

Resonant Inelastic X-ray Scattering (RIXS) confirmation of $\text{Ce}^{3+}/\text{Ce}^{4+}$

Because the Ce L_3 – edge XANES is dominated by the Ce^{3+} white line, one cannot be absolutely certain that the intensity variation in the higher energy XANES peak originates from Ce^{4+} ; therefore, we also used RIXS to confirm, at least qualitatively, the presence of Ce^{4+} . In the RIXS technique, as the excitation energy approaches the Ce L_3 – edge (Fig. S1a, c, e), the inelastically scattered X-ray exhibits distinctly different features between Ce^{3+} and Ce^{4+} due to the presence and the absence of a $4f$ electron respectively. The analysis of the RIXS process is discussed elsewhere (e.g., Sham et al., 2005; Rubensson, 2000).

To examine the RIXS behavior for Ce^{3+} and Ce^{4+} , we analyzed the model compounds (CePO_4 and CeO_2) at a range of different excitation energies in the pre-edge region of the XANES spectra. The RIXS spectra for these compounds are presented using X-ray emission intensity versus emission wavelength (Fig. S1). The CePO_4 compound displays a normal RIXS behavior (Fig. S1b) showing a gradual increase in intensity and an energy dispersion of the $L\alpha_{1,2}$ (shift to lower emission wavelength) as the excitation energy approaches the threshold (Bartolome et al., 1999). However, the CeO_2 compound (Fig. S1d) exhibits a more complex pattern as the excitation energy approaches the threshold (number 13 in Fig. S1c). Instead of a well-defined $L\alpha_{1,2}$ –like doublet, the RIXS spectra appear to be a considerably broadened multiplet (Fig. S1d) while a gradual increase in intensity and a characteristic energy dispersion can still be observed. This anomaly in Ce^{4+} RIXS has been attributed to $f^1 (2p)^6$ to $f^2 (2p)^5$ quadrupole transition (Hague et al. 2004, Sham et al. 2005).

The XANES spectra for the green titanite at the Ce L_3 – edge and the pre-edge region is shown in Figure S1e. In the pre-edge region, where the RIXS is most sensitive to the oxidation state, the green titanite RIXS (Fig. S1f) resembles neither the clean doublet of the Ce^{3+} (Fig. S1b) nor the broadened multiplet of the Ce^{4+} (Fig. S1d), but a mixture. Although the green titanite spectra are noisy due to the low concentration of Ce, it is possible to qualitatively examine the spectra. For example, at ~ 5720 eV excitation energy the green titanite RIXS shows a doublet (Fig. S1f) reminiscent of Ce^{3+} but the main peak is significantly distorted and at lower excitation energy, the shoulder (emerging to become $L\alpha_2$) that was clearly noticeable in the Ce^{3+} RIXS was not detected. These observations are consistent with a mixed contribution from both oxidation states.

SUPPLEMENTARY REFERENCES

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FIGURE S1: a) XANES spectra showing excitation energies used for the RIXS investigations of Ce³⁺PO₄. b) RIXS spectra for the Ce³⁺PO₄ compound. c) XANES spectra showing excitation energies used for the RIXS investigations of Ce⁴⁺O₂. d) RIXS spectra for the Ce⁴⁺O₂ compound. e) XANES spectra showing excitation energies used for the RIXS investigations of the green titanite. f) RIXS spectra for the green titanite.

