

Supplementary Material: Distribution of aluminum over different T-sites in ferrierite zeolites studied with aluminum valence to core X-ray emission spectroscopy

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I. ENERGY CALIBRATION OF THE SPECTROMETER

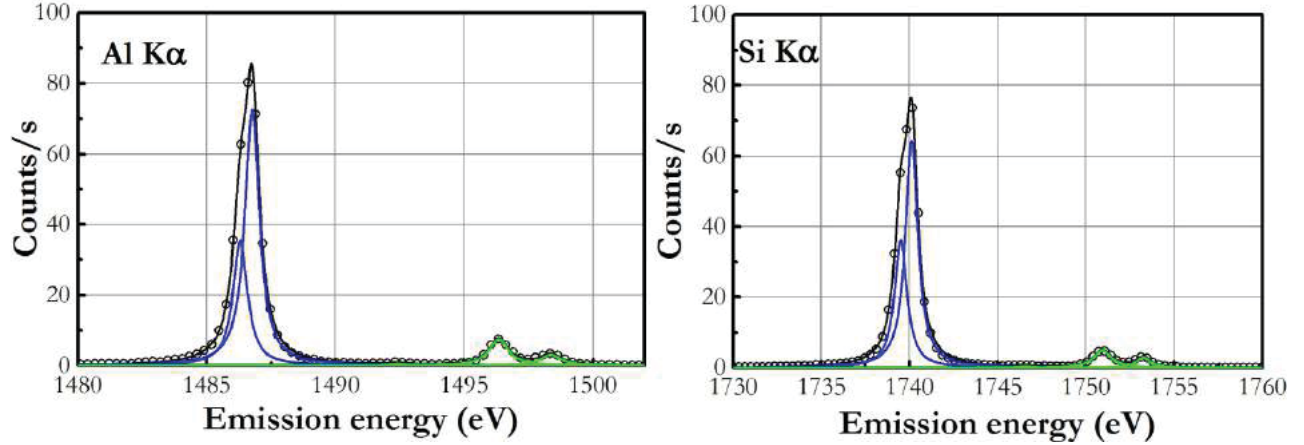


FIG. S1. Reference $K\alpha$ x-ray spectra of elemental Al and Si. For the fit Lorentzian profiles were used. The FWHM experimental energy resolution was derived from the fitted Lorentzian widths by subtracting the natural lifetime broadening of 0.41 eV for Al, and 0.48 eV for Si. The widths were adopted from the recommended values of Campbell and Papp (reference [33] in the manuscript). FWHM experimental energy resolution of 0.27 eV at 1.487 keV, and 0.38 keV at 1.740 keV was obtained. The lines occurring around 1497 eV and 1752 eV correspond to the $K\alpha_{1,2}L_1$ satellites of Al and Si, respectively.

II. SI VtC SPECTRA

In addition to Al VtC spectra, Si VtC spectra of the ferrierite samples have been recorded. The measurement of the Si VtC spectra was performed under the same conditions as for the Al VtC spectra. The instrumental response for Si VtC spectra was determined by a fit of a Lorentzian function with FWHM of 0.26 eV at 1740 eV (Si $K\alpha$). The measuring time for a single spectrum was 15 min. Figure S2 shows the background subtracted Si VtC spectra. The spectral differences between the samples observed in the Si VtC spectra are

