Supplementary Information

Iron speciation in iron-organic matter nanoaggregates: A kinetic approach coupling Quick-EXAFS and MCR-ALS chemometry

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SI contente

SI-1 – Details of MCR-ALS analysis

In the following figures are reported the details of the MCR-ALS analysis performed on the set of data provided by the two experiments Exp-Air and Exp-N2 performed in Quick-XAS.

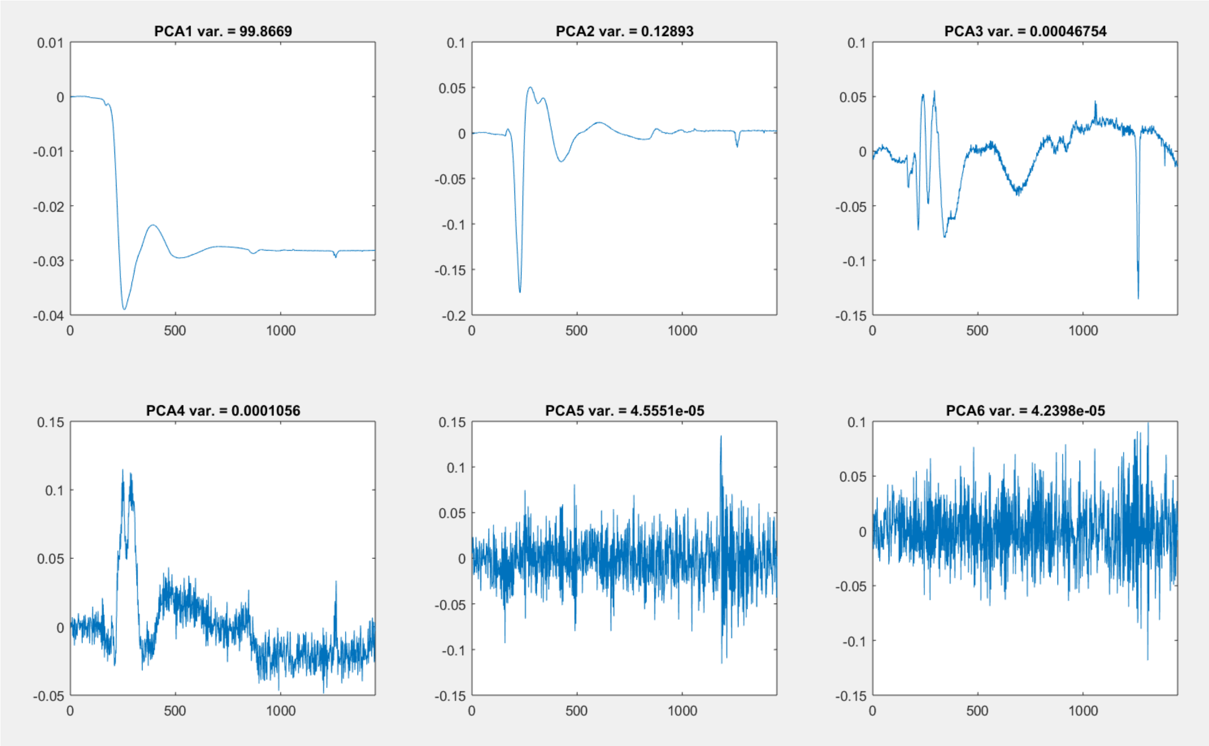

Fig. SI-1-a: Six firsts Principal Component (PC) Eigenvectors (PCA1, PCA2, PCA3, PCA4, PCA5, PCA6) obtained through the Singular Value Decomposition (SVD) of the data set made of Exp-Air and Exp-N2 quick-XAS experiments.

