APPENDIX A

1) $\sigma_{N'_{Fe^{3+}}}$ error of $N'_{Fe^{3+}}$, the atomic fraction of Fe^{3+}, calculated for N_O oxygens and N_{CT} cations:

$$\sigma_{N'_{Fe^{3+}}} = \frac{2N_O - N'_{Fe^{3+}}}{N_{CT}} \sqrt{\sum \sigma^2{}_{N'_i} + \left(1 + \frac{N'_{Fe^{3+}}}{N'_{Fe^{2+}}}\right)^2 \sigma^2_{N'_{Fe^{2+}}}},$$

where $\sigma_{N'_i}$ is the standard deviation of the atomic fraction i different from $N'_{Fe^{2+}}$.

1bis) σ' mean error of the atomic fraction of Fe^{3+}:

$\sigma' = \frac{\sigma_{N'_{Fe^{3+}}}}{\sqrt{n}}$where n is the number of point analyses.

2) $\sigma_{e^-_{ref}}$ error of the total electrons from site occupancy refinement in the A, B, C, and D sites for chevkinite formula $A_4BC_2D_2O_8(Si_2O_7)_2$:

$$\sigma_{e^-_{ref}} = \sqrt{\left(2\sigma_{e^-_{refA1}}\right)^2 + \left(2\sigma_{e^-_{refA2}}\right)^2 + \left(\sigma_{e^-_{refB}}\right)^2 + \left(2\sigma_{e^-_{refC1}}\right)^2 + \left(\sigma_{e^-_{refC2A}}\right)^2 + \left(\sigma_{e^-_{refC2B}}\right)^2}.$$

3) $\sigma_{e^-_{chem}}$ error of the total electrons from chemical analysis in the A, B, C, and D sites for chevkinite formula $A_4BC_2D_2O_8(Si_2O_7)_2$:

$$\sigma_{e^-_{chem}} = \sqrt{\sum(\sigma_i Z_i)^2},$$

where σ_i and Z_i are the estimated standard deviation and the atomic number of each analyzed element, respectively.

4) $\overline{x}_w$ weighted average of the bond distances:

$$\overline{x}_w = \frac{\sum \frac{x_i}{\sigma_i}}{\sum \frac{1}{\sigma_i}},$$

where x_i is each individual bond length, and σ_i is its estimated standard deviation.

4bis) $\sigma_{\overline{x}_w}$ error of the weighted average of the bond distances:

$$\sigma_{\overline{x}_w} = \sqrt{\frac{\sum \frac{1}{\sigma_i}(x_i - \overline{x}_w)^2}{\sum \frac{1}{\sigma_i}}}.$$