

## Appendix I: Calculations of the ion contributions

The relation between the numbers extracted from the analysis of Figure 7 and the magnetite to maghemite ratio is not straightforward. One supposes that

$$\text{XMCD}(\text{biotic}) = \text{XMCD}[\text{Fe}^{2+}(\text{Oh})] + \text{XMCD}[\text{Fe}^{3+}(\text{Oh})] + \text{XMCD}[\text{Fe}^{3+}(\text{Td})]$$

where  $\text{XMCD}[\text{Fe}^{2+}(\text{Oh})]$  stands for XMCD contribution for a fully magnetized  $\text{Fe}^{2+}$  on an octahedral site and similar definitions for the other XMCD terms. From Figure 7, one finds that

$$\text{XMCD}(\text{abiotic}) - \text{XMCD}(\text{abiotic}) = 4.5\% \text{ XMCD}[\text{Fe}^{2+}(\text{Oh})] - 3\% \text{ XMCD}^{3+}(\text{Oh})] - 1.5\% \text{ XMCD}[\text{Fe}^{3+}(\text{Td})]$$

(the precision on these figures is estimated to  $\pm 0.5\%$ ), so that

$$\text{XMCD}(\text{biotic}) = 95.5\% \text{ XMCD}[\text{Fe}^{2+}(\text{Oh})] + 103\% \text{ XMCD}[\text{Fe}^{3+}(\text{Oh})] + 101.5\% \text{ XMCD}[\text{Fe}^{3+}(\text{Td})]$$

If  $\text{XMCD}(\text{abiotic})$  can be written

$$\begin{aligned} \text{XMCD}(\text{abiotic}) &= y \text{ XMCD}[\text{Fe}_3\text{O}_4] + x \text{ XMCD}[\text{Fe}_{8/3}\text{O}_4] \\ &= y \text{ XMCD}[\text{Fe}^{2+}(\text{Oh})] + (y+5x/3) \text{ XMCD}[\text{Fe}^{3+}(\text{Oh})] + (y+x) \text{ XMCD}[\text{Fe}^{3+}(\text{Td})] \end{aligned}$$

then one is dealing with three linear equations

$$\begin{aligned} y &= 0.955 ; \\ y &= 1.03 - 5x/3 ; \\ y &= 1.015 - x \end{aligned}$$

that are plotted in Appendix Figure 3. The black square with coordinates  $X = 4\%$  and  $Y = 97\%$  is the center of the incertitude triangle.

One should notice that  $X + Y$  is slightly larger than 1. This is expected from the fact that the two isotropic spectra for biogenic and abiogenic particles have the same intensity far from the edge (740 to 760 eV) though  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  have slightly different radial matrix elements for 2p to 3d transitions (as can be seen from Fig. 5) so that a small variation of their respective concentrations is expected to yield a small variation of the total number of iron ions. To come back to usual concentrations that sum up to 1, one should consider  $X/(X + Y) = 4\%$  and  $Y/(X + Y) = 96\%$ .

Taking the center of the incertitude triangle to calculate the maghemite and magnetite proportion, we find  $4 \pm 1\%$  maghemite ( $\text{Fe}_{8/3}\text{O}_4$ ) and  $96 \pm 1\%$  magnetite ( $\text{Fe}_3\text{O}_4$ ). The uncertainty ( $\pm 1\%$ ) comes from the uncertainties on the numbers extracted from Figure 7 and the standard deviation associated to the incertitude triangle ( $\pm 0.7\%$ ). The amount of vacancies on the octahedral sites is 0.7%. It is simply given by  $4\% / 6 = 0.7\%$  since one sixth of the magnetite octahedral sites are empty in maghemite.