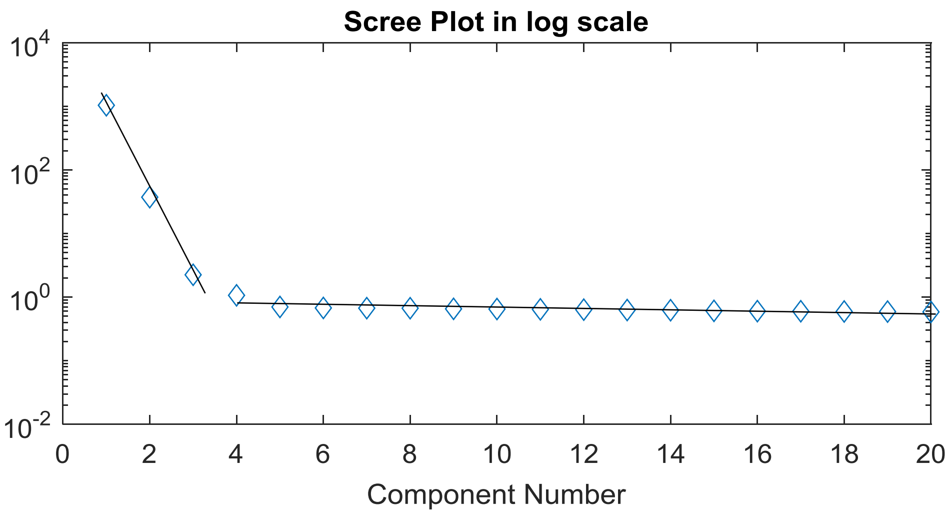

Fig. SI-1-b: log-scale scree plot representing the PC eigenvalues sorted out as a function of their importance regarding to the variance that their related PC.

Figure SI-1-a displays the firsts six Principal Component (PC) Eigenvectors obtained through the Singular Value Decomposition (SVD) of the data set made of Exp-Air and Exp-N2. It is evident that the fifth and sixth PCs (PCA5 and PC6, respectively) do not contain any signal but only noise. On the contrary, the first 3 PCs (PCA1, PCA2 and PCA3) display well defined features which have to be considered to explain the variance of the data set. The fourth PC (PCA4) which is noisier than the first 3 PCs still exhibits however a signal which could suggest the requirement of a fourth component in the MCR-ALS analysis. However, the log-scale scree plot (Fig. SI-1-b), which represents the PC eigenvalues sorted out as a function of their importance regarding to the variance that their related PC can explain in the whole dataset (the variance being defined as the square of the eigenvalue) allows us to conclude that only 3 PCs are relevant. Namely, the required number of PCs is ascribed to the slope break between the straight line formed by the first PCs and a second asymptotic line which aim to pass through the other dots corresponding to components of lower eigenvalues with no contribution to explain system variance. These representations evidence thus that three components can be extracted from the data set made of Exp-Air and Exp-N2

SI-2 – Details of EXAFS shell by shell fitting

In the following figures are reported the EXAFS (left) and corresponding Fourier transform (right) of the pure Fe phases extracted by MCR-ALS together with several IFEFFIT calculations results.

CPt-1.

