

small methods

Supporting Information

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Mapping Heterogeneity of Pristine and Aged Li- and Na-Mnhcf Cathode by
Synchrotron-Based Energy-Dependent Full Field Transmission X-ray Microscopy

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1. Samples and Electrochemistry

Table S1. List of the samples.

Sample ID	Specifications
Pristine	As prepared electrode
LiC01	Fully Charged, 1 st cycle
LiD01	Fully Discharged, 1 st cycle
LiC50	Fully Charged, after 50 th cycles
LiD50	Fully Discharged, after 50 th cycles
NaC01	Fully Charged, 1 st cycle
NaD01	Fully Discharged, 1 st cycle
NaC50	Fully Charged, 50 th cycles
NaD50	Fully Discharged, 50 th cycles

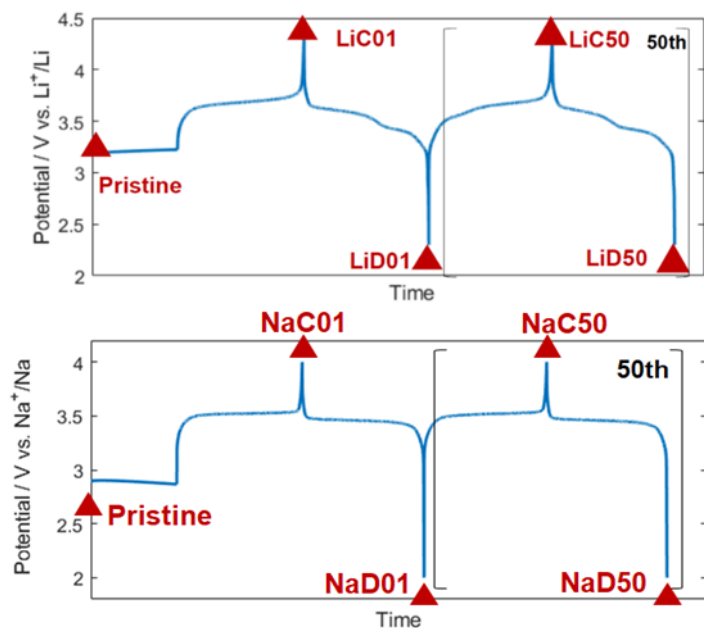


Figure S1. Nomenclature of the electrodes used in this paper.

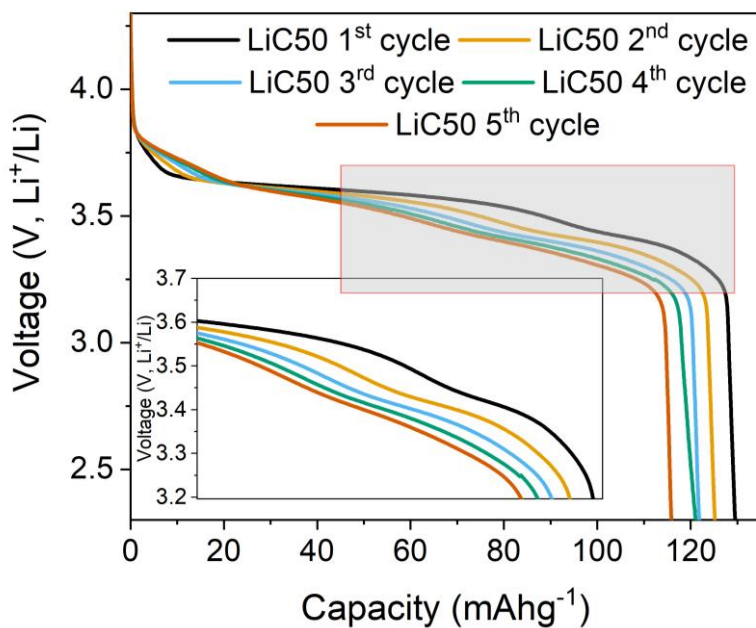


Figure S2. Galvanostatic discharge curves of the first five cycles of LiC50 sample with magnification on the area of plateaus.

2. Electronic Structures and Spectral Details

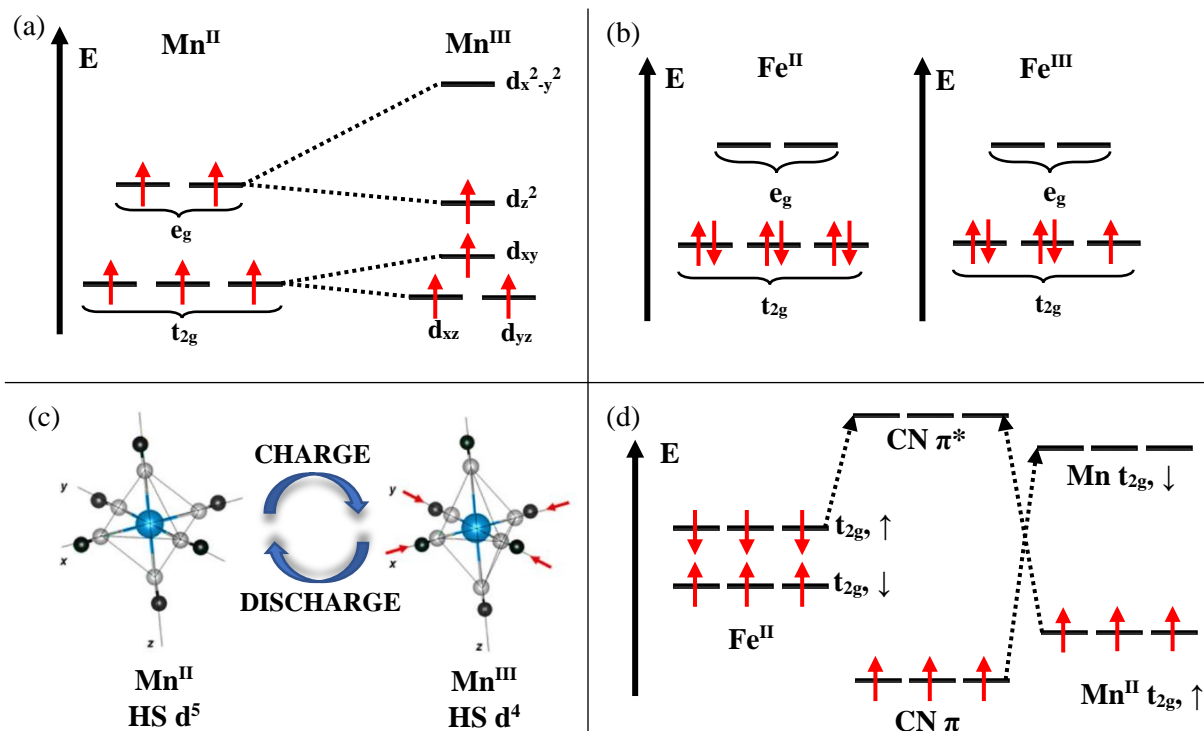


Figure S3. (a) Schematic diagram of Mn^{II} and Mn^{III} 3d orbitals; (b) Schematic diagram of Fe^{II} and Fe^{III} 3d orbitals; (c) schematic diagram of Mn 3d orbitals after JT-elongation; and (d) charge transfers from between Mn, Fe 3d (t_{2g}) and CN 2pπ/2pπ*.

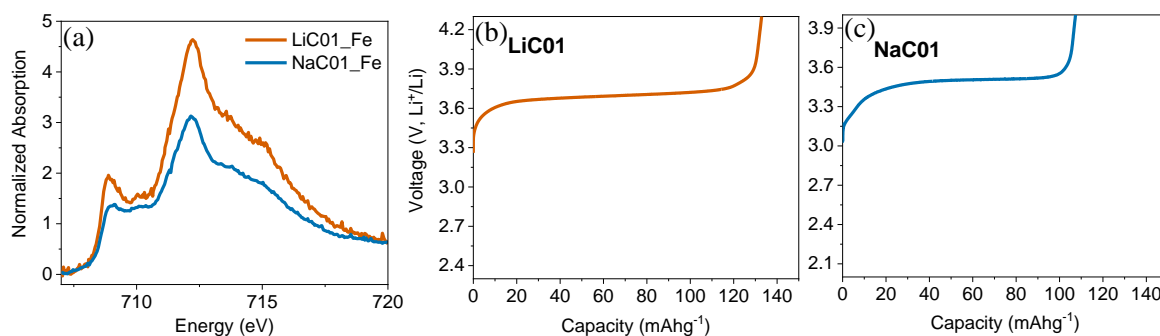


Figure S4. Average Fe L-edge spectra of LiC01 vs. NaC01 (a), and corresponding galvanostatic charge curves: LiC01 (b), NaC01(c).

The average spectra of Mn and Fe L-edges reflects the results obtained from the GCD of the corresponding samples, including the problems of cell performance, if any. For example, in the first cycle, CDG showed that NaC01 capacity was lower, compared to its Li-analogue (Fig. S3). In agreement to this phenomenon, in the corresponding spectra characteristic Peak A of Fe^{III} is less evident in NaC01 than in LiC01.

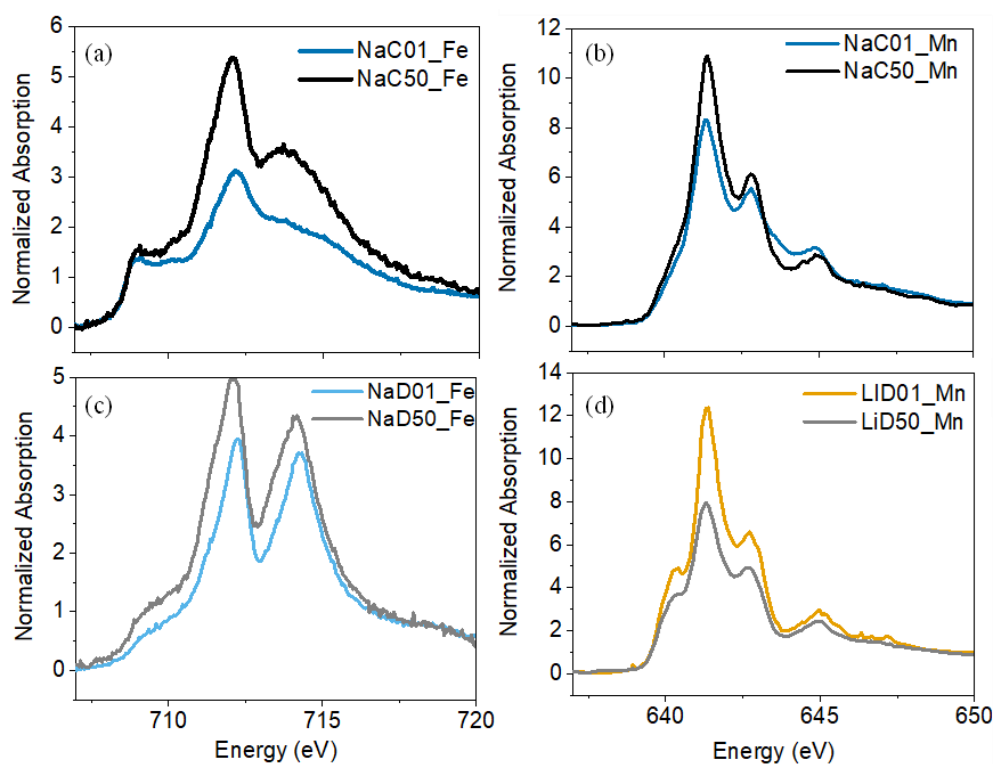


Figure S5. Average spectra of NaC01 vs. NaC50 of Fe L-edge (a), Mn L-edge (b), Fe L-edge spectra of NaD01 vs NaD50 (c), Mn L-edge spectra of LiD01 vs. LiD50 (d).

