



	<b>Experiment title:</b> Molecular Mechanisms of Antimony(V) Binding to Natural Organic Matter	<b>Experiment number:</b> EV347
<b>Beamline:</b> BM20	<b>Date of experiment:</b> from: 25.01.2022 to: 31.01.2022	<b>Date of report:</b> 26.03.2022
<b>Shifts:</b> 18	<b>Local contact(s):</b> Damien Prieur	<i>Received at ESRF:</i>
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## Report:

### Experiment

Organic matter-rich soils have a high potential to retain antimony (Sb) and serve as a natural sink for anthropogenic Sb emissions. This suggests that particulate natural organic matter (NOM) is an important sorbent for this potentially toxic metalloid. Under oxidizing conditions, antimonate [Sb(V),  $\text{Sb}(\text{OH})_6^-$ ] is the predominating Sb form in soils and aquatic environments. However, molecular-scale information on Sb(V) complexation by intrinsically heterogeneous NOM is entirely missing. Our study aims to fill this gap. This includes experiments on Sb(V) binding to pure NOM as well as to NOM enriched with polyvalent metal cations bound to the organic material, which is a prerequisite for the potential formation of ternary Sb(V) complexes with NOM. The NOM was obtained from an ombrotrophic peat soil (Federseetorf, Bad Buchau, Germany), wet-sieved (particle size: 40-250  $\mu\text{m}$ ), and freeze-dried. Part of the NOM samples was loaded with Fe(III) (0-7820 ppm) or Sr (0-14250 ppm), washed, and redried. Afterwards, all samples were loaded with different Sb(V) concentrations (610-6100 ppm) at pH 3 and pH 5, which represents the pH range most relevant for sorptive interactions between Sb(V) and NOM in soil environments.

### Measurement

A total of 18 samples were prepared and sent to ESRF. These included two reference samples [Sb(III) and Sb(V)] and 16 NOM samples (half of them loaded with Sr + Sb(V) and Fe(III) + Sb(V), respectively). Reference samples were analyzed in transmission mode by Sb K-edge XANES spectroscopy in order to infer the oxidation state of Sb in the Sb(V)-reacted NOM samples. All other samples were analyzed by Sb and Fe or Sr K-edge XANES and EXAFS spectroscopy in fluorescence mode, except for two NOM samples (Sr K-edge), which were also measured in transmission mode. Six samples were measured at the Sr K-edge and eight samples at the Fe K-edge. Since the beamline was calibrated 500 eV too high for the Sb K-edge, all Sb data had to be manually corrected after the measurements. In total, 32 measurements were performed at ca. 10 K using a He cryostat.

