

## Towards Quantitative Maps of Lithium in the Scanning Electron Microscope

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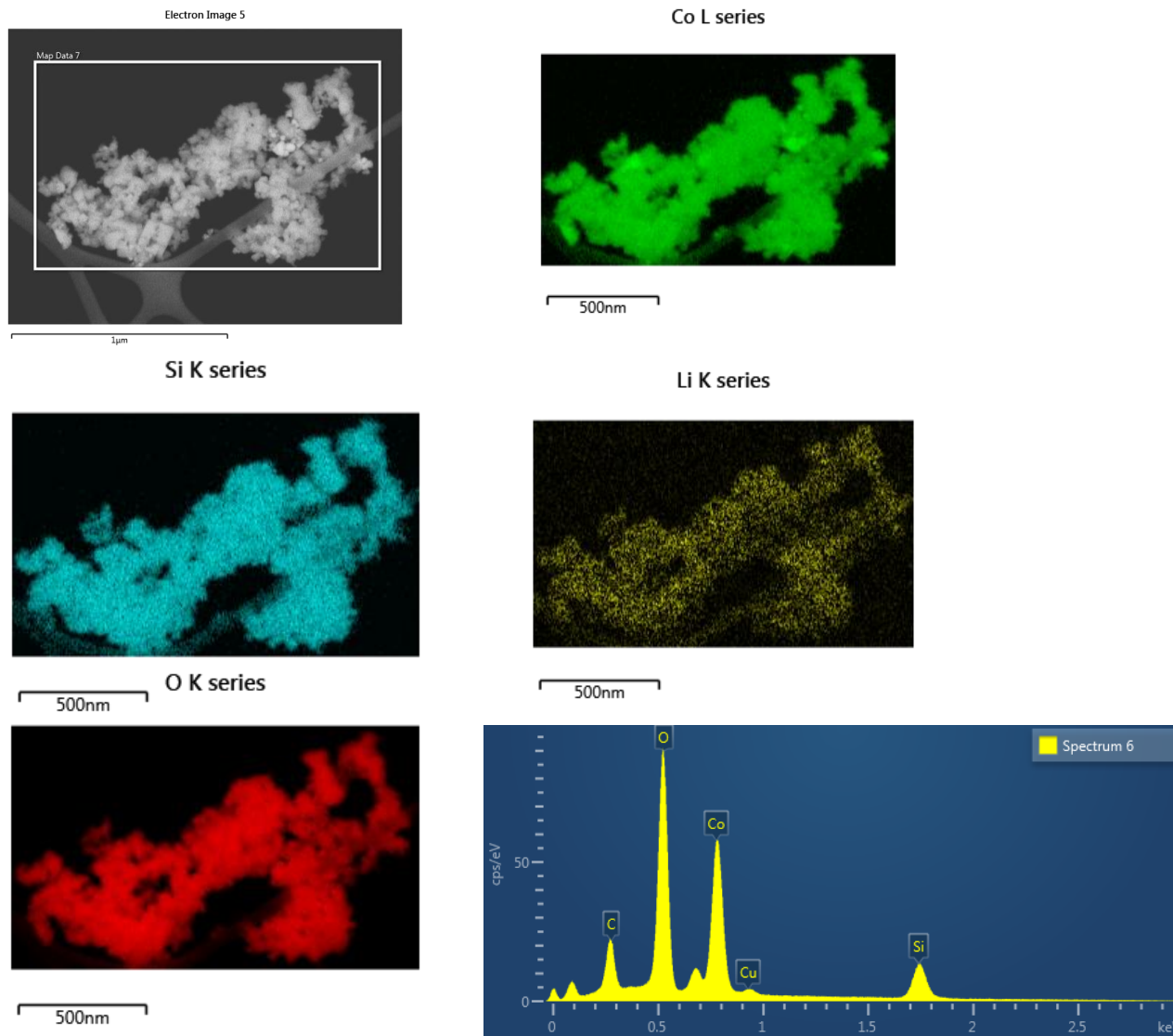
This paper will present new achievements in performing quantitative EDS and EELS maps of lithium-based materials in the scanning electron microscope. State of the art results acquired with the SU-9000 dedicated STEM will be shown. This microscope has EELS capabilities that allows Li detection [1]. It is also equipped with the Extreme EDS system from Oxford Instruments that can detect the K line of lithium [2]. The SU-9000 has a resolution of 0,22 nm in bright field STEM without aberration correctors and it allows lattice imaging.