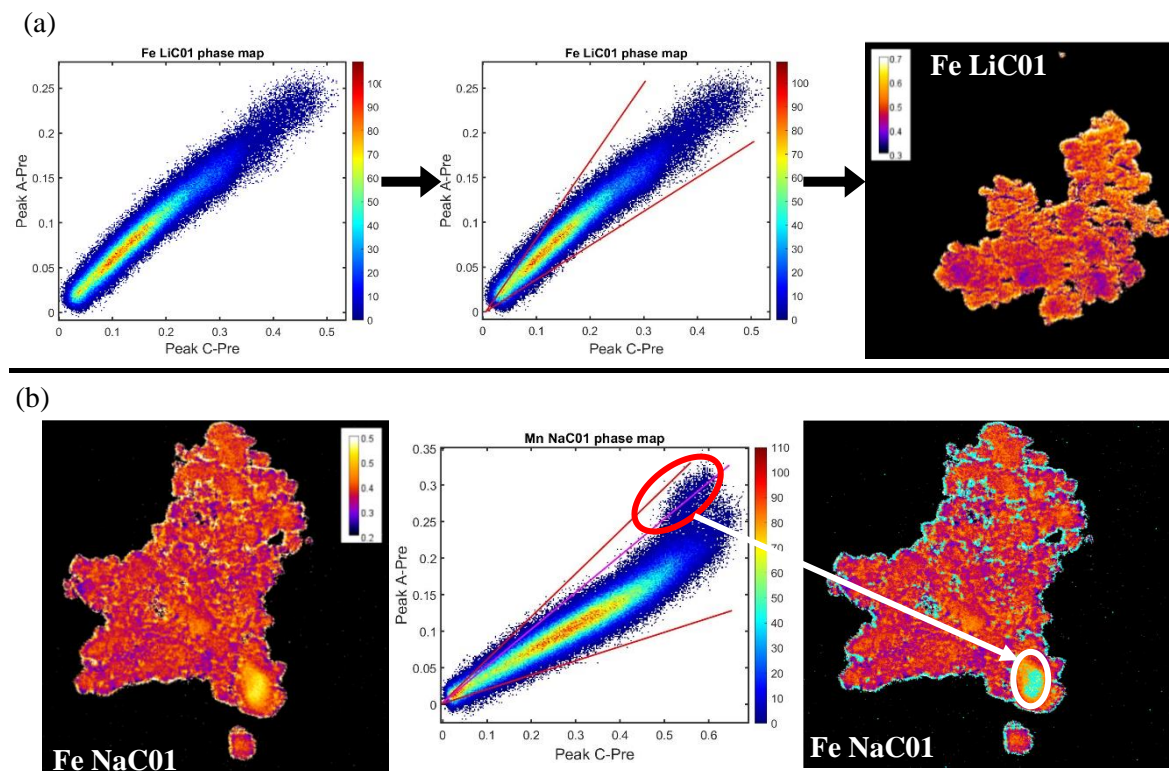


Figure S6. Fe L-edge scatter plot of LiC01 sample with corresponding arctangent ratio image (a); and the arctangent ratio image of Mn L-edge of the NaC01, its corresponding scatter plot, with the highlighted deviated part from the general "cloud" and its corresponding portion of the sample on the arctangent image (b).

3. Phase maps of the samples, and their selections with corresponding spectra

After image treatment on every sample, the corresponding phase maps were obtained. Thanks to the visible contrast, achieved after the procedure, set of selections were able to be chosen, and afterwards, their corresponding spectra were also retrieved.

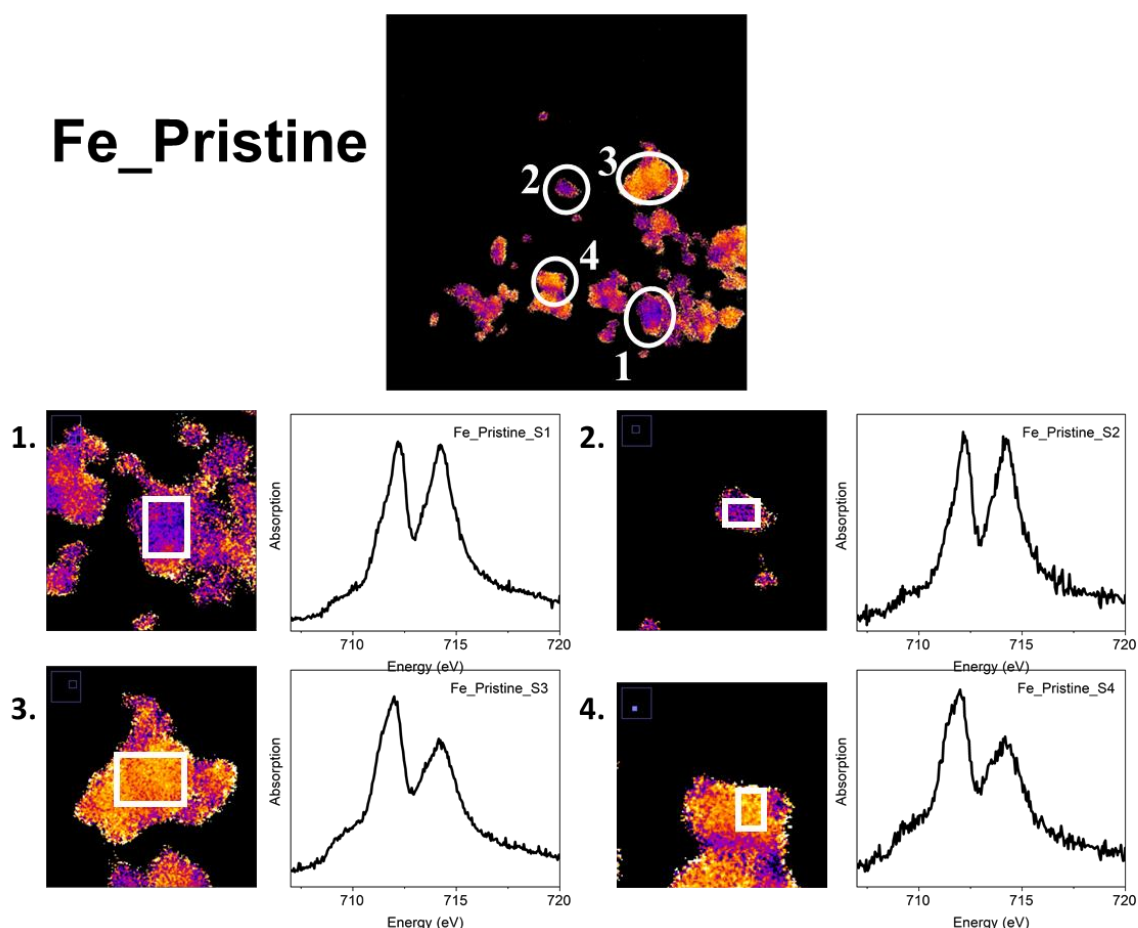


Figure S7. Phase map of Fe_Pristine, magnified selections and corresponding spectra.

Mn_Pristine

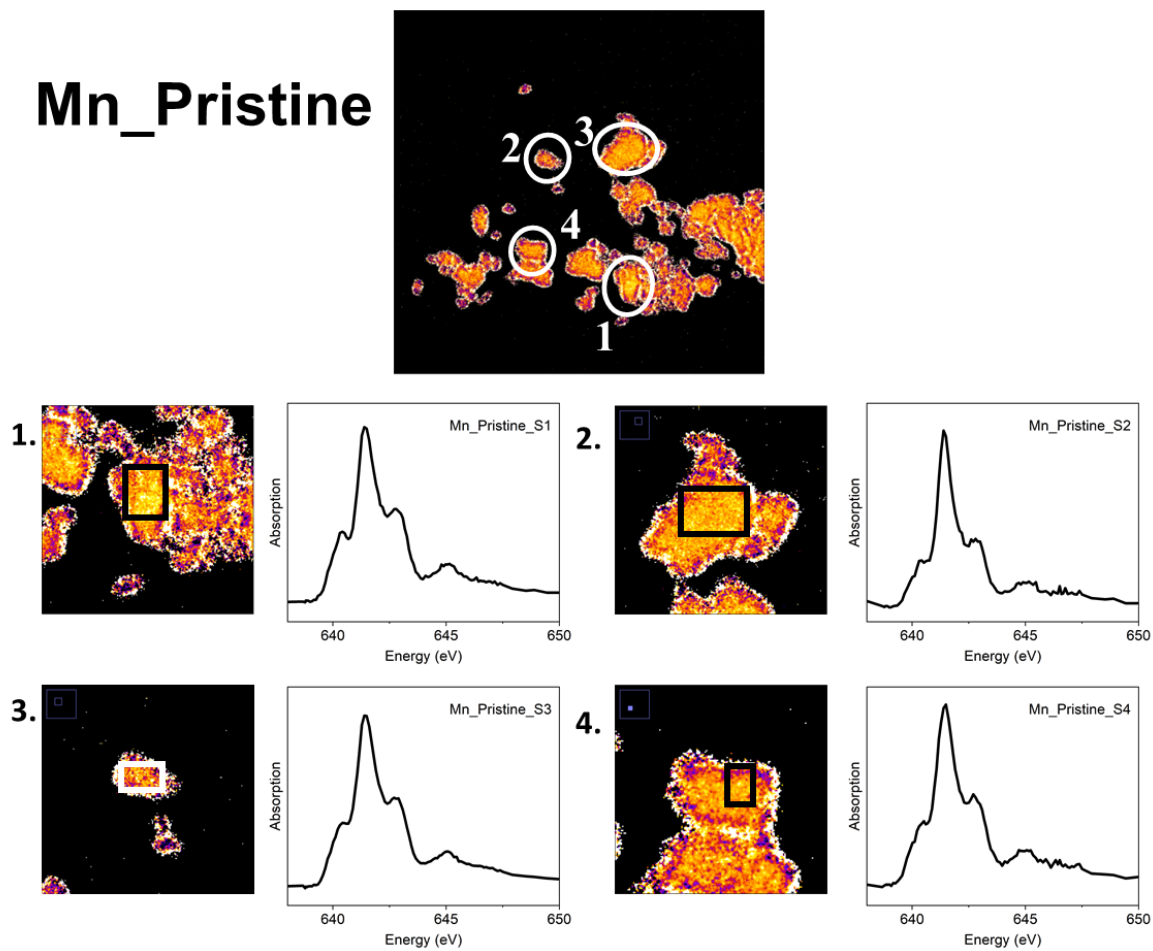


Figure S8. Phase map of Mn_Pristine, magnified selections and corresponding spectra.

