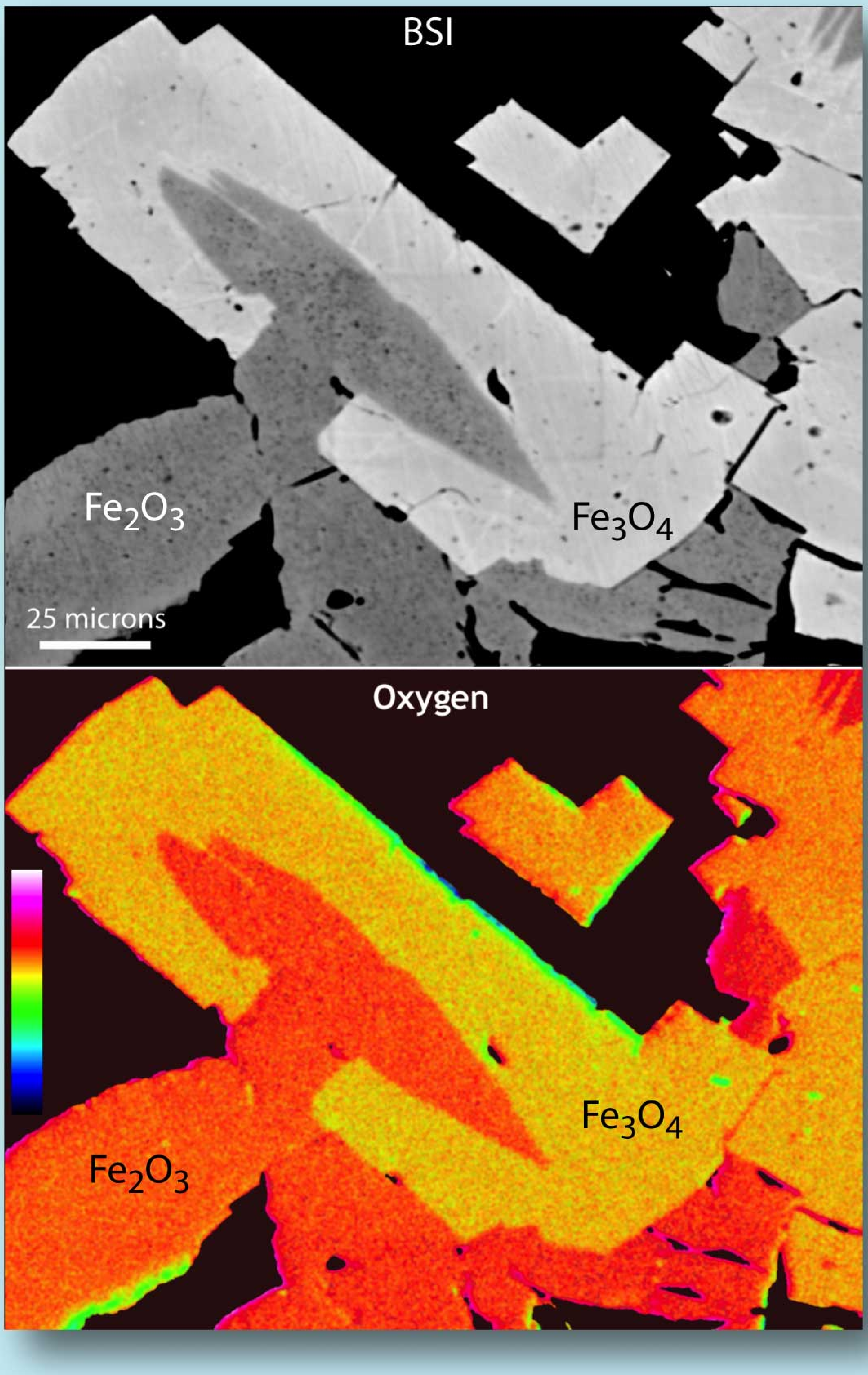
McSwiggen & Associates

TECH Notes

Oxygen

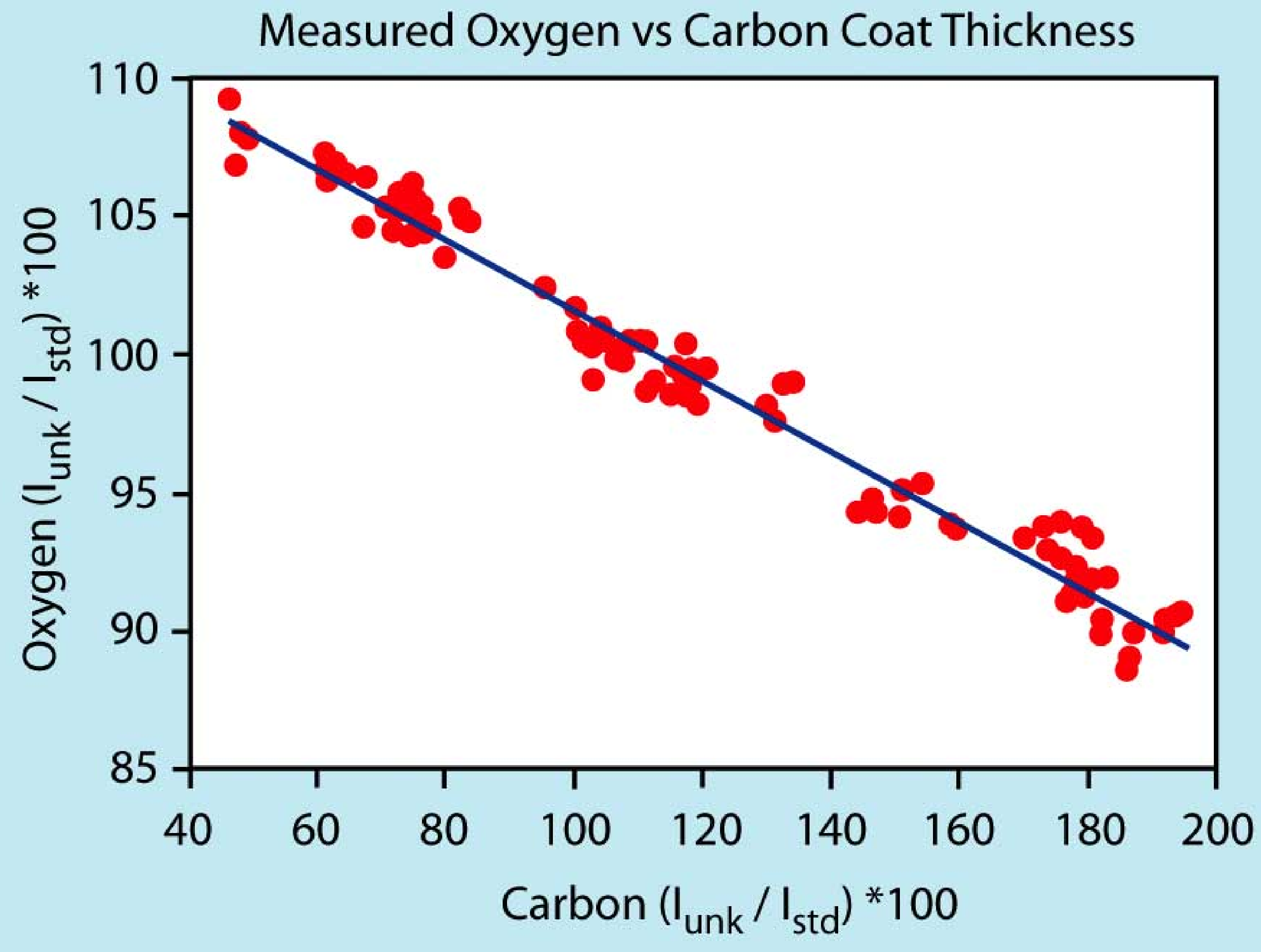
Oxygen (O, Z=8) is a particularly important element in many different systems. In geologic systems it is the most abundant element. In metallurgical systems, oxygen's importance comes from its role in corrosion. Yet for all of its importance, it is arguably the least analyzed of the major elements. The reason for this is the difficulty in getting good results. Most quantitative analyses of oxides do not measure the oxygen abundance directly, but calculate it assuming a fixed stoichiometry for each oxide. This works in most cases, but for some oxides there is not a single fixed oxidation state. The best example of this is iron, which occurs both as $Fe^{2+}O$ and $Fe^{3+}_2O_3$.

The biggest problem with analyzing for oxygen is that it produces very low-energy X-rays, and these X-rays are easily absorbed. Add to this the problem that most oxides are non-conductive; therefore they need a conductive coating deposited onto their surface before being analyzed with an electron beam. Typically, a carbon coating is used for quantitative analyses because carbon's low atomic number means fewer of the generated X-rays will be absorbed. However even thin carbon coatings can greatly absorb very low energy X-rays like those from oxygen. The plot below shows the range in measured oxygen from SiO_2 glasses that were coated using normal coating procedures, but at different times. It demonstrates that even when trying to be consistent with the carbon coating a significant range in carbon thicknesses may be deposited, and this impacts the oxygen analyses by as much as ±10 weight percent. The best solution is to carbon coat the standards and the unknown at the same time to ensure identical thicknesses.