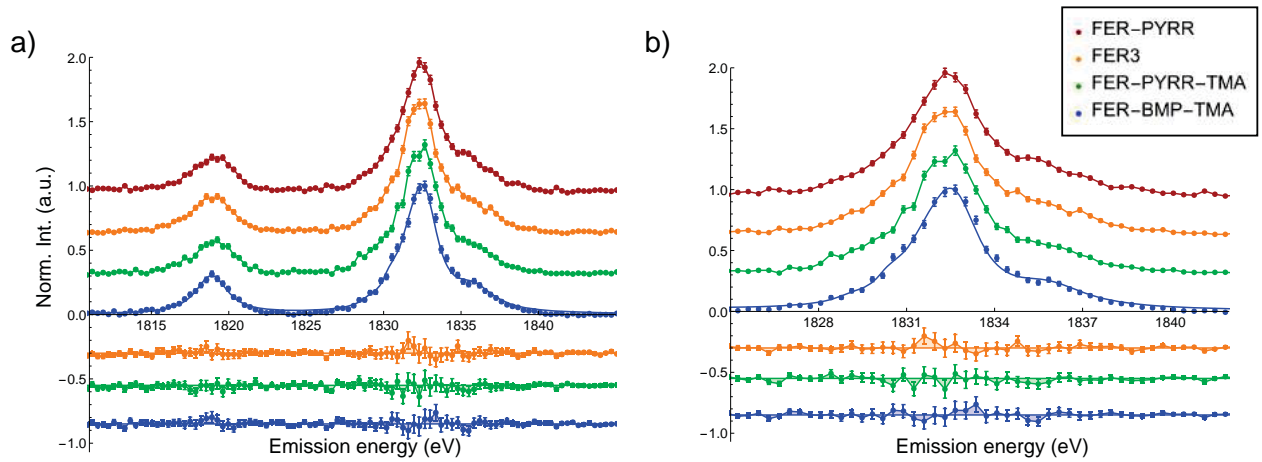


FIG. S2. a) Background subtracted experimental Si VtC emission spectra of FER-BMP-TMA, FER-PYRR-TMA, FER-PYRR and FER3 samples. b) Zoom in of the main emission peak. The full lines represent the fitted functions. The difference spectra correspond to differences with respect to the spectra of FER-PYRR.

small compared to differences in the Al VtC spectra and feature shifts in the $K\beta_{1,3}$, $K\beta'$, and $K\beta''$ features.

III. LABELLING OF CONFIGURATIONS

Considering the occupation of α - and β - sites there are 12 configurations in which one or two aluminum atoms can occupy either of the two 6-rings. Figure S3 shows the labelling convention for these configurations used in the manuscript.