Fe_LiC01

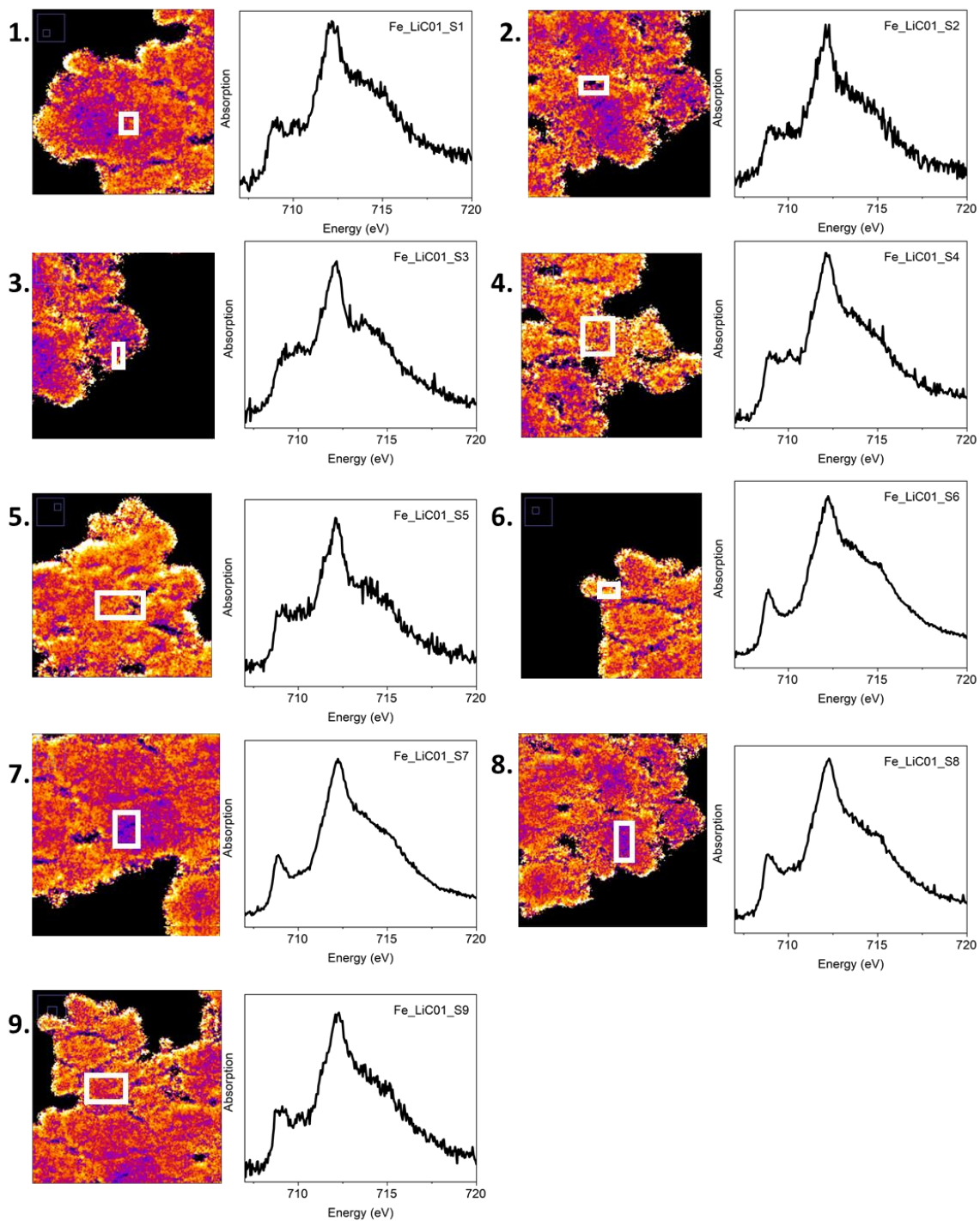
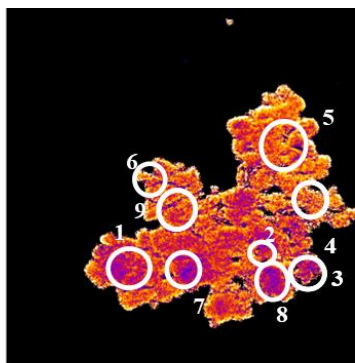


Figure S9. Phase map of Fe_LiC01, magnified selections and corresponding spectra.

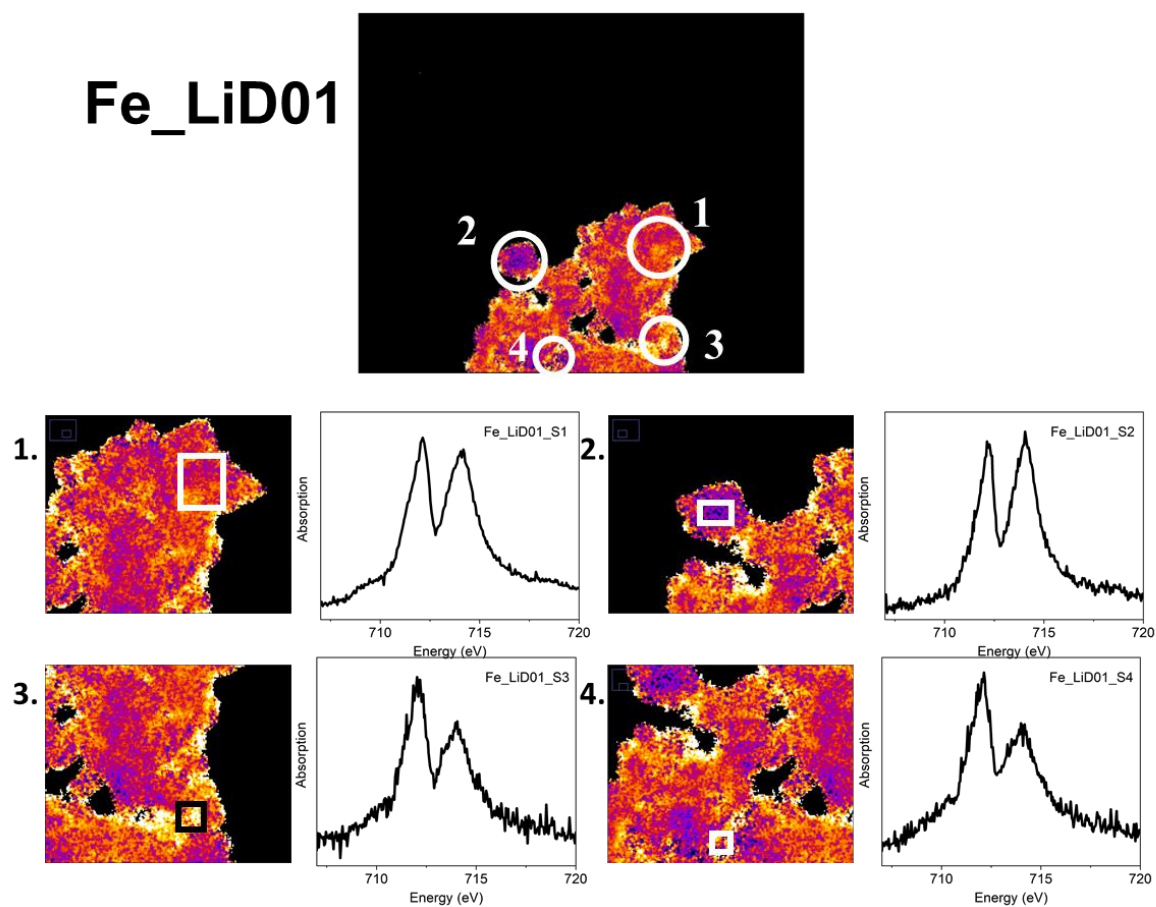


Figure S10. Phase map of Fe_LiD01, magnified selections and corresponding spectra.

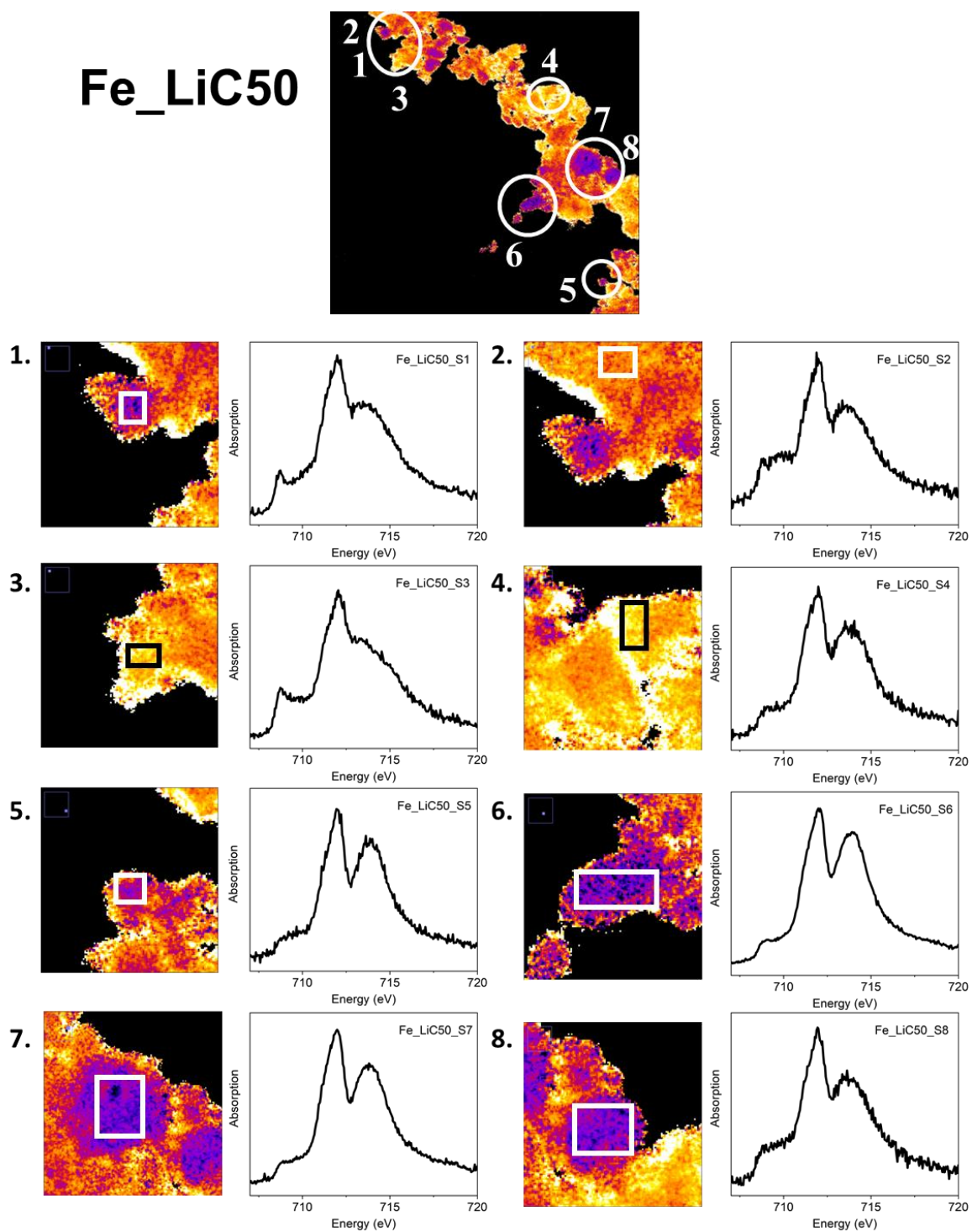


Figure S11. Phase map of Fe_LiC50, magnified selections and corresponding spectra.

