside the bivalve, at location D is a better match for Limestone than that for Area A, outside the shell. In fact the ratio of Calcium to Carbon to Oxygen at location D was 20:18:61, which within the expected accuracy of the measurements is very close to CaCO_3 .

Figure 2c is included for completeness. The brightness output from the secondary electron detector is dependent upon the angle of the surface to the electron beam.

The fact that there is any contrast at all is due to the fact that despite the material having been cut flat, there is some inherent roughness.

I mentioned earlier that I had been wondering whether my measurements might have been "wrong". This could arise if the EDS system was not working properly, or more likely if my preparation had not been up to scratch. All I can say is that my collaborators and other experts approached for comment have preferred to believe the results rather than query them, even where it has led to them needing to re-think their original conclusions.

I have to say, that coming to this side of microscopy somewhat late in the day, there have been times, while trying to interpret the EDS outputs, when I wished that my lab smelt of xylene and my fingers were glued to the bench with Praktamount. Perhaps I should go back "On Circuit" and look at microscope slides once more.