Table EA-1. Empirical bond-valences for Mn-Zn precipitate[a].

	O1[b]	O1[c]	O1[d]	O1[e]	O2, O3	O3	O4	Σ	Formal valence
Mn1	0.628 ×6→ ×3↓	0.628 ×2↓	0.628 ×2↓	0.628 ×2↓				3.8	4
Mn2, Mn3		0.469 ×3→			0.433 ×3→			2.7	3
Zn1			0.403 ×3→			0.372 ×3→		2.3	2
Zn2				0.731 ×3→			0.543	2.7	2
H^+	0.11[f]								
Σ	1.9 – 2.0[g]	1.7	1.7	2.0					

(a) Bond valences in valence unit (v.u.) were calculated using the Valence for Dos program (v. 2.0 - http://www.ccp14.ac.uk/solution/bond_valence/index.html) and the parameters from Brese and O' Keeffe (1991).

(b) O1 coordinated to 3 Mn^{4+} in Mn1 (Table 1).

(c) O1 coordinated to 2 Mn^{4+} in Mn1 and 1 Mn^{3+} in Mn2 or Mn3.

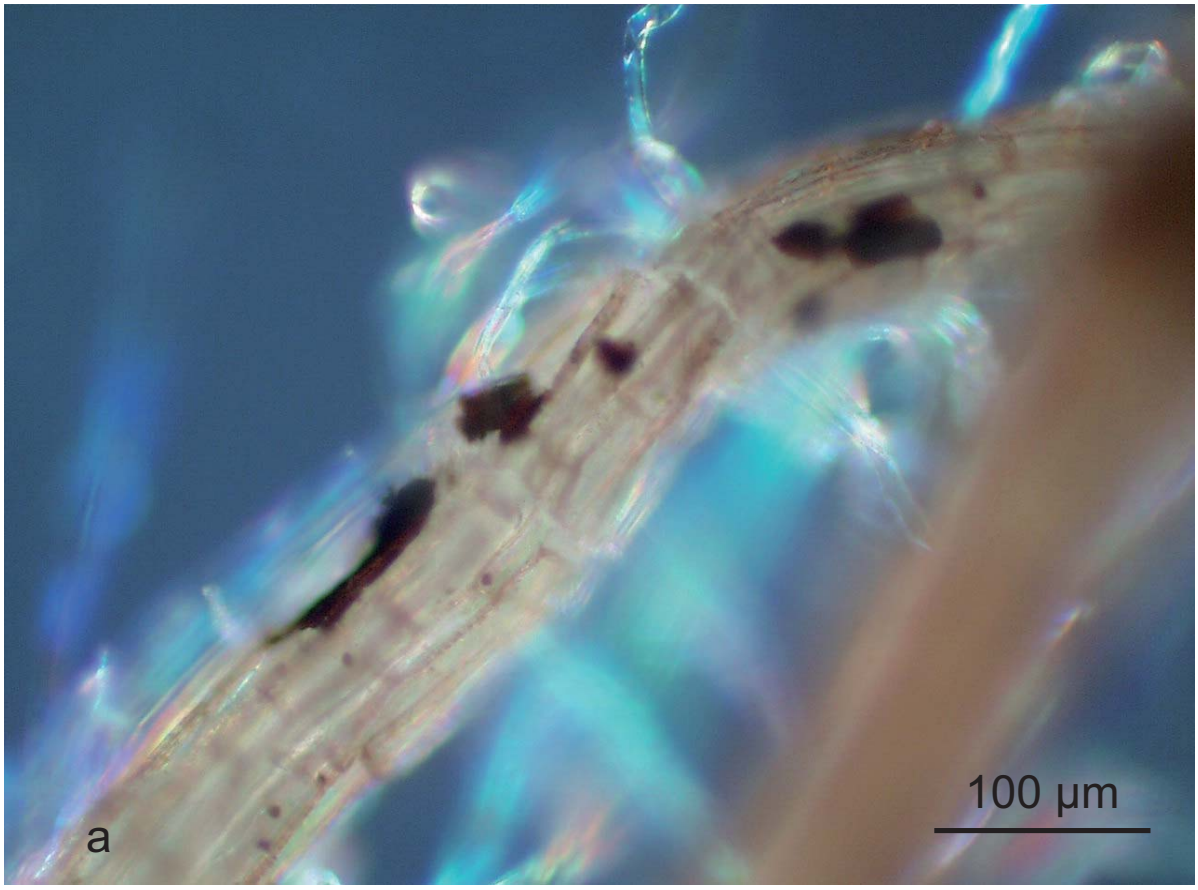
(d) O1 coordinated to 2 Mn^{4+} in Mn1 and 1 Zn^{2+} in Zn1.