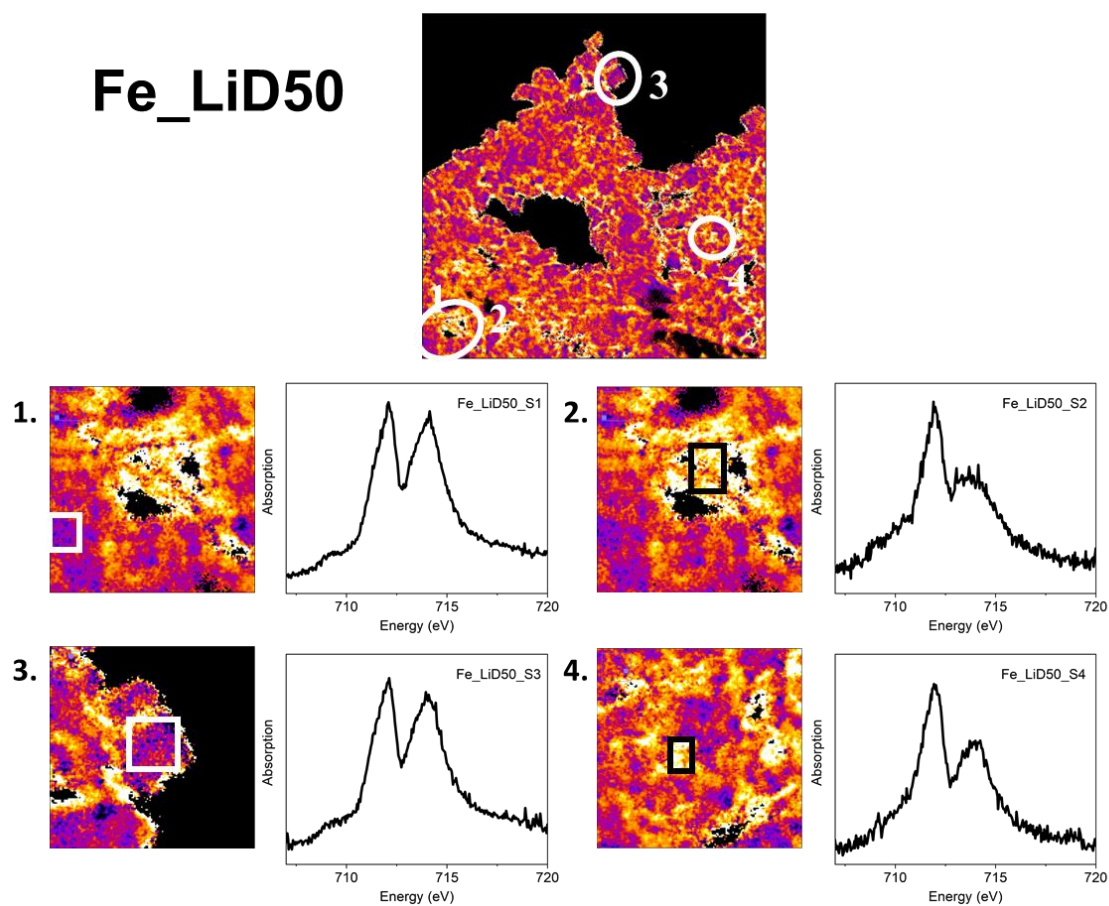


Figure S12. Phase map of Fe_LiD50, magnified selections and corresponding spectra.

Fe_NaC01

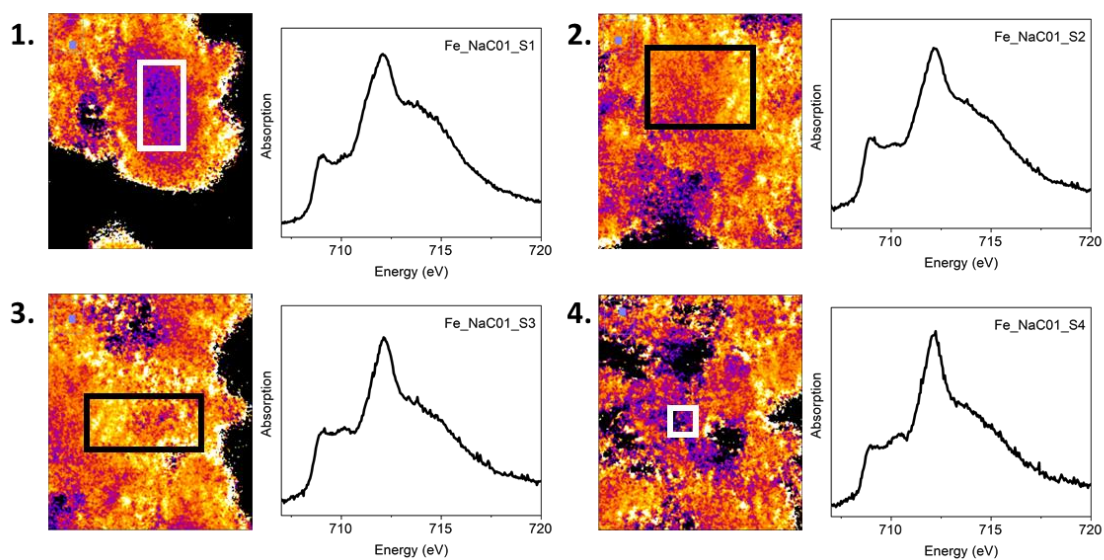
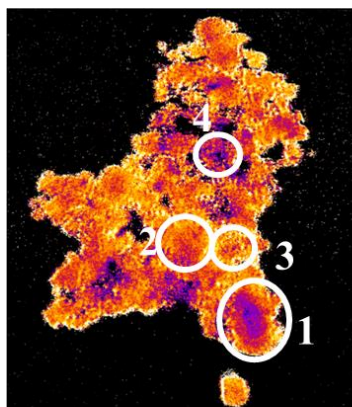


Figure S13. Phase map of Fe_NaC01, magnified selections and corresponding spectra.

Fe_NaD01

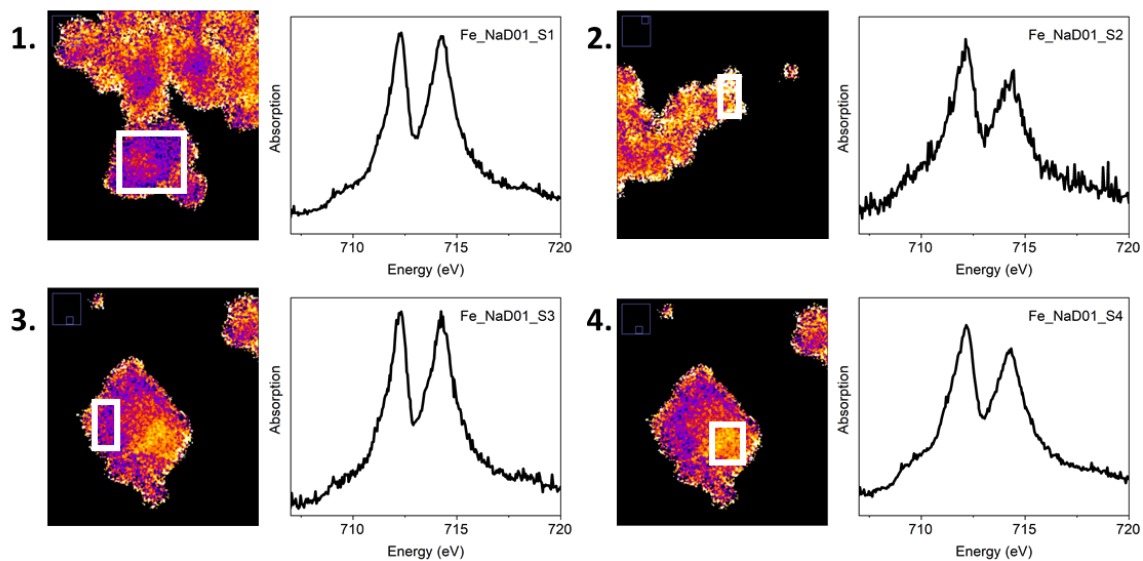
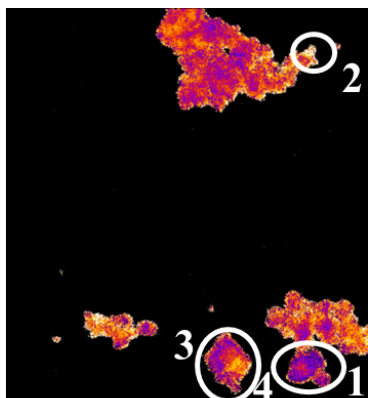


Figure S14. Phase map of Fe_NaD01, magnified selections and corresponding spectra.