### Results

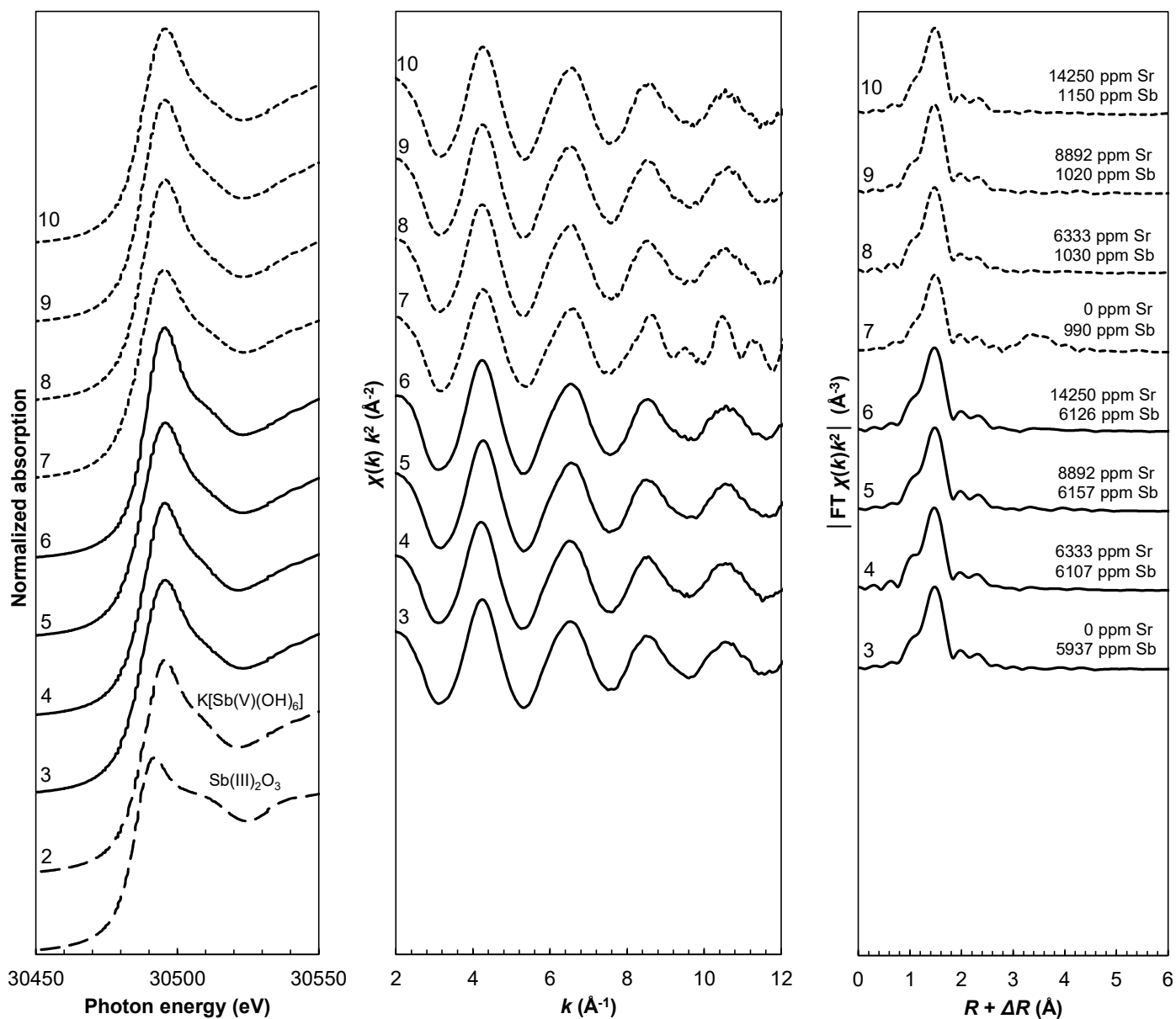
Hardly any differences of Sb K-edge XANES and EXAFS spectra were observed for different element loadings (Sb, Sr, Fe) and pH values. Figures 1 and 2 show  $k^2$ -weighted Sb K-edge EXAFS spectra and their corresponding

Fourier-transform (FT) magnitudes for NOM samples pre-loaded with Sr and Fe(III) and reacted with Sb(V) at pH 3 and 5. The XANES spectra of all samples are similar to that of the pentavalent Sb reference  $K[Sb(OH)_6]$ , indicating that Sb(V) was little or not at all reduced after reaction with NOM under oxic conditions. In accordance with previous findings, Sb(V) binding seems to occur directly to O-C-groups regardless of metal-loading and pH. The Sb concentration slightly increased in the Sr-loaded compared to the non-loaded NOM, which may suggest ternary complex formation. However, EXAFS data delivered no indication of Sr backscattered of Sb in Sr-loaded NOM samples (Figure 1). An opposite behavior was observed for the Fe-loaded NOM samples (Figure 2). Here, the Sb concentration of NOM decreased with increasing Fe content, indicating that Fe(III) competes with Sb(V) for the same binding sites. Again, no differences were detected in EXAFS spectra between the Sb(V)-reacted pure and Fe(III)-loaded NOM samples, implying the absence of ternary Sb(V)-Fe(III)-NOM complexes.