(e) O1 coordinated to 2 Mn^{4+} in Mn1 and 1 Zn^{2+} in Zn2.

(f) O5-H-O1 H-bond.

(g) Depending on whether this O1 receives additional valence from H^+ through H-bond.

REFERENCE: Brese N.E. and O' Keeffe M. (1991) Bond-valence parameters for solids. *Acta Crystallogr*. **B47**, 192-197.



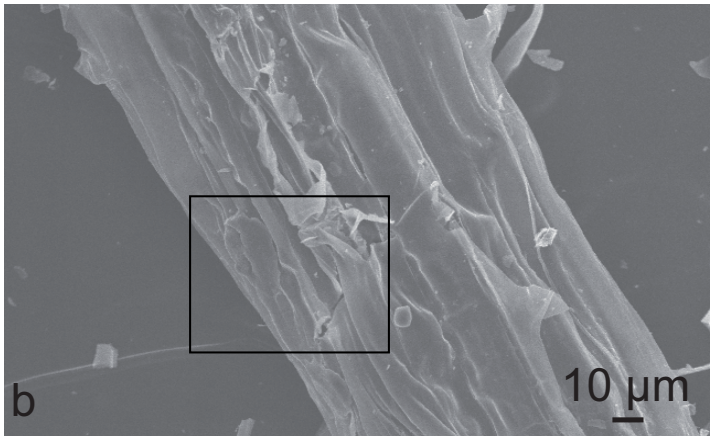


Fig. EA-1: Roots of *Festuca rubra* grown on a Zn-contaminated sediment. (**a**) Close-up photograph from Fig. 1a. (**b**) Lower magnification of Fig. 1c.