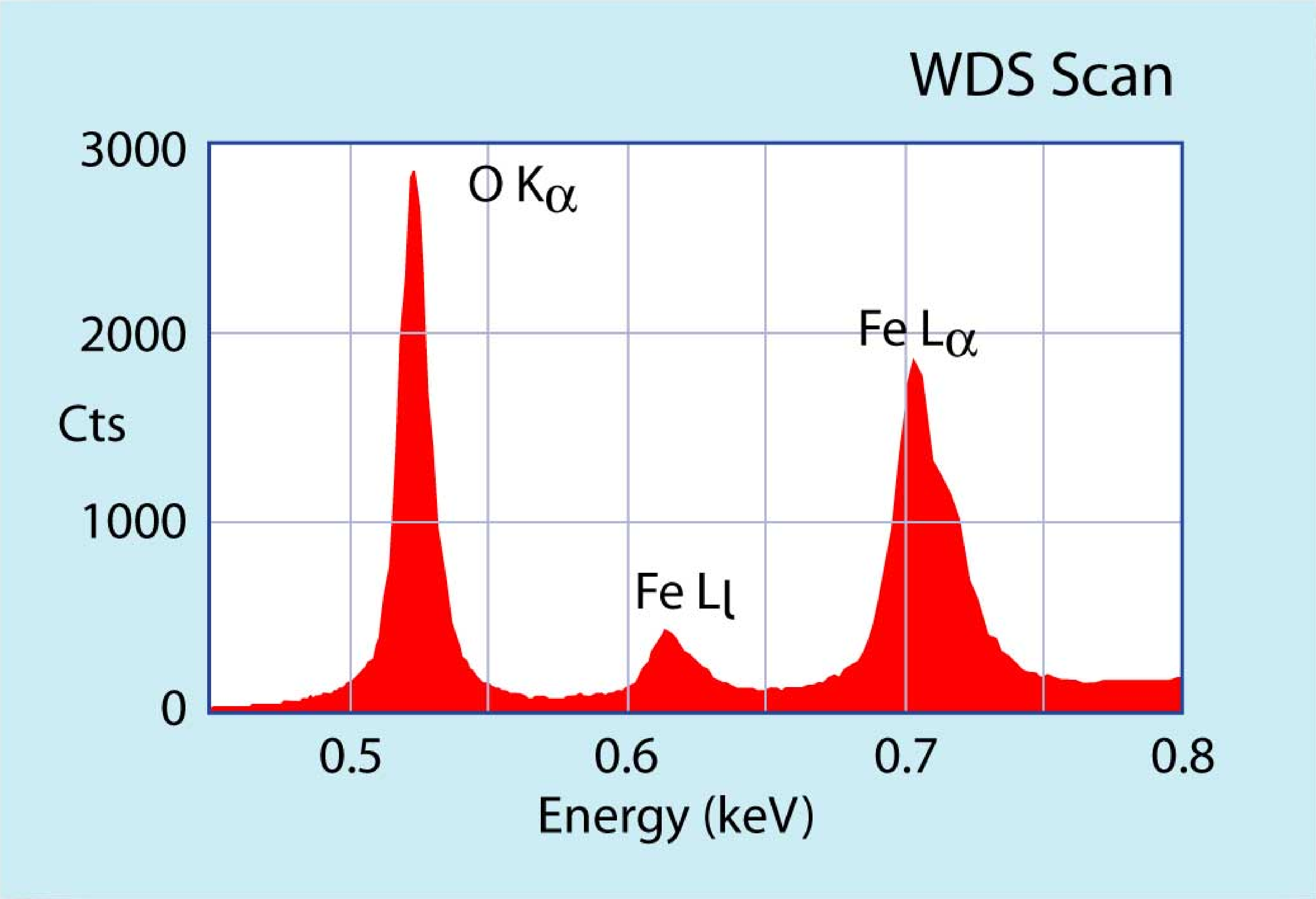


Backscattered electron image (BSI) and oxygen element map of magnetite (Fe_3O_4) and hematite (Fe_2O_3) grains. The hematite has about 2.5% more oxygen than the magnetite.