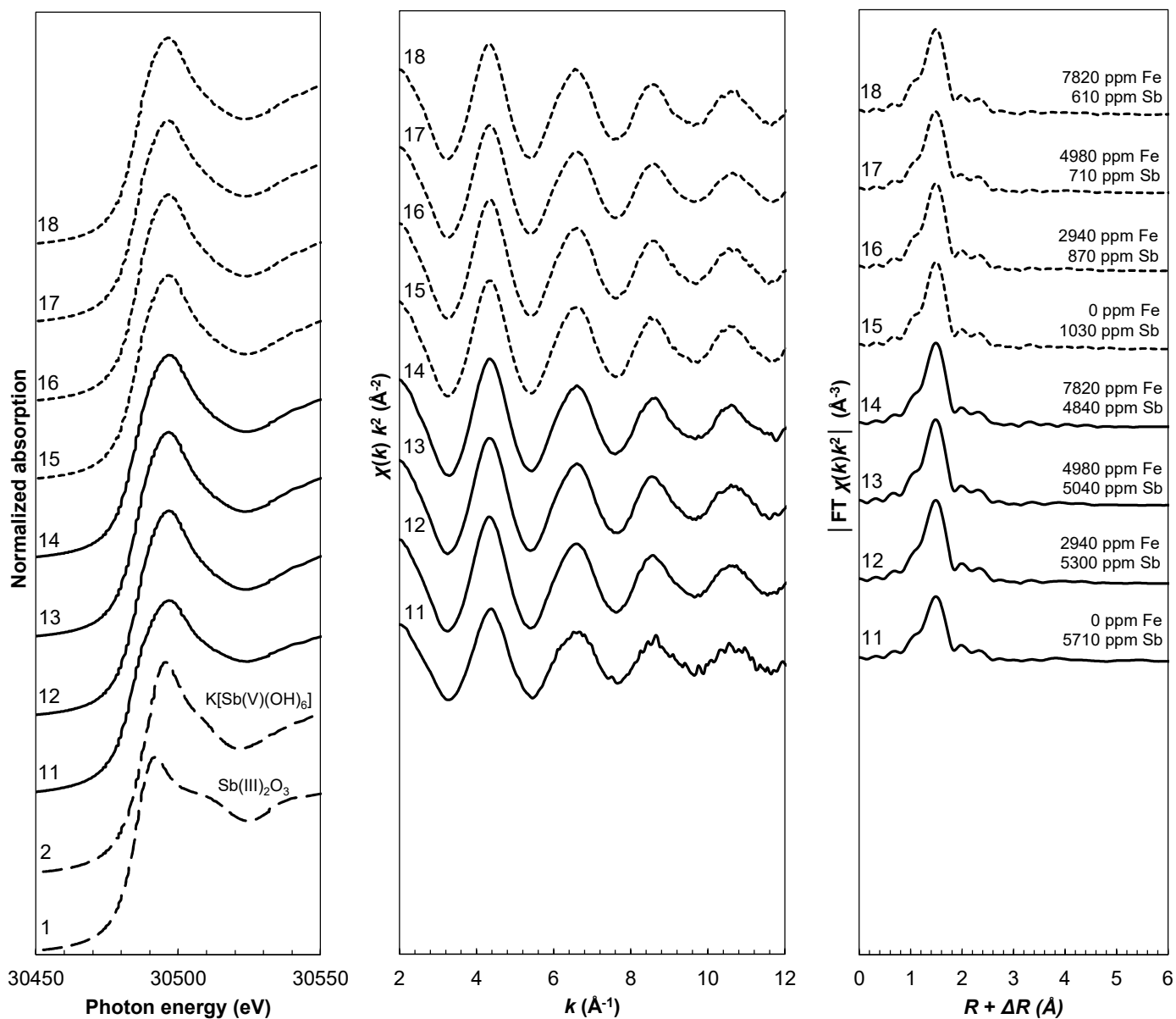
A fundamentally different Sb K-edge EXAFS spectrum was obtained for a pure NOM sample reacted with Sb(V) at pH 5 (Figure 1, sample 7). The broad Fourier-transform peak between 3-4 Å suggests the precipitation of an Sb(V) (oxyhydr)oxide phase and/or the formation of polynuclear organic Sb(V) complexes. Interestingly, a similarly prepared NOM sample reacted with Sb(V) at pH 3 did not show this spectral feature (Figure 1, sample 3).

Figures 3 and 4 illustrate normalized  $k^2$ -weighted Sr and Fe K-edge EXAFS spectra and their corresponding FT magnitudes, respectively, for all NOM samples prepared at pH 3 and 5. No spectral differences were observed for the Sr-loaded NOM samples reacted with Sb(V). The absence of Sb-related FT-peaks beyond the first O shell implies the absence of Sb(V)-Sr-NOM complexes. A higher spectral variation was observed for the Fe K-edge EXAFS spectra (Figure 4). All Fe K-edge EXAFS FTs showed a prominent peak at ca. 2.4 Å (uncorrected for phase shift), implying Fe(III) complexation by carboxyl/hydroxyl groups of NOM. Regardless of the specific Fe coordination, the FTs of Sb K-edge EXAFS spectra of Fe-loaded and Sb(V) reacted NOM samples showed no signs of Fe neighbors of Sb (Figure 2).