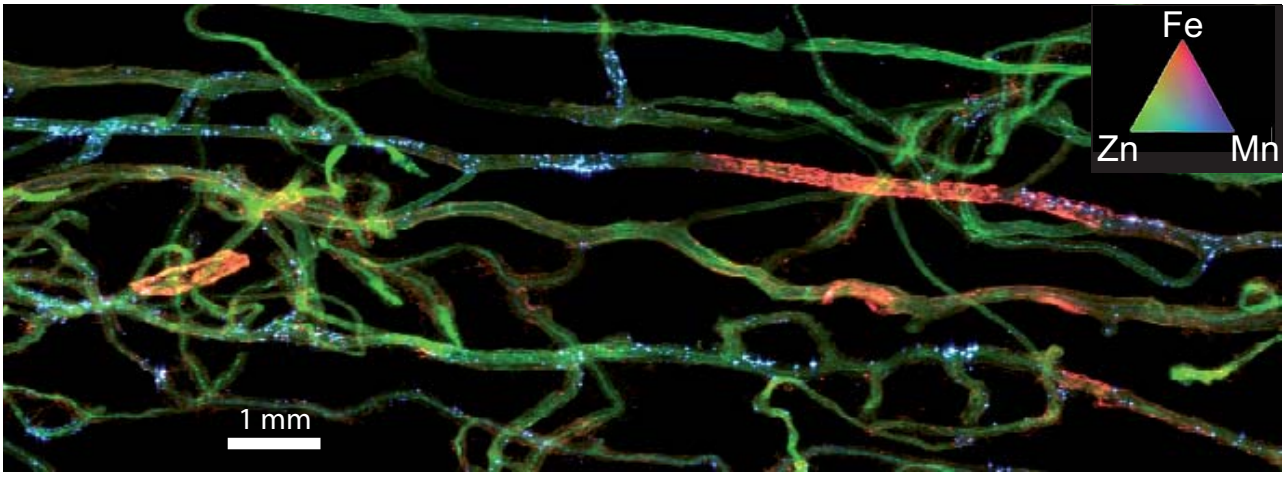


Fig. EA-2: Tricolor (RGB) μ-XRF map of a bundle of roots. Red codes for Fe, green for Zn, and blue for Mn. Each pixel is colored in proportion to Fe-, Zn- and Mn-Kα signals. Pixel size is 18 × 15 μm^2.