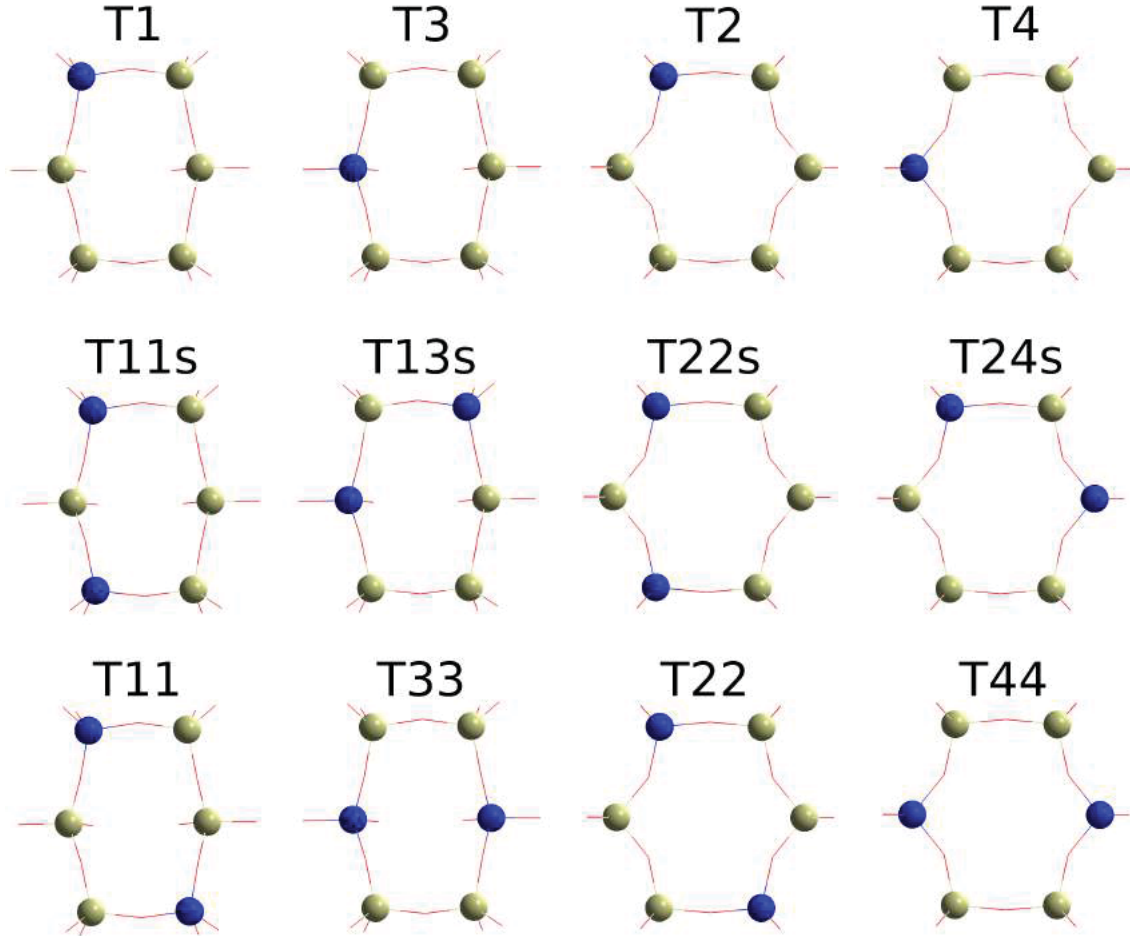


FIG. S3. Labelling of configurations of α - (left) and β - (right) sites. Blue and yellow spheres represent aluminum and silicon atoms, respectively, while the connection to the oxygen atom is marked with a red line.

IV. $K\beta'$ SHAPE

The $K\beta'$ peak in the measured Al VtC has found to have an symmetric shape for all the measured samples. This peak shape was not reproduced by our theoretical spectra. To verify that the observed discrepancy is not caused by an insufficient size of our model, T-sites corresponding to the second coordination shell of the 6-rings were included. The $K\beta'$ peak of the calculated spectra shows no substantial differences with regards to the one from our model (see Fig. S4). The origin of the shape of the experimental $K\beta'$ peak is therefore not fully understood.

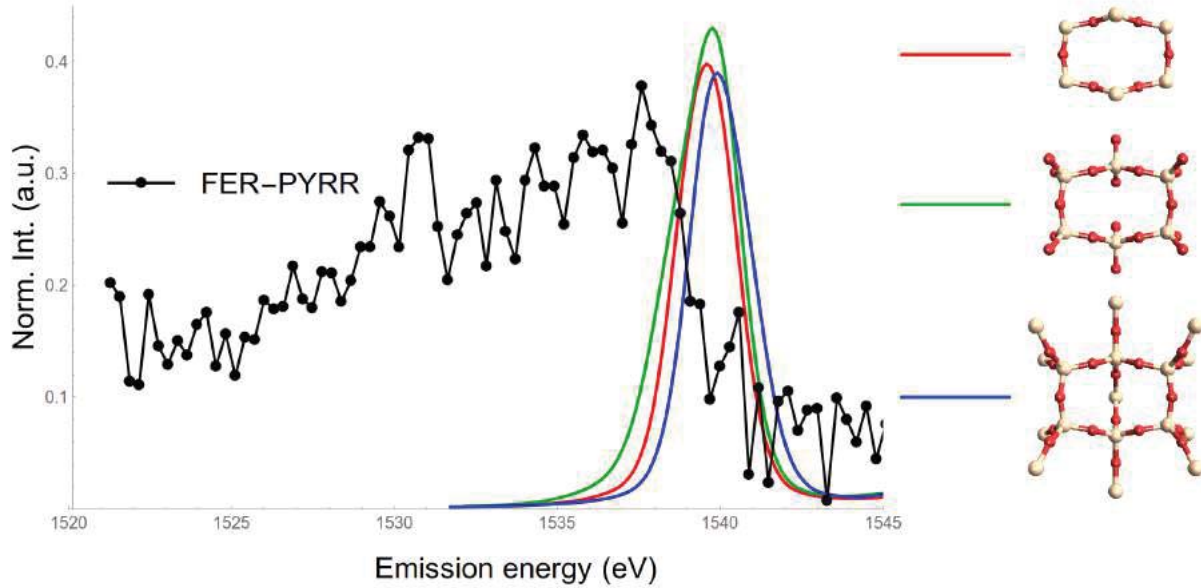


FIG. S4. A comparison between the shapes of the $K\beta'$ peak of the T1 site calculated on models with different sizes along with the experimental spectra of the FER-PYRR sample. The augmentation of the model size does not seem to have a noticeable effect on the shape of the $K\beta'$ peak.

V. FITTING AND ERROR ESTIMATION

To obtain the concentration of configurations present in the samples, the raw emission spectra were fitted with constant and linear terms, describing the background, and theoretical reference spectra f_i , describing $K\beta_{1,3}$, $K\beta_x$, and $K\beta''$ features, by the chi-square method. The fitting function

$$F(a_1, a_2, b_1, \dots, b_{12}, E) = (a_1 + a_2 * E) + \sum_{i=3}^{14} a_i * f_i(E), \quad (1)$$

was evaluated on the energy grid between 1542.3 eV and 1560.5 eV. The χ^2 parameter was calculated as

$$\chi^2(a_1, \dots, a_{14}) = \sum_j^N \left(\frac{G_j - F_j(a_1, \dots, a_{14})}{\sigma_j} \right)^2, \quad (2)$$