Fe_NaC50

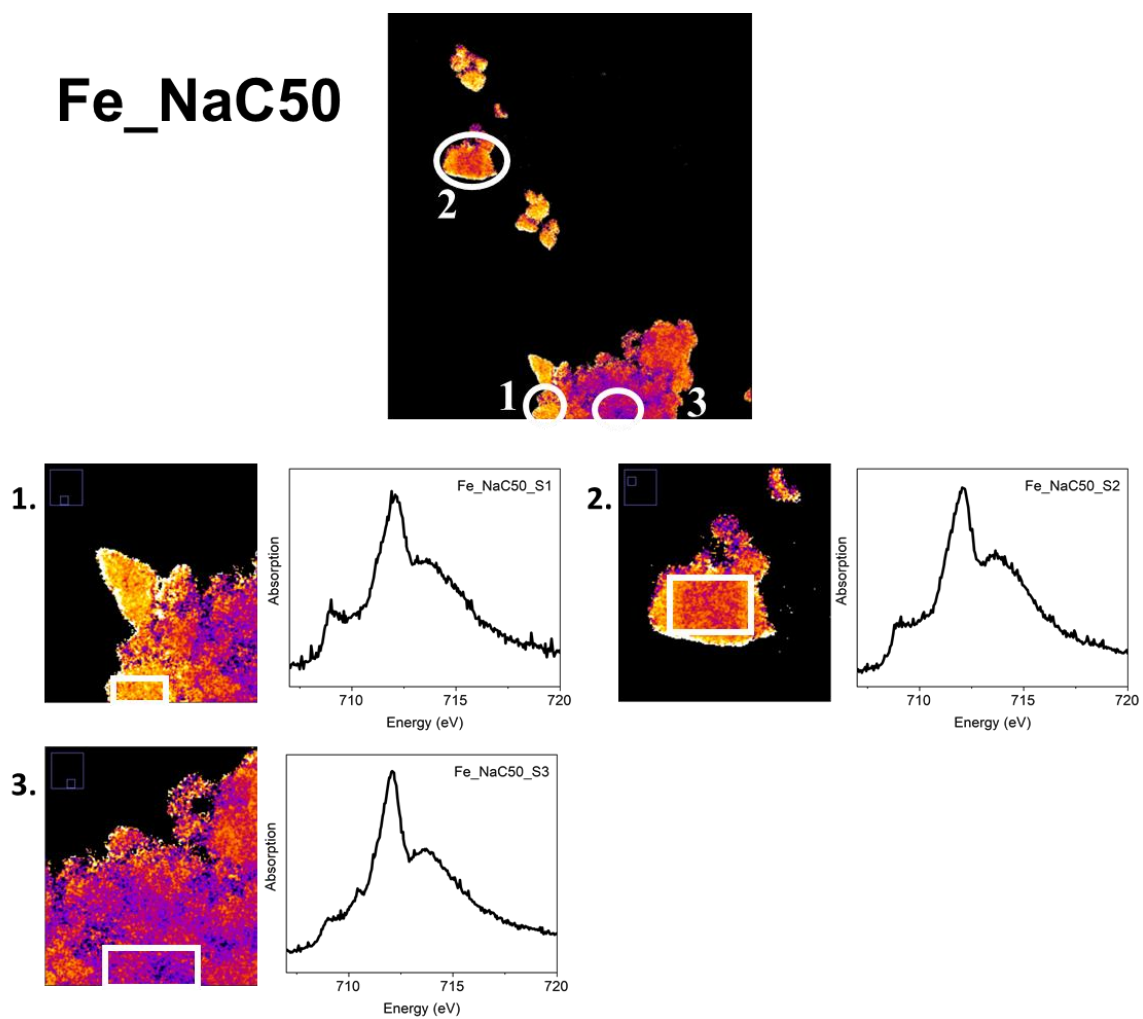


Figure S15. Phase map of Fe_NaC50, magnified selections and corresponding spectra.

Fe_NaD50

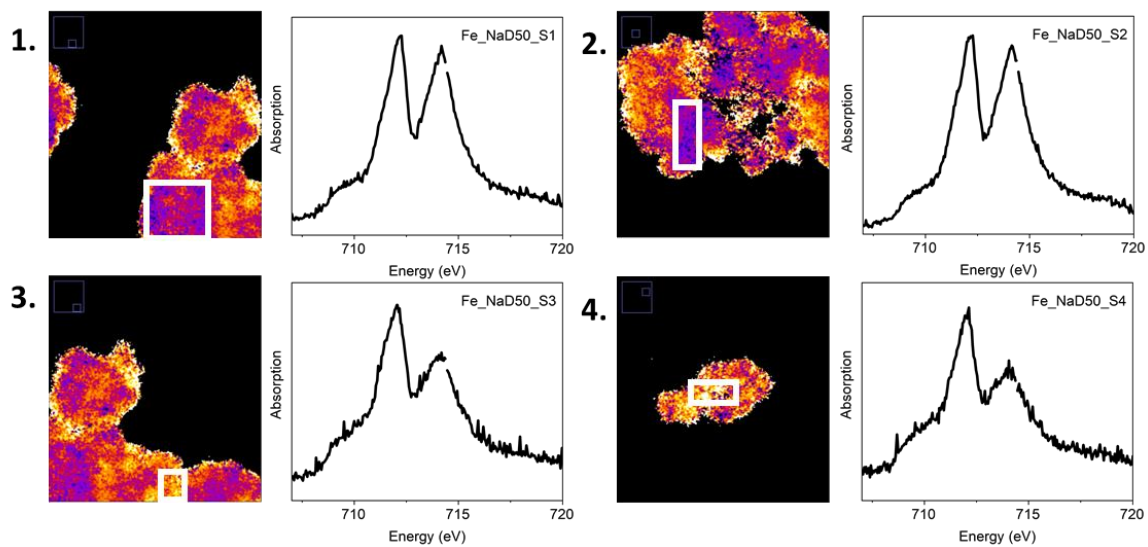
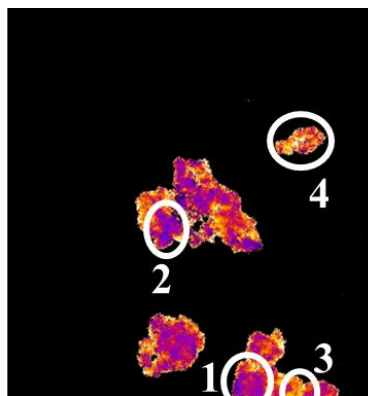


Figure S16. Phase map of Fe_NaD50, magnified selections and corresponding spectra.

Mn_LiC01

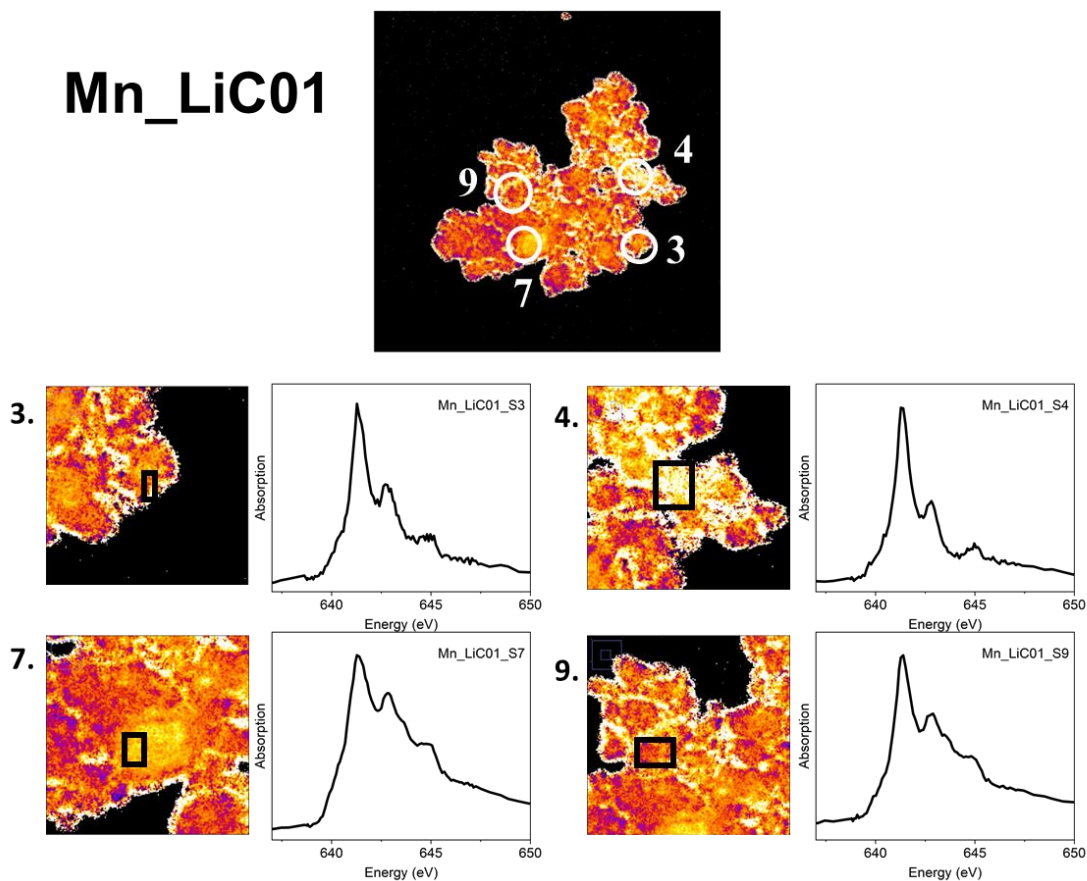


Figure S17. Phase map of Mn_LiC01, magnified selections and corresponding spectra.

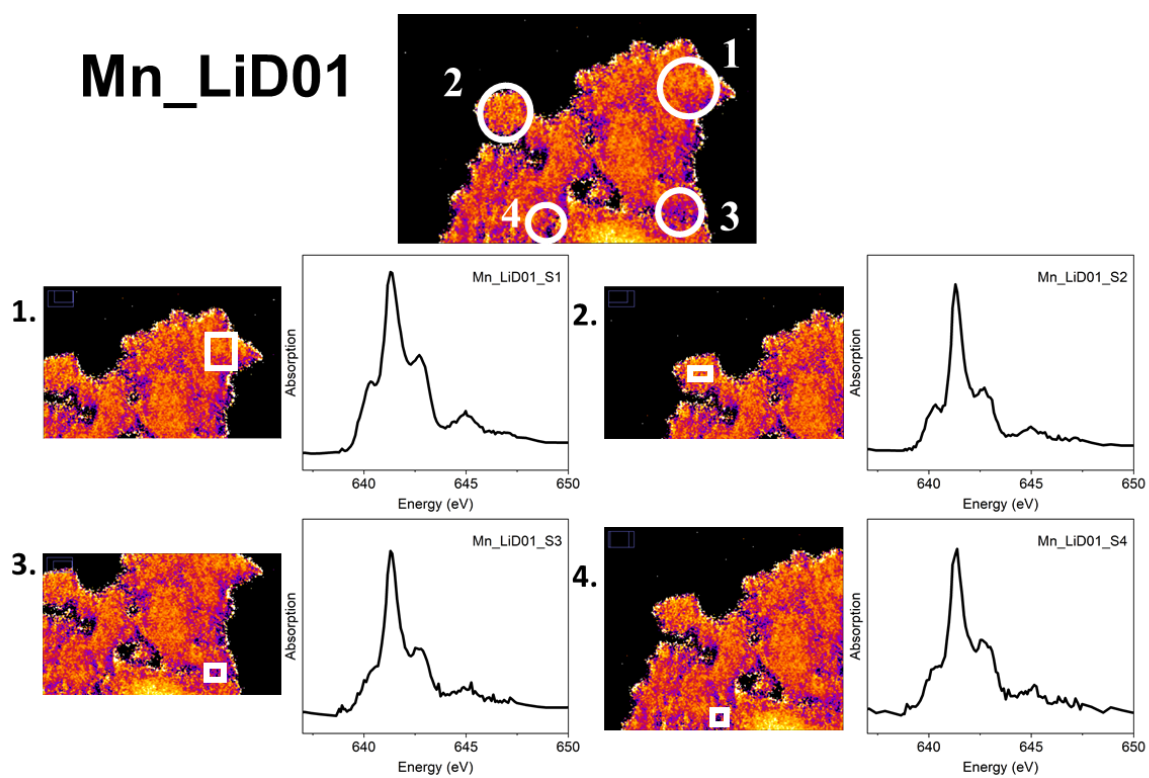


Figure S18. Phase map of Mn_LiD01, magnified selections and corresponding spectra.