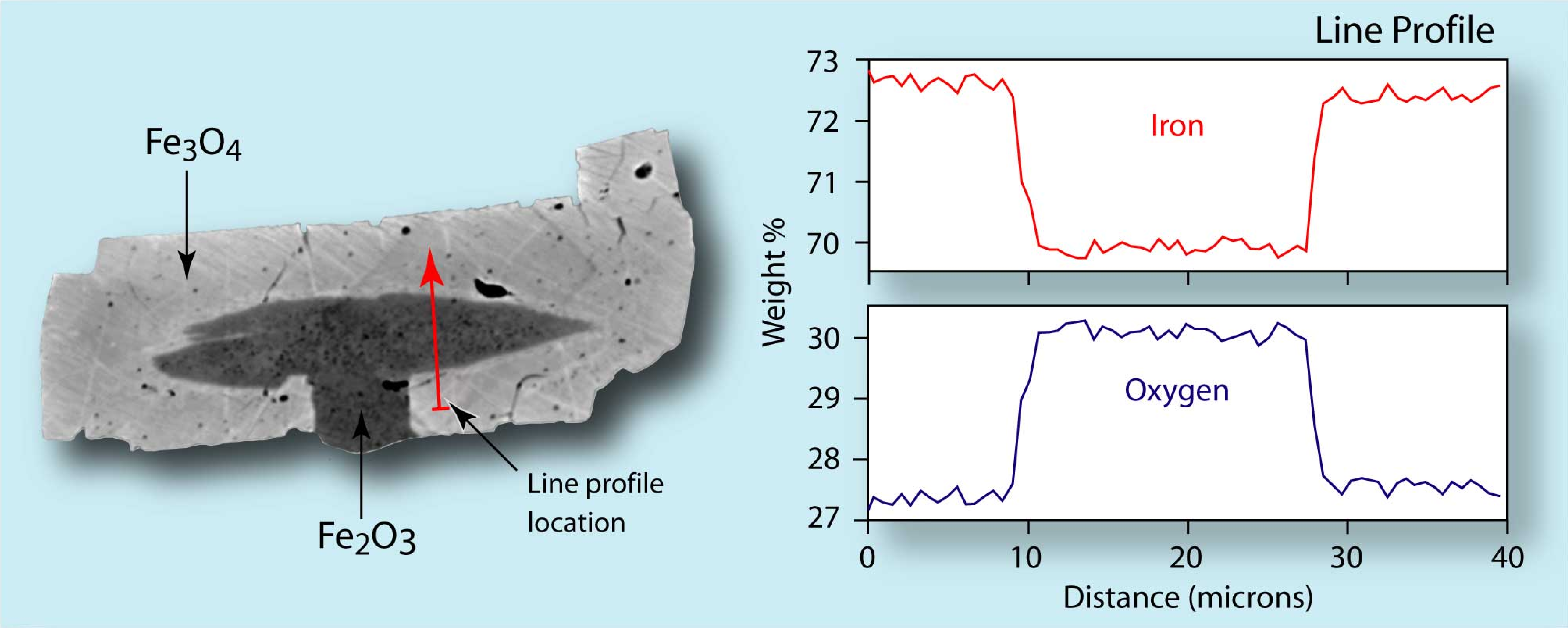
(Sample is from the Biwabik Iron Formation.)



Measured oxygen abundance relative to variations in the carbon coating thickness, as measured by carbon abundance. Samples were SiO_2 glasses that were carbon coated at different times. The standards were quartz (SiO_2) and its carbon coating.



Wavelength dispersive spectrometer (WDS) scan over the oxygen Kα X-ray line and neighboring peaks. A similar spectrum from an energy dispersive spectrometer (EDS) would not be able to separate these three peaks. There would be a significant overlap between the O Kα and Fe Lα peaks and the Fe Ll peak would be completely hidden.



Line analyses are an efficient way to determine the change in oxygen abundance spatially across a sample. They are semi-quantitative because the data are not corrected for matrix effects. The recorded values are X-ray intensities that have been converted to weight percent using a calibration curve, but they can clearly show relative changes in abundance.

Another problem that can occur with quantitative oxygen analyses is that the oxygen peak can shift or undergo a shape change from one material to another. This is a result of a change in the bonding energy of the oxygen atom. When this occurs it is critical to integrate the area under the oxygen peak to get the total number of counts.

True quantitative analyses, such as those shown to the right, have been corrected for differences in the average atomic number, and for differences in the amount of absorption and fluorescence in the standards versus the unknowns. With proper preparation, wavelength dispersive, quantitative analyses can measure differences in oxygen down to fractions of a weight percent.

Quantitative Analyses

	Magnetite - Fe_3O_4			Hematite - Fe_2O_3		
	weight percent					
Fe	72.54	72.57	72.30	70.10	69.78	69.91
O	27.61	27.61	27.39	30.35	30.20	30.04
Total	100.15	100.09	99.69	100.45	99.98	99.95