Figure 1 shows a set of EDS maps acquired at 3 keV on  $\text{Li}_2\text{CoSiO}_4$  for Co, Si, O and Li as well as the corresponding sum spectrum. Clearly, the intensity of the Li map is much weaker than for the Co L, Si K and O K lines. It is even possible to see that some 50 nm particulates are richer in Co. The sum spectrum shows that if there are Li K net X-ray intensities, it is very weak. The Li K map is likely to be the background map and possibly the Co M line that has an energy of 58 eV compared to 54,3 eV for Li K. The emission of the Li K line is difficult because of strong x-ray absorption in the material following ionization with a very weak fluorescence yield of roughly 1 over 10000. Also, the electrons coming from these two lines are from the valence band and some of these electron's are likely to be bounded to other elements, making the x-ray emission difficult, if not impossible. This was demonstrated in LiCl by Gauvin et al [3] where Li emission was not occurring initially under electron irradiation but only after Cl evaporation following the formation of metallic Li where the electron could jump from the L to K shell. These results also showed that beam damage is common with the microanalysis of Li compounds.

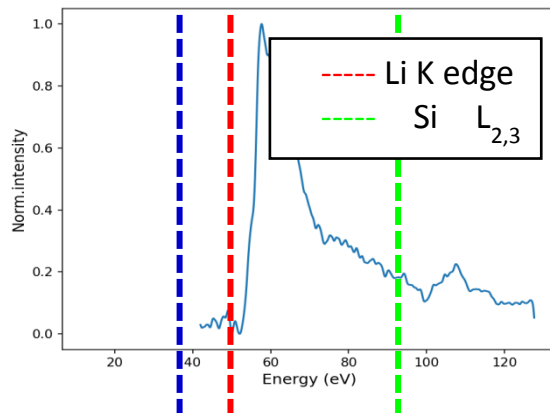
Figure 2 shows a EELS spectrum of  $\text{Li}_2\text{FeSiO}_4$  taken with the Hitachi SU-9000 at 30 keV. Even if X-ray emission was not detected with the EDS detector for this material for the same reasons stated above for  $\text{Li}_2\text{CoSiO}_4$ , the ionization edges are clearly visible for Fe, Li and Si. This shows the strong advantage of EELS over EDS (or WDS) for Li quantification. This is clearly seen in figure [3] that shows a Li EELS edge to background ratio map of an Al-Li 2099 alloy recorded with the three-detectors system on the Hitachi SU-9000 at 30 keV. This map shows the round  $\delta'$  precipitates ( $\text{Al}_3\text{Li}$ ) of 5 to 20 nm and the  $T_1$  plates ( $\text{AlCuLi}$ ) that have thicknesses between 1 to 2 nm. The fact that the edges are always ionized is a strong advantage for EELS since the electron transition leading to the emission of an X-ray is not necessary to observe the ionization event. Also, the emission rate is greater than about 10 000 owing to the fluorescence yield. The downside of EELS is the need for a very thin transparent specimen and beam damage can also occur at 30 kV. Results obtained with a cryo-holder to evaluate possible minimization of beam damage will be presented.

### References:

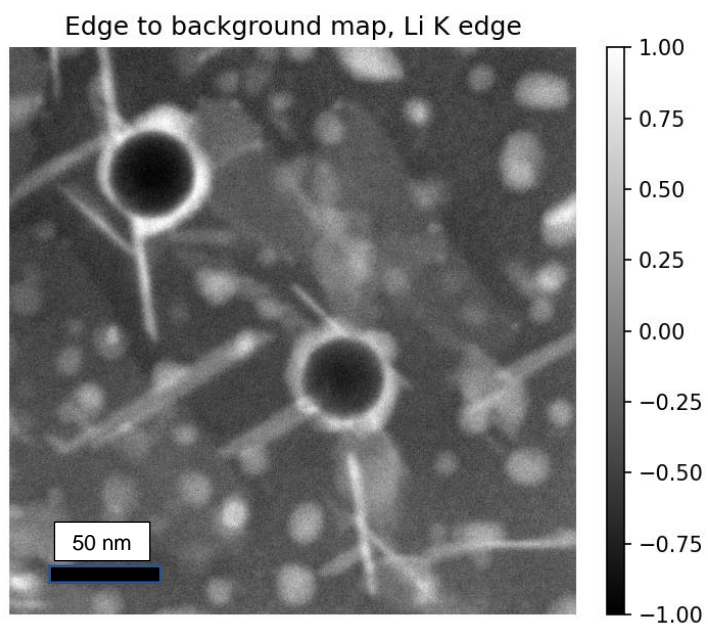
- [1] N. Brodusch et al., *Ultramicroscopy* 203 (2019), p.1.
- [2] P. Hovington et al., *Scanning* 38 (2016), p. 571.
- [3] R. Gauvin et al., *Microscopy and Microanalysis* 27 (2021), p. 1868.



**Figure 1.** EDS map of  $\text{Li}_2\text{CoSiO}_4$  acquired at 3 keV with the Extreme EDS detector installed on the Hitachi SU-9000. The Li map is a false map.



**Figure 2.** EELS spectrum of  $\text{Li}_2\text{FeSiO}_4$  taken with the Hitachi SU-9000 at 30 keV.



**Figure 3.** Li EELS edge to background ratio map of an Al 2099 alloy taken with the Hitachi SU-9000 at 30 keV.