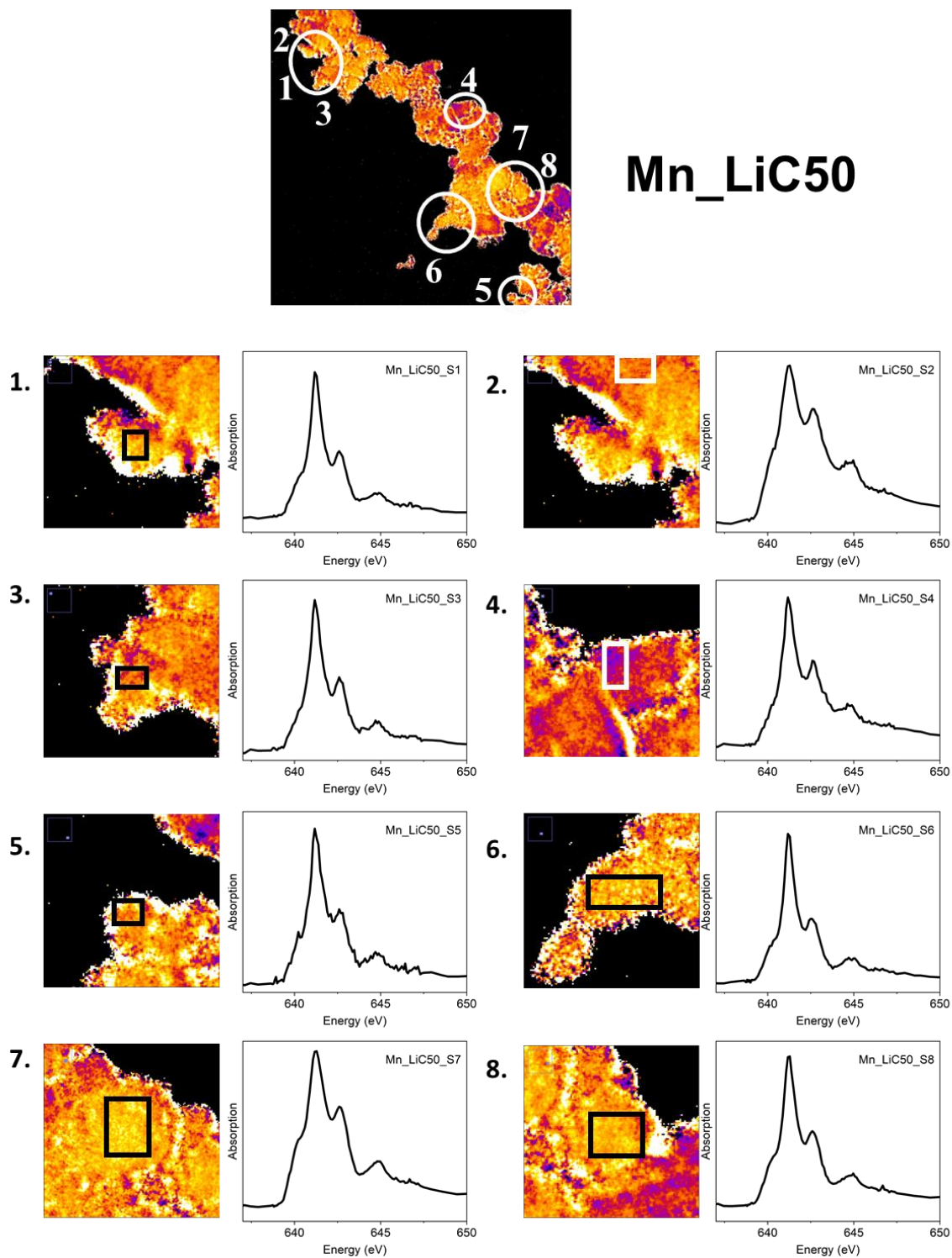


Figure S19. Phase map of Mn_LiC50, magnified selections and corresponding spectra.

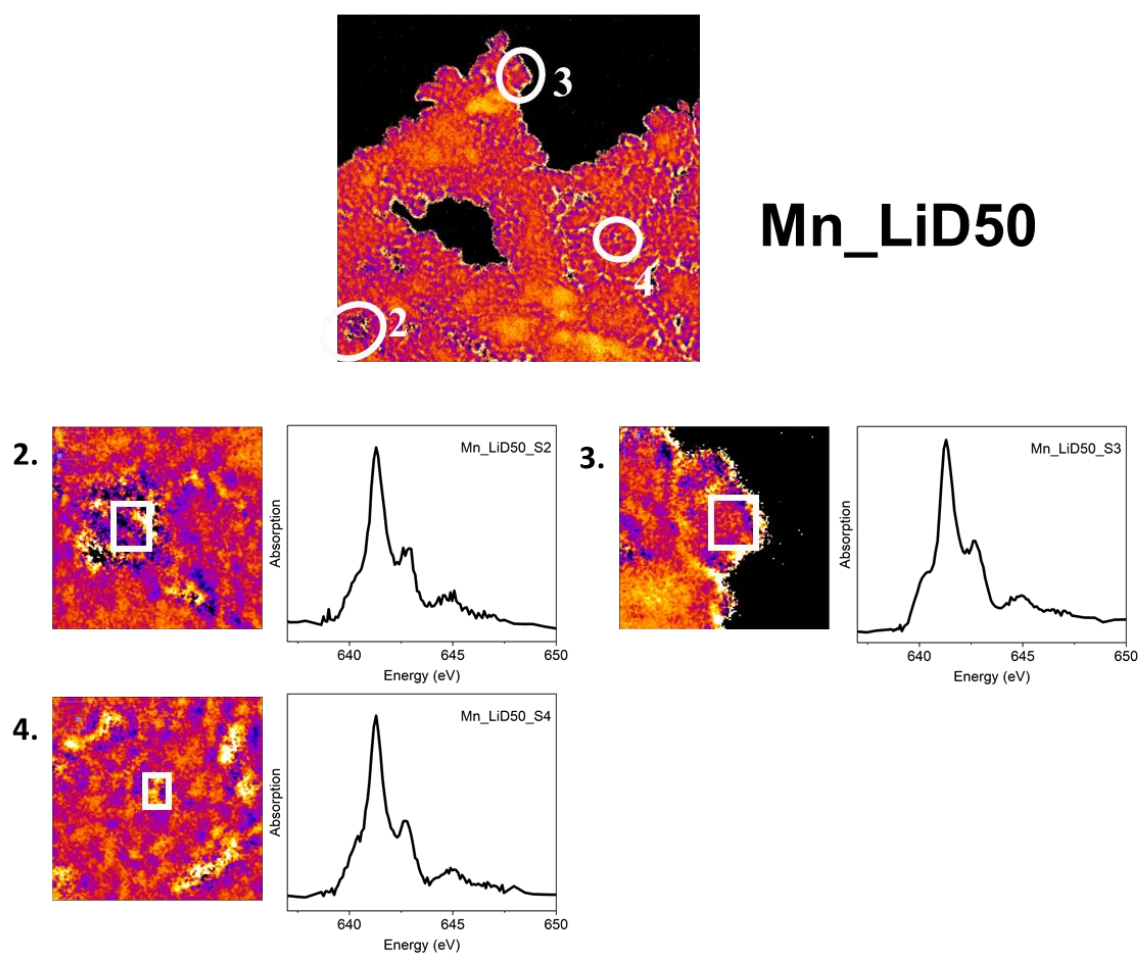


Figure S20. Phase map of Mn_LiD50, magnified selections and corresponding spectra.

Mn_NaC01

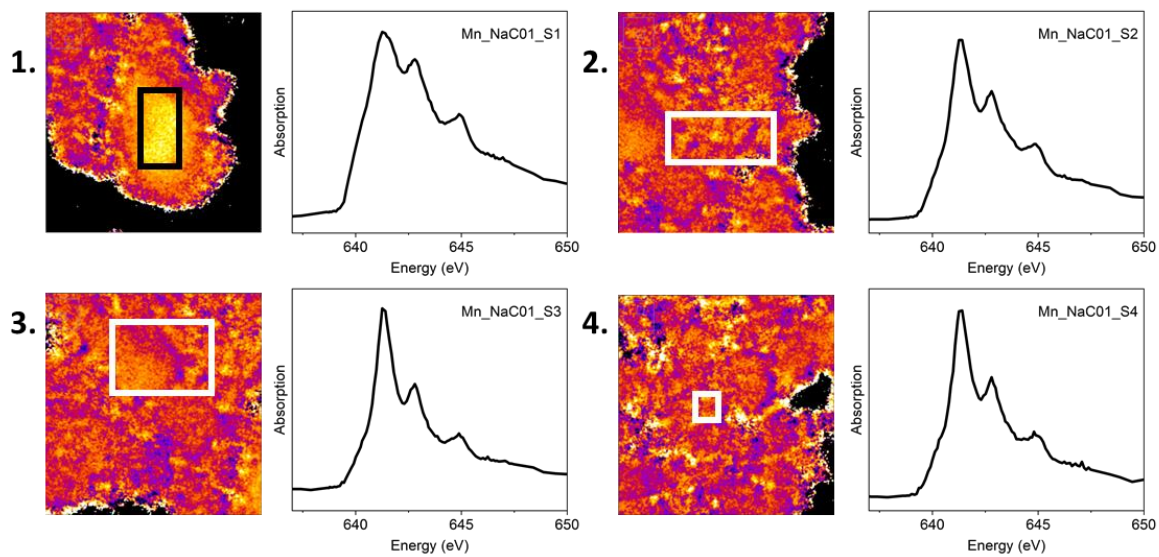
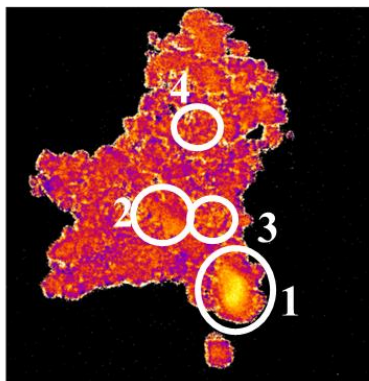


Figure S21. Phase map of Mn_NaC01, magnified selections and corresponding spectra.