where G_j is the measured value at the j -th energy point, σ_j is the associated error of that energy point, estimated as $\sqrt{G_j}$, and N is the number of experimental points. The concentration of the m -th configuration in the fit is computed by normalizing a_m as $c_m(t_k) = a_m / \sum_i^{14} a_i$. The error in the concentration c_m was estimated by maximizing the a_m component in the manifold defined as $\chi^2(a_1, \dots, a_{14}) = \chi^2(a_1^{opt}, \dots, a_{14}^{opt}) + 1$, where the superscript *opt* corresponds to the optimized parameters at which χ^2 is minimal¹. The fitted concentrations along with the comparison between experimental and fitted Al VtC XES spectra are shown in Fig. S5.

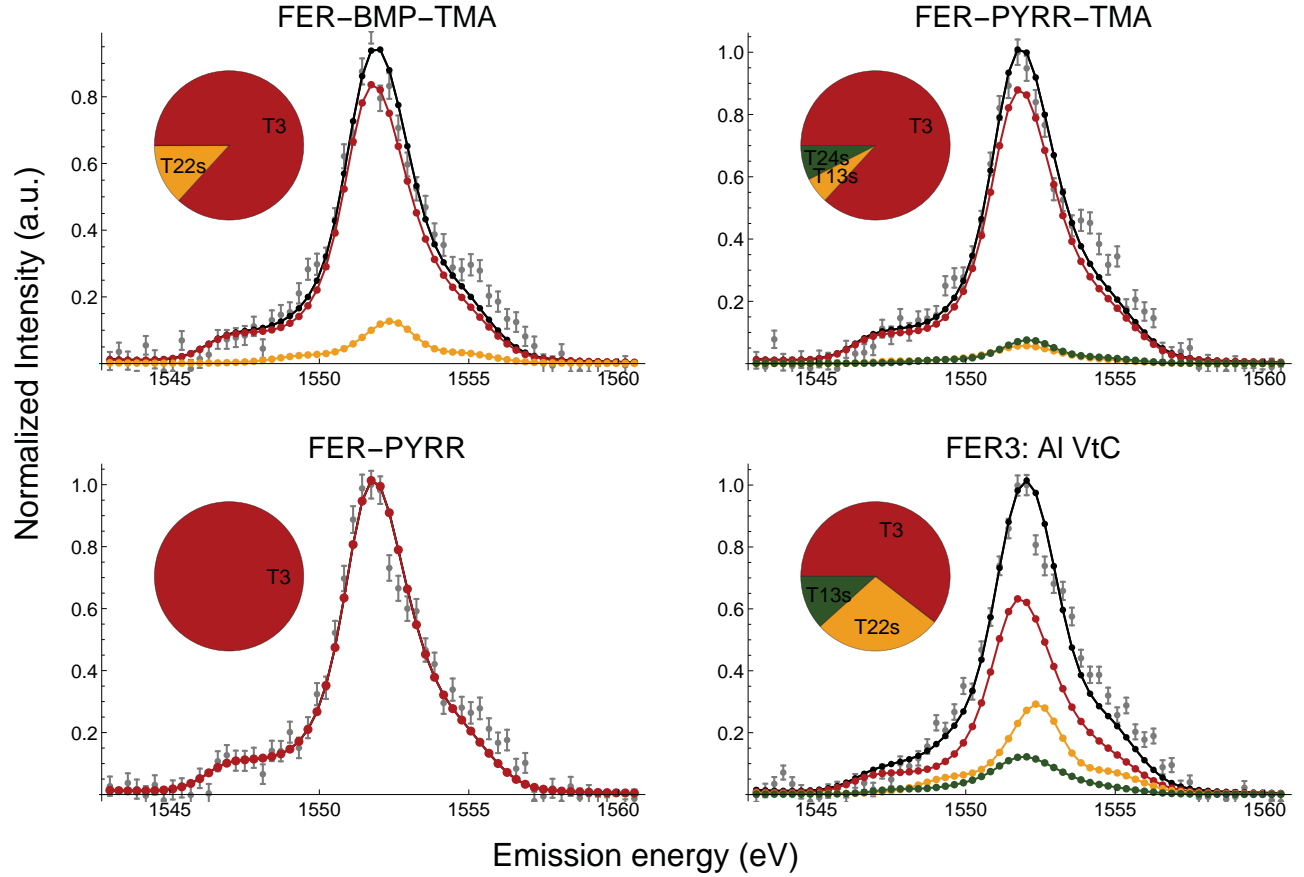


FIG. S5. Comparison between background subtracted experimental (gray markers) and theoretical fitted Al VtC XES spectra (black line) for the ferrierite samples. The contribution of individual configurations to the emission spectra is indicated with coloured lines and dots with the pie chart showing the corresponding composition.