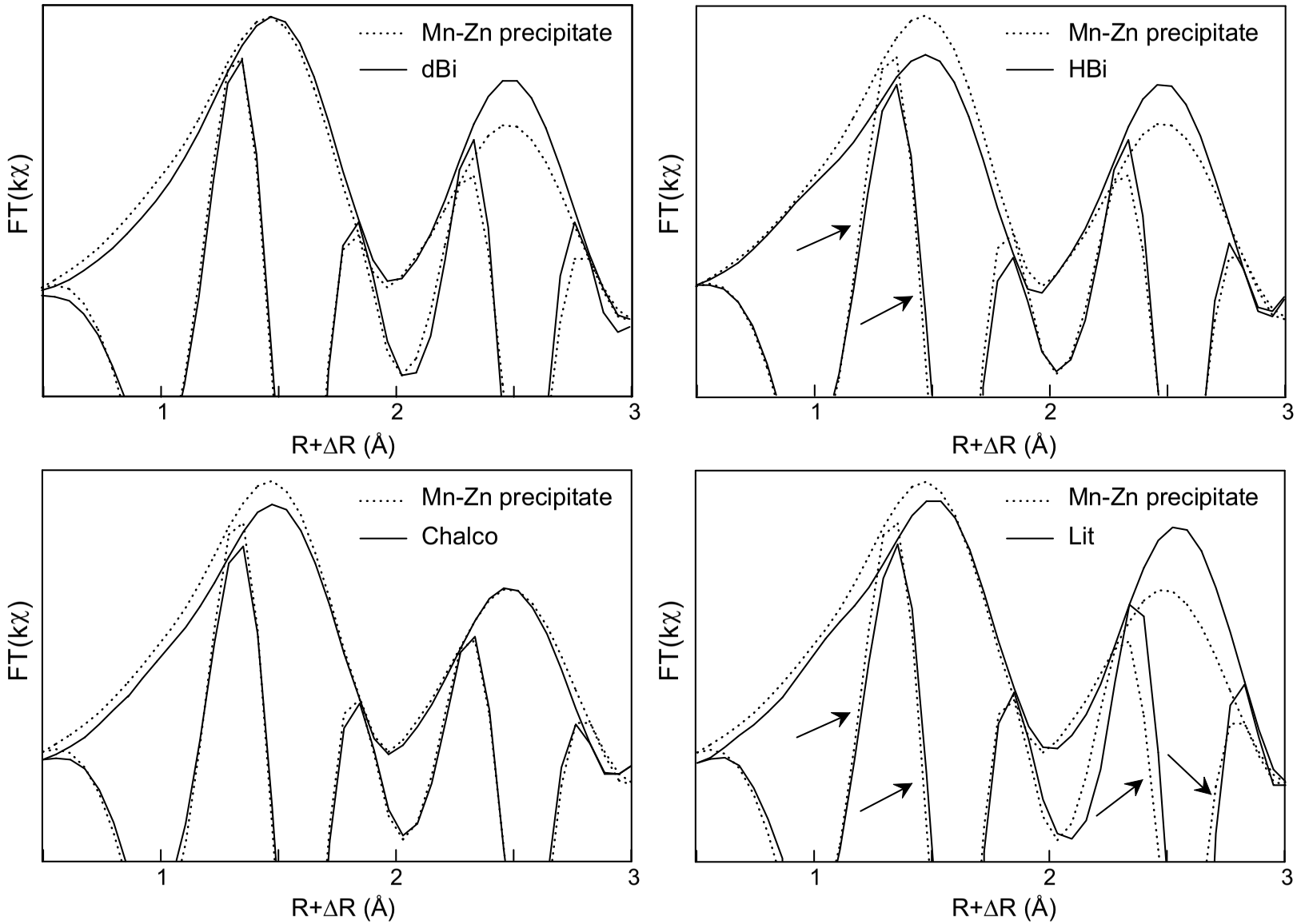


Fig. EA-3: Fourier transforms (FTs) of the manganese K-edge *k*-weighted EXAFS spectra for the Mn-Zn root precipitate and synthetic ^{VI}Zn-sorbed δ-MnO_2 (dBi, synthetic turbostratic birnessite), chalcophanite (Chalco), hexagonal birnessite (HBi), and lithiophorite (Lit). Expansion of the [1-3 Å] R+ΔR interval.