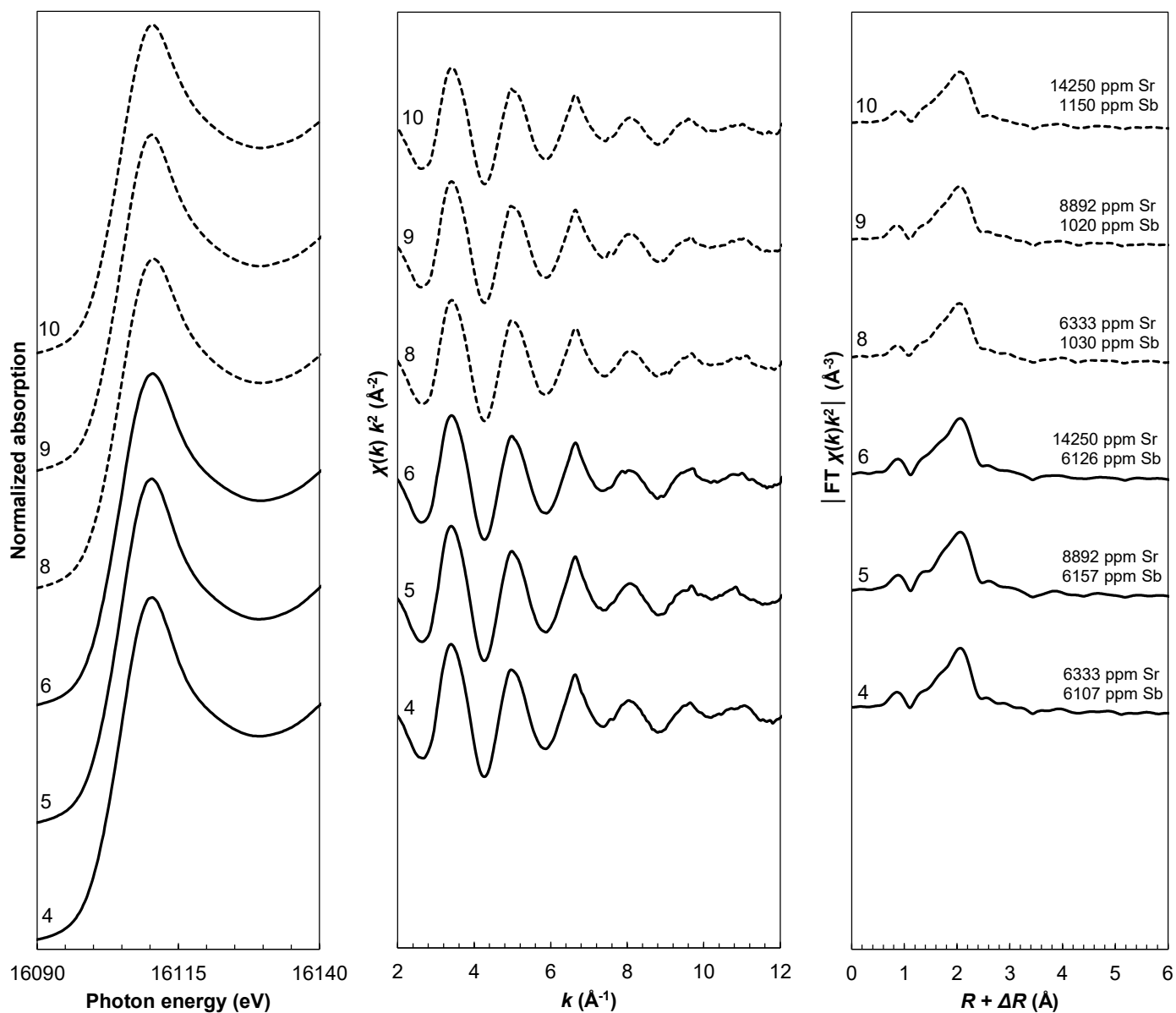
Based on qualitative data analysis, our tentative conclusion is that Sb(V) does not form ternary NOM complexes with Sr and Fe(III) at pH 3 and pH 5. We will support this conclusion by detailed shell-fit analyses and wish to thank Mr. Damien Prieur for