VI. BACKGROUND SUBTRACTED SPECTRA

The background subtraction of raw data was performed in the fit of the theoretical model (see Equation 1). At the border values of the energy interval considered in the fit, i.e., 1542.3 eV and 1560.5 eV, the contribution from Al VtC emission is expected to be negligible. The constant and linear terms can therefore model possible variations in the offset and slope of the experimental spectra. Fig. S6 shows the raw data, the background, and the background subtracted data.

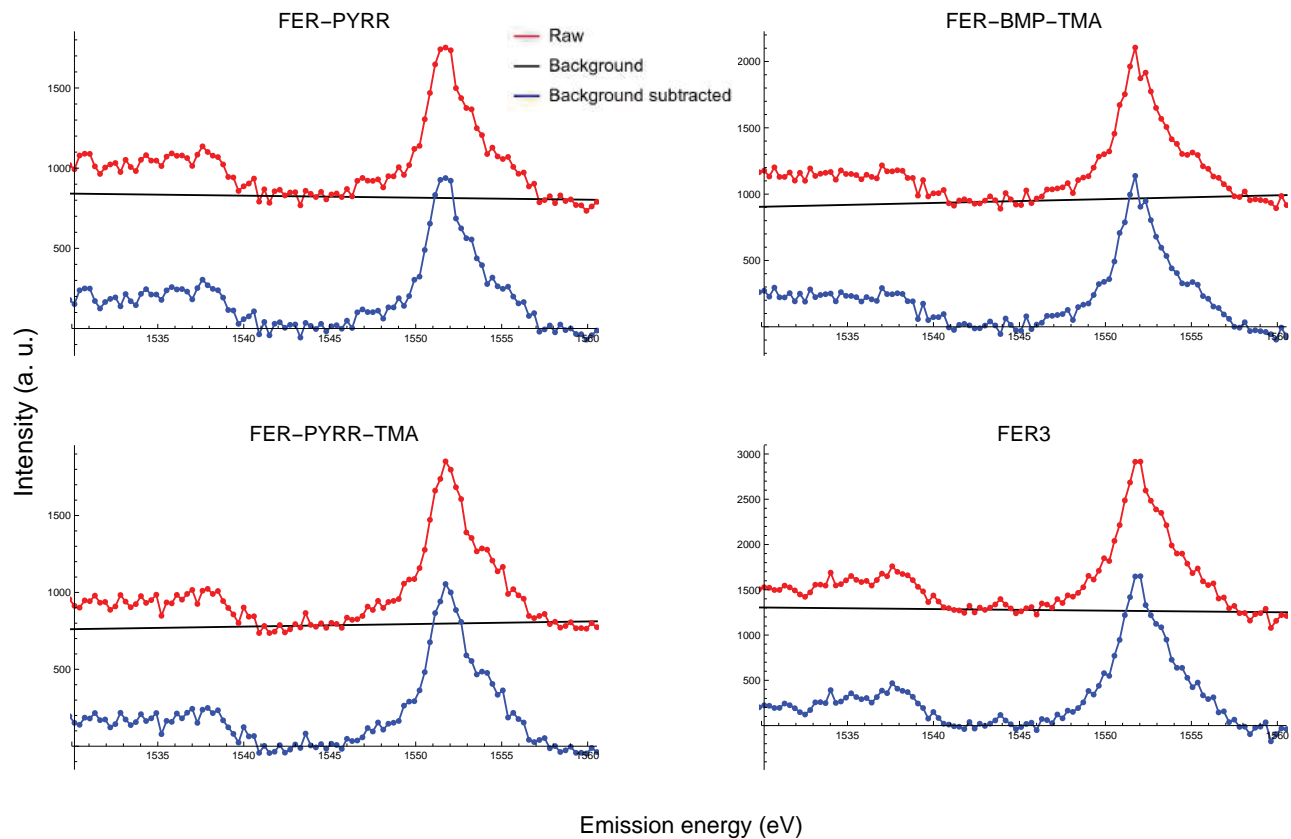


FIG. S6. Raw Al VtC spectra along with the background fit and the background subtracted data. The background subtraction was performed in the fit of the theoretical model

REFERENCES

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