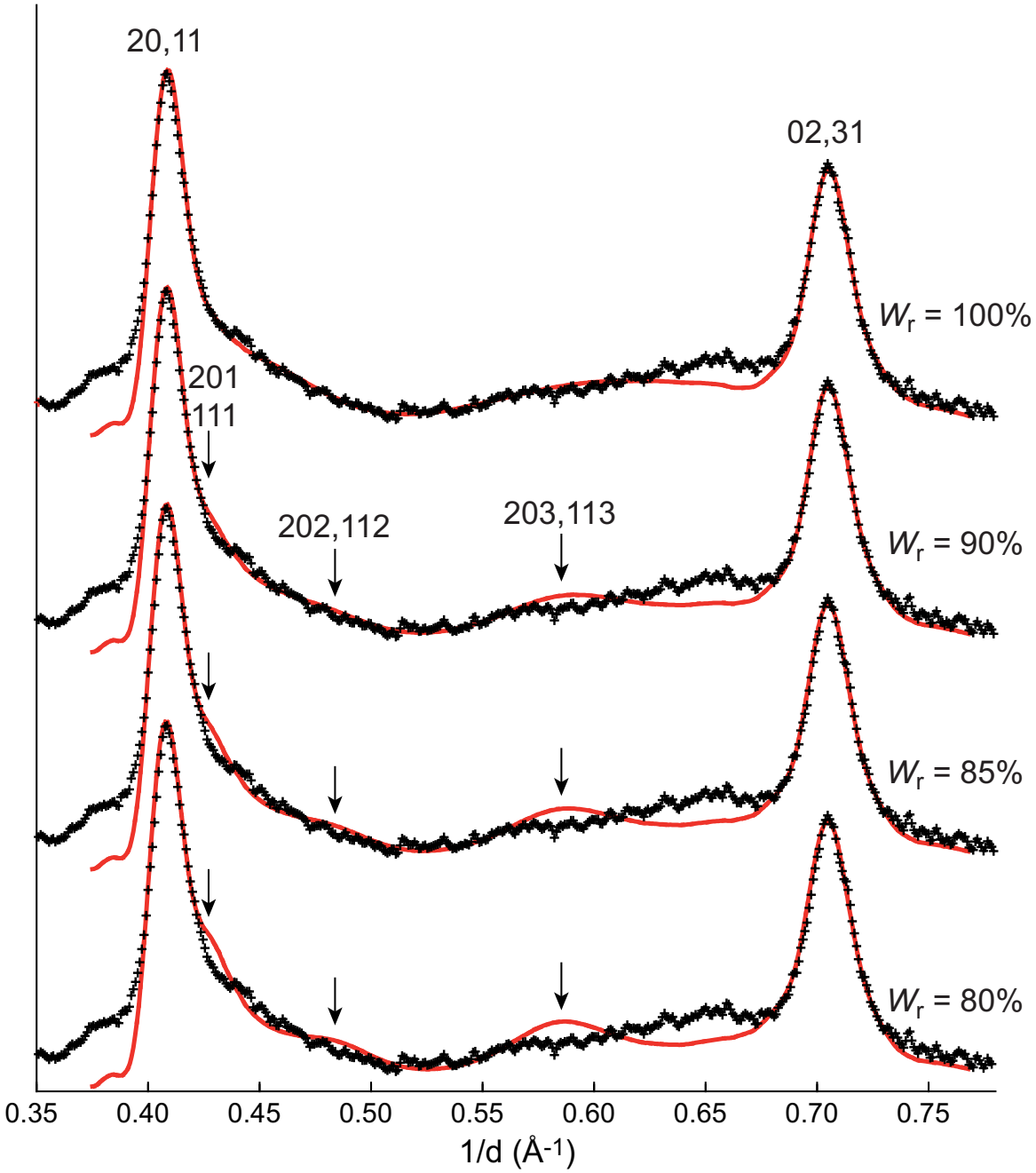
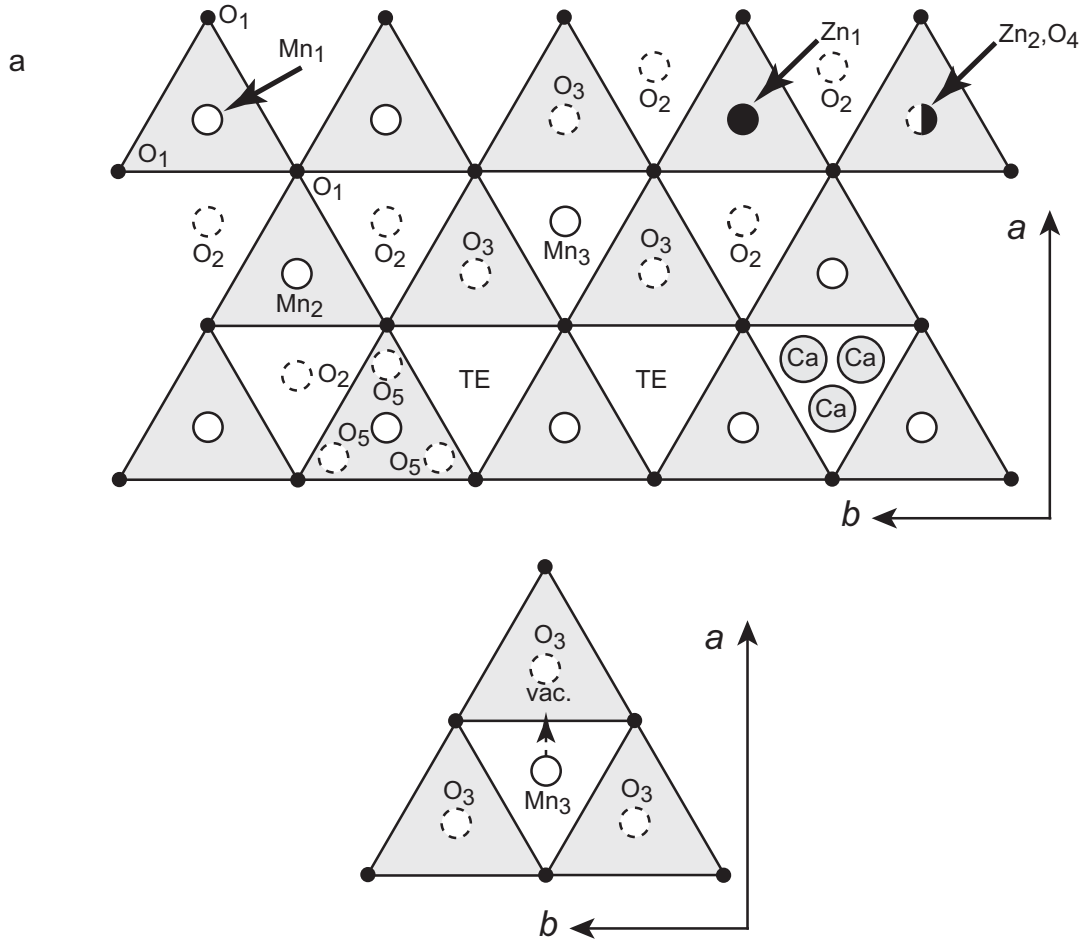