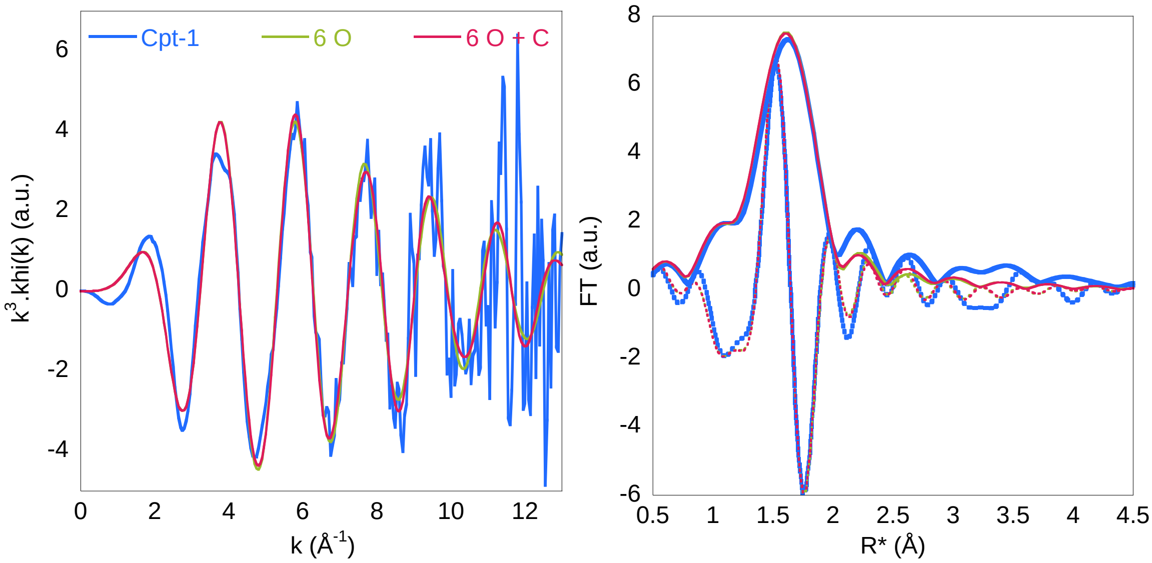

Fig. SI-2-a. The Cpt-1 EXAFS spectrum is reported in blue line. In green line is reported the spectrum corresponding to 6 O in the first shell. The fitting parameters are reported in Table 1. In red line is reported the spectrum corresponding to the best fit with 6 O in the first shell and C in the second shell (best fit returns 0.7 C at 3.16 Å).The imaginary parts of the Fourier transforms are reported in dotted lines

The figures SI-2-a left and right illustrate the very slight improvement of the fit with the addition of C neighbors against the Cpt-1 data.

CPt-2.

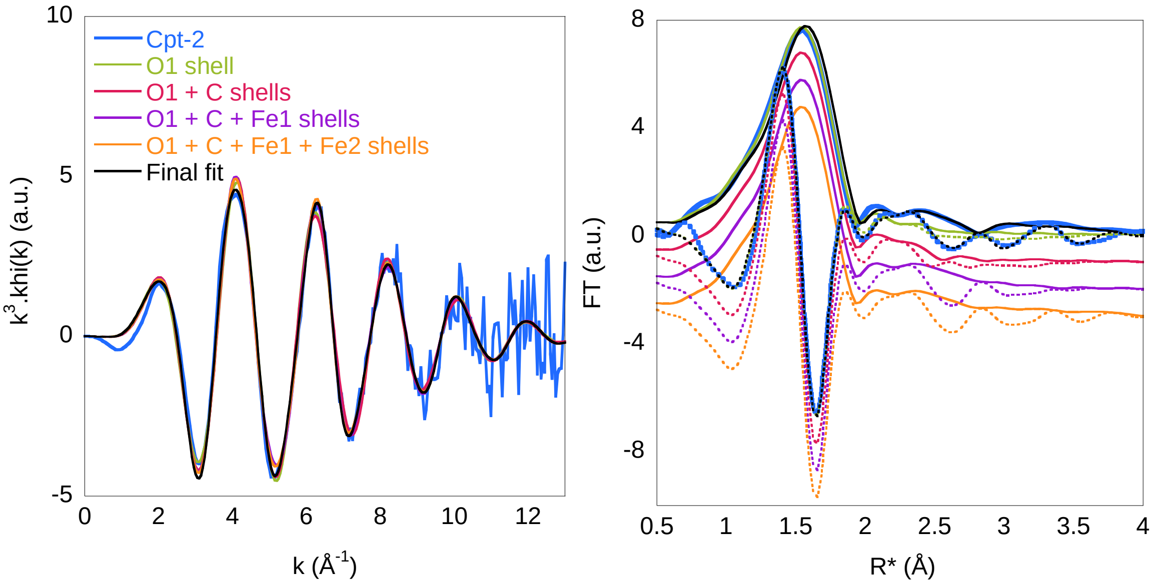

Fig. SI-2-b. The Cpt-2 EXAFS spectrum is reported in blue line. In green line is reported the spectrum corresponding to the first O shell. In red line is reported the spectrum corresponding to the fit with the first O and C shells. In purple line is reported the spectrum corresponding to the fit with the first O, the C and the first Fe shells. In orange line is reported the spectrum corresponding to the fit with the first O, the C and the two Fe shells. In black line is reported the spectrum corresponding to the final fit that includes the multiple scattering path. The imaginary parts of the Fourier transforms are reported in dotted lines. The fitting parameters are reported in Table 1.