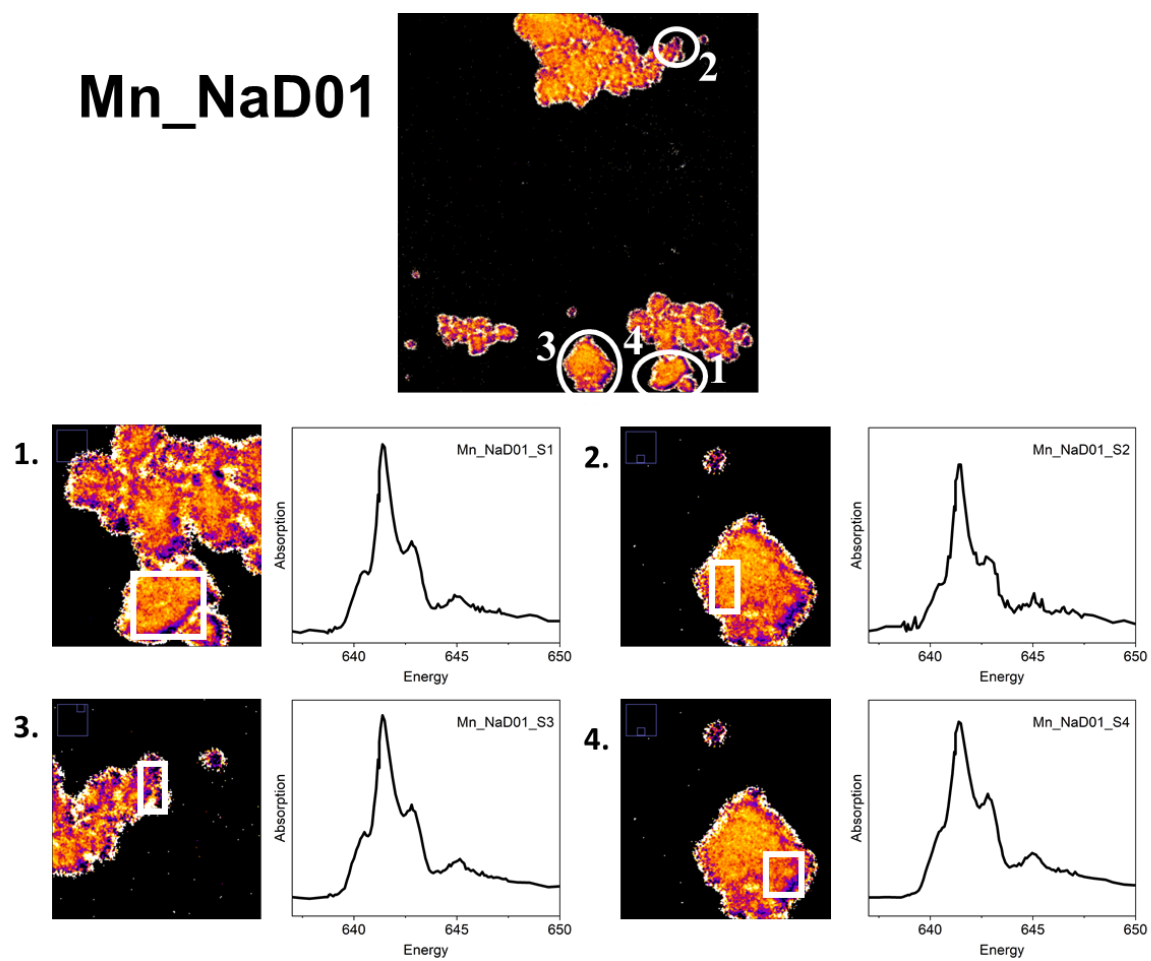


Figure S22. Phase map of Mn_LiD01, magnified selections and corresponding spectra.

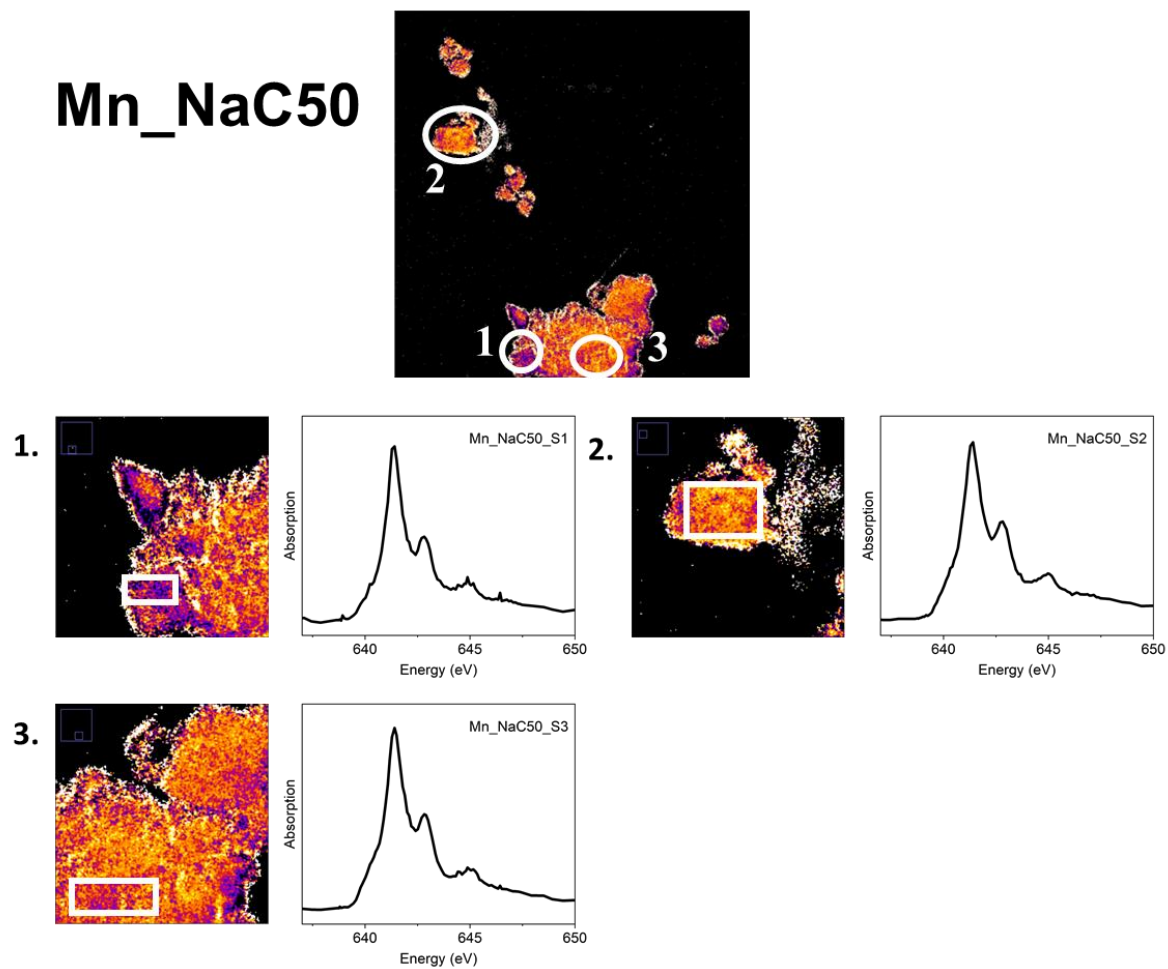


Figure S23. Phase map of Mn_NaC50, magnified selections and corresponding spectra.

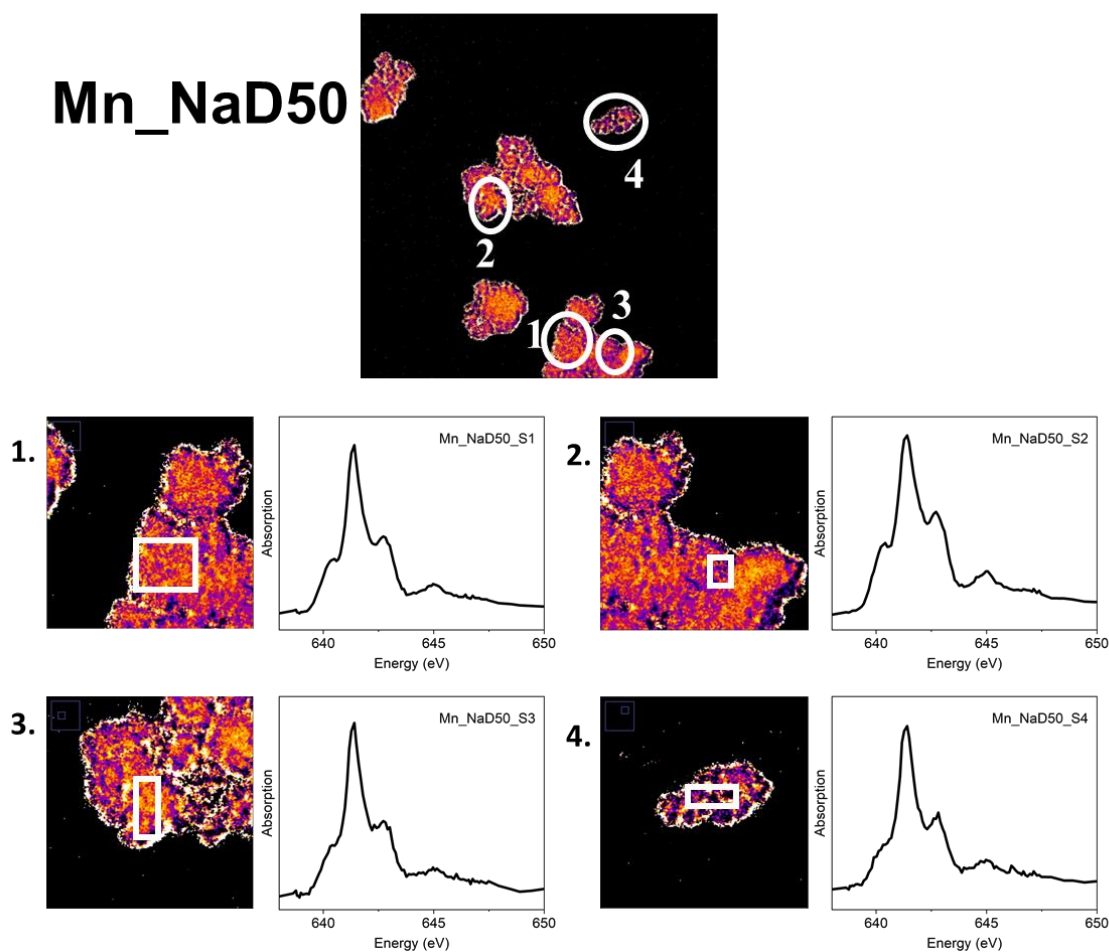


Figure S24. Phase map of Mn_NaD50, magnified selections and corresponding spectra.

4. Stacked spectra

The spectra of the different selections in every sample, ordered by Peak A intensity, corresponding to the oxidation state, stacked on top of each other from the most oxidized region (in the bottom) towards the most reduced region (on the top). From each sample at least two selections are reported. In Na containing charged samples show systematically higher oxidation state than discharged ones. Instead, in Li containing samples the order is more mixed, with selections of the cycled samples spread along the series, so that some selections of the reduced sample are more oxidized than others of the oxidized one.