Fig. EA-4: Simulations of the [20,11] and [02,31] X-ray scattering bands (black crosses, C-centered layer cell). Intensities (red lines) were calculated for the optimal structure model (Table 1) with different occurrence probabilities of random stacking faults (W_r). Arrows indicate the positions of *hkl* reflections.



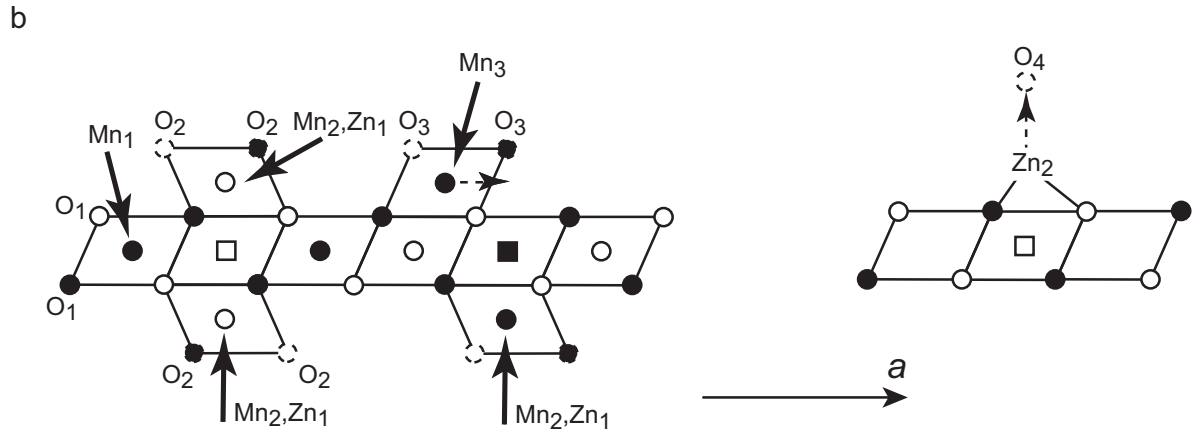


Fig. EA-5: Idealized structure of Mn-Zn precipitate. (**a**) Projection on the *ab* plane. The upper surface of the layer is shown as light shaded triangles, and the atomic notations are the same as in Table 1. (**b**) Projection along the *b* axis. Open and solid symbols indicate atoms at $y = 0$ and $y = \pm½$, respectively. Squares represent vacant layer octahedra.The Mn_3 and Zn_2 atoms can be shifted from their positions as indicated by the dashed arrows to obtain more realistic interatomic distances (see Table EA-1).