The figures SI-2-b left and right evidence that the fit of the first O shell (green curve) does not allow reconstructing the whole Cpt-2 signal. Adding C neighbors (red curve) improves the fit, while adding Fe neighbors (purple and orange curves) strongly improves the fit quality, as evidenced by the reproduction of the Fourier transform broad peaks around 2.5 and 3.5 Å. The addition of a multiple scattering path slightly optimized the final fit (black curve).

CPt-3.

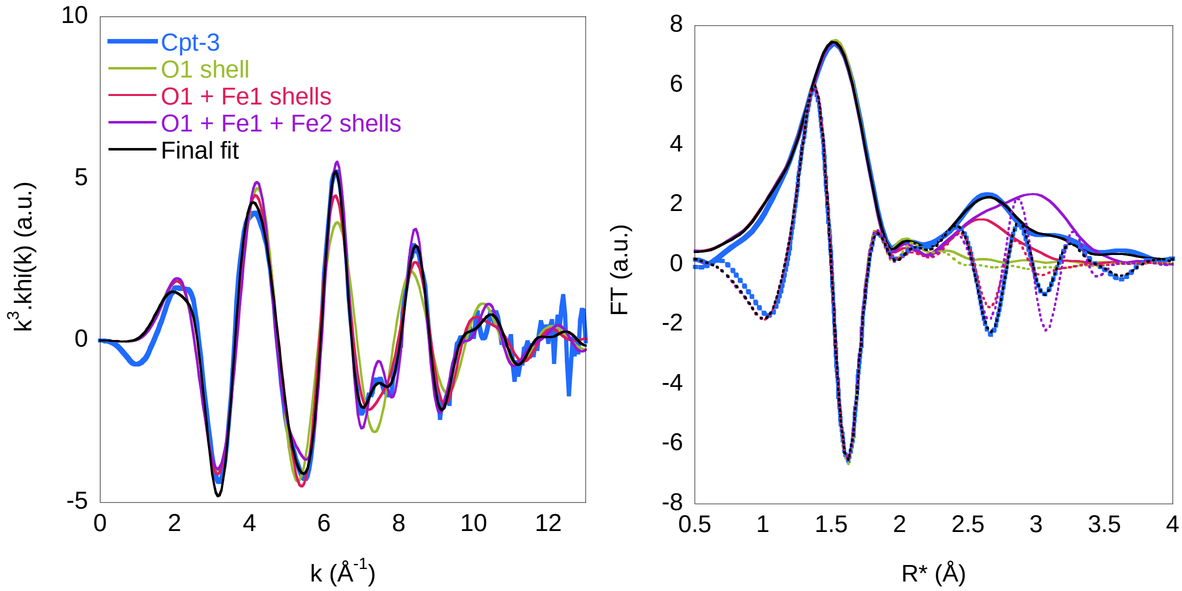

Fig. SI-2-c. The Cpt-3 EXAFS spectrum is reported in blue line. In green line is reported the spectrum corresponding to the first O shell. In red line is reported the spectrum corresponding to the fit with the first O and the first Fe neighbors. In purple line is reported the spectrum corresponding to the fit with the first O, and the first and second Fe shells. The signal of the Fe second neighbors is voluntary enlarged to highlight its contribution to the overall EXAFS signal, especially to the reproduction of the EXAFS feature at 8 Å^{-1}. In black line is reported the spectrum corresponding to the final fit that includes O neighbors in the second coordination shell. The imaginary parts of the Fourier transforms are reported in dotted lines. The fitting parameters are reported in Table 1.

The figures SI-2-c left and right evidence that the fit of the first O shell (green curve) does not allow to reconstruct the whole Cpt-3 signal. Adding Fe neighbors at two distances is necessary to reproduce the EXAFS feature at 8 Å-1 and the peak of the Fourier transform from 2.5 to 3.5 Å. The final fit (black curve) shows that the addition of O neighbors as second and third neighbors contributes to improve the fit quality.