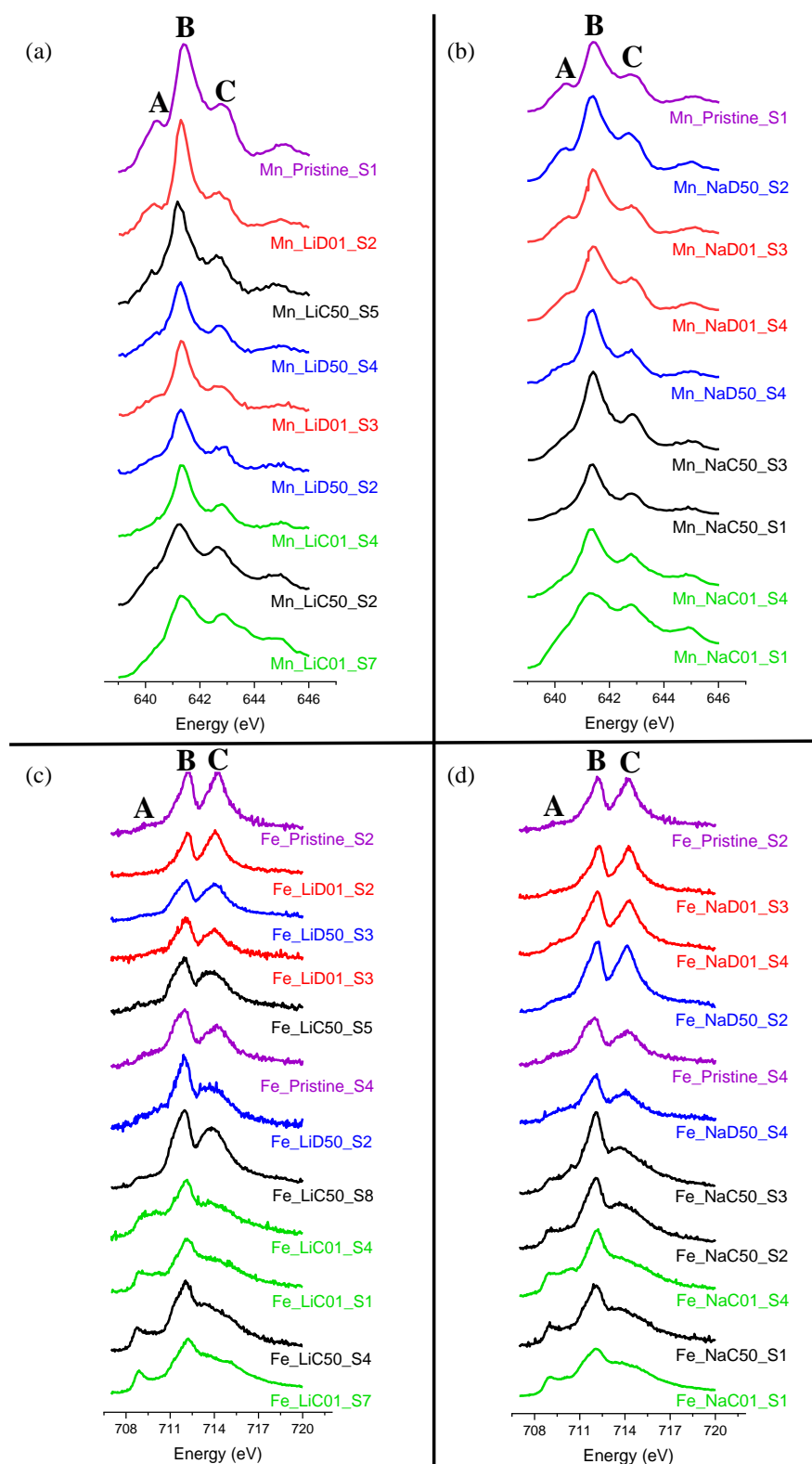


Figure S25. Spectra of the different selections: Li-containing samples Mn L-edge (a), Na-containing samples Mn L-edge (b), Li-containing samples Fe L-edge (c), and Na-containing samples Fe L-edge (C01 - green, D01 - red, C50 - black, D50 - blue, pristine - purple) (d).

5. Image Treatment – Avoiding the Saturation

For controlling the absorption intensity in the reliable ranges, sample absorbance was checked, based on the calculator available at https://henke.lbl.gov/optical_constants/filter2.html. Density was assumed to be 1.9 g/cm^3 (according to the previously published XRD refinement^[31]), and thickness – 1 micron. The MISTRAL beamline presents a level of baseline intensity so-call stray light of about 7%^[32] which implies an absorbance saturation at 1.2, as shown in Figure S26.

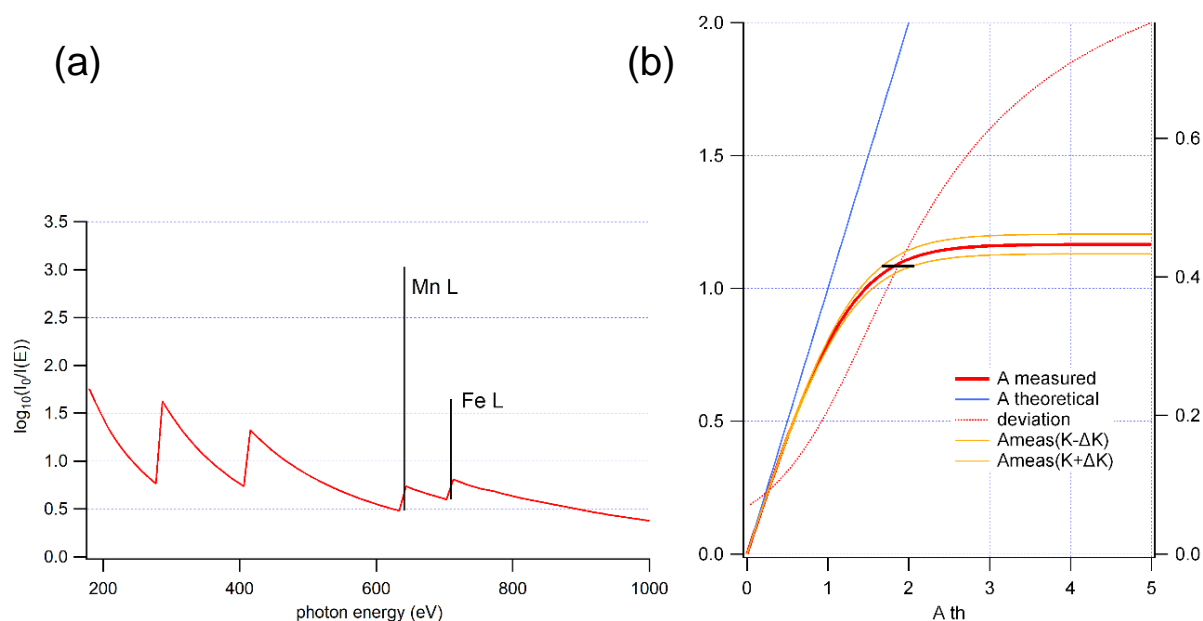


Figure S26. The relationship of absorption intensity on the photon energy (a), theoretical and experimental estimation of the linearity limit, based on the absorbance value (b).

According to this estimation, theoretical absorbance of 1 is observed as 0.78. After the distortion correction, reliable linearity up to absorbance of 2 is achieved. Higher values of absorbance are too close to saturation to give meaningful contrast. Based on these figures, thickness of $<700 \text{ nm}$ has been estimated as reliable at the images taken with energy of strongest absorption, while above $1 \text{ }\mu\text{m}$ saturation is reached. However, the thickest parts may occasionally contribute with some distortion at the maximum, the vast majority of the sample lies well below 500 nm . Furthermore, for peaks A and C of Mn L absorption is about half of the maximum (absorbance ≈ 2 for $1 \text{ }\mu\text{m}$ thickness), consequently, the chemical composition maps are even less affected.

6. Analysis of Possible Bulk-Border Effects

After the image treatment, it was also observed, that in the phase maps of Mn L-edge are the eye noticeable differences near the edges of the particles compare to the bulk, almost depicting the borderline. We call this phenomenon the “bulk-border” effect, which is not observable in the Fe L-edge (Figure S7 a and b). The spectra of the bulk have slightly more tendency to share the features characteristic to their corresponding charge state than border parts. As Figure S7 c, d and e shows, for NaD01 sample, on high energy the spectra extracted from both the bulk and the border part have similar features, but peak A region shows lower intensity for the border part, indicating to be slightly more oxidized compared to the bulk.

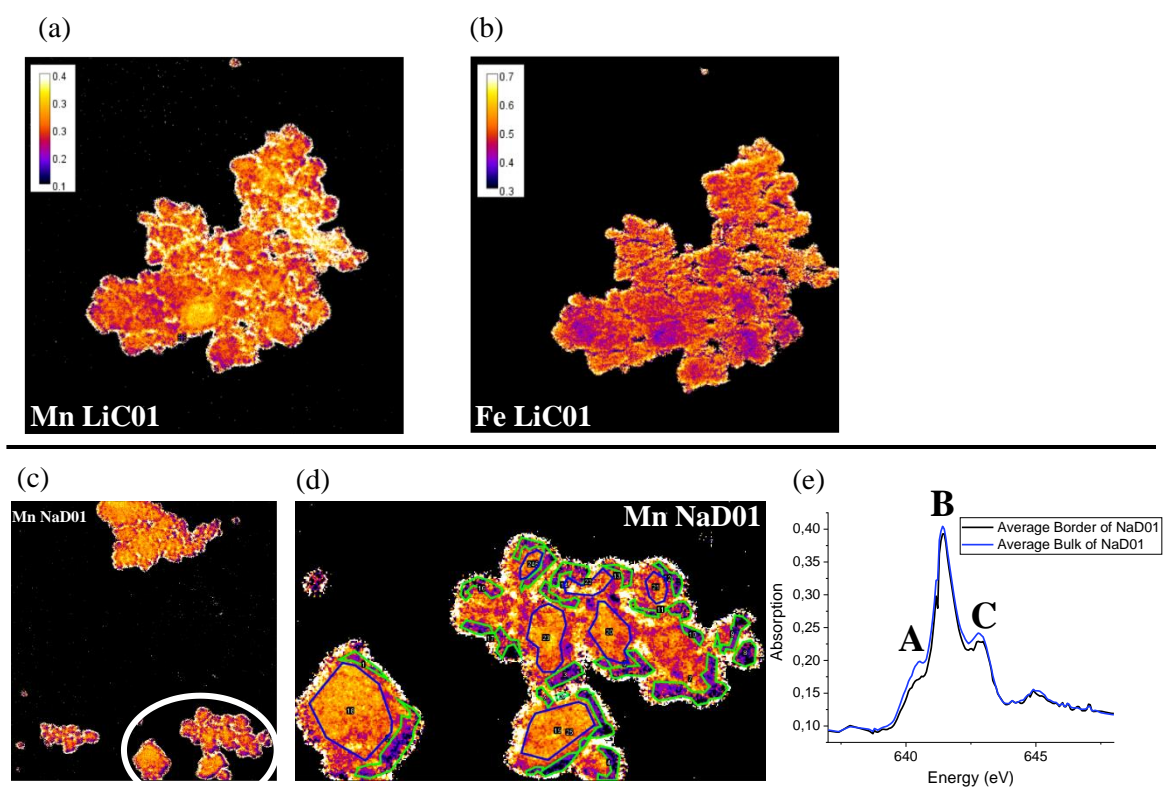


Figure S27. The comparison of LiC01 sample: Mn L-edge (a) and Fe L-edge (b); Bulk-border effect on Mn L-edge of NaD01 sample (c), zoomed region (d) and corresponding spectra (e).