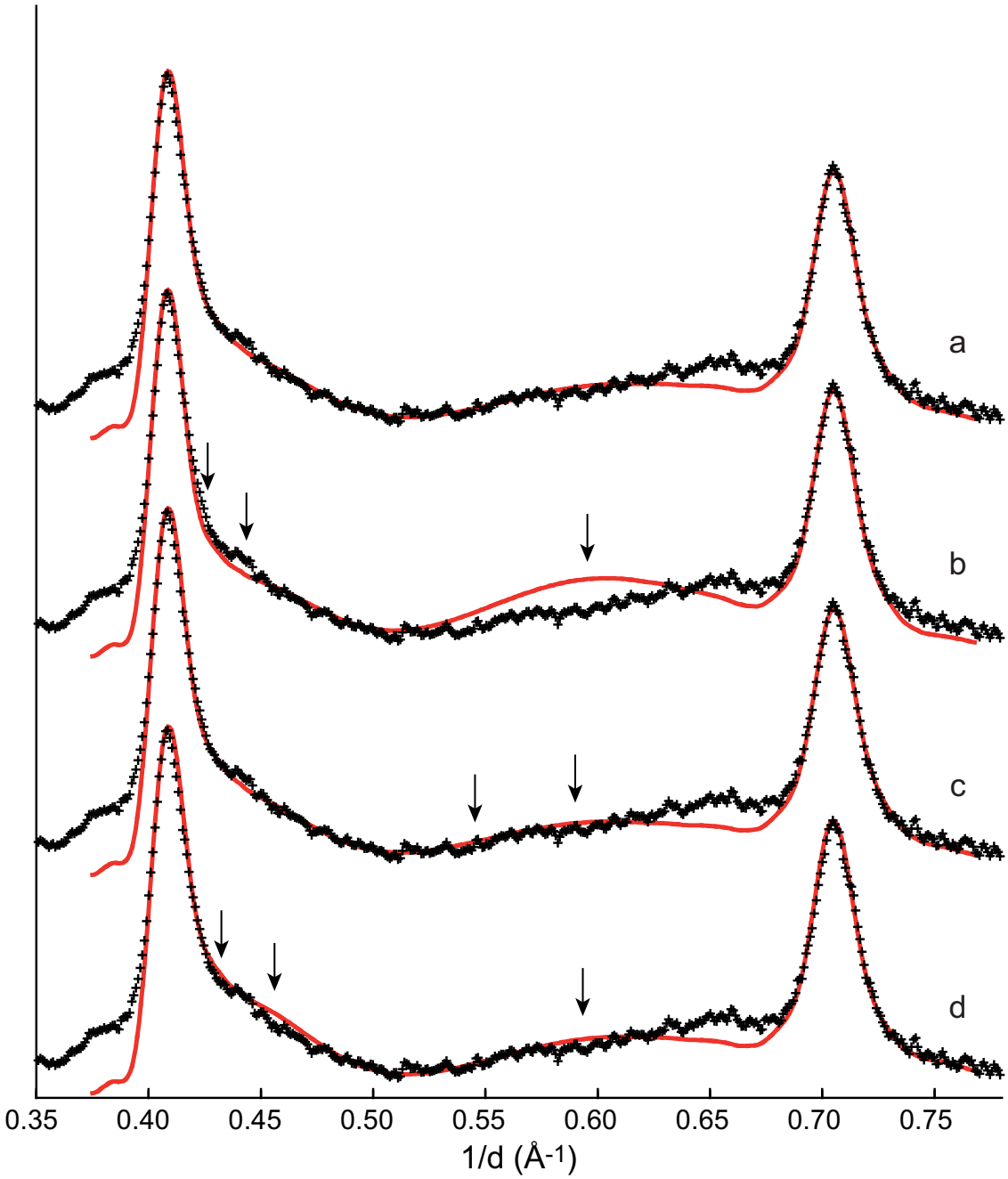


Fig. EA-6: Simulations of the [20,11] and [02,31] X-ray scattering bands (C-centered layer cell, black crosses). Small but significant misfits between experimental and calculated patterns are pointed out with arrows. Intensities (red lines) were calculated with a turbostratic layer stacking (no interlayer correlation). (a) Optimal model (Table 1; Figs. 8 and EA-5); R_{wp} = 3.49%. (b) Model with ^{IV}Zn (Zn2) in (0, 0, 1.97 Å), instead of (0, 0, 1.77 Å) in the optimal fit, so as to increase the Zn-O bond length from 1.82 À (Table 2) to 1.91 Å. Coordinated H_2O molecules (O4) were moved from (0, 0, 3.70 Å) to (0, 0, 3.90 Å); R_{wp} = 3.92%. (c) Model with ^{VI}Zn (Zn1) in (0, 0, 2.30 Å), instead of (0, 0, 2.20 Å) in the optimal fit so as to decrease the sum valence of Zn1 from 2.3 (Table EA-1) to 2.0. Coordinated H_2O molecules (O2) were moved from (-0.333, 0, 3.45 Å) to (-0.333, 0, 3.65 Å); R_{wp} = 3.55%. (d) Model with Ca in (-0.333, 0, 3.60 Å), instead of (-0.410, 0, 3.60 Å) and equivalent positions in the optimal fit; R_{wp} = 3.51%. Unless specified, all parameters used in calculations are those of the optimal model.

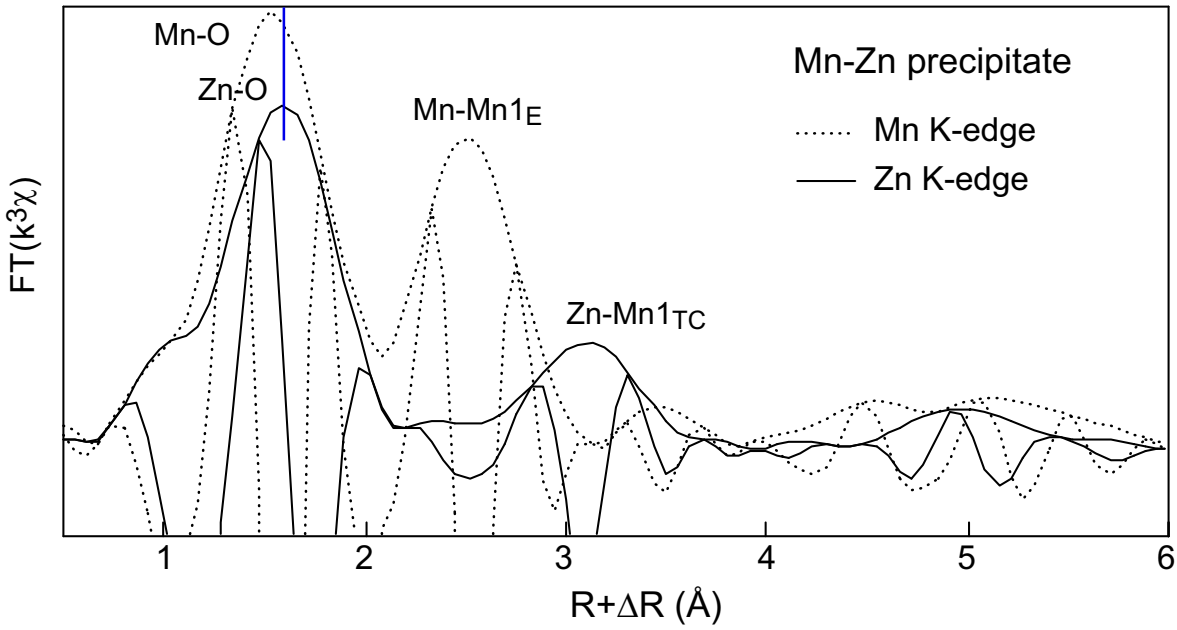


Fig. EA-7: Fourier transform of the EXAFS spectra for the Mn-Zn precipitate at the Mn and Zn K-edges. The average Mn-O and Zn-O EXAFS distances (R values) are 1.90 Å and 2.00 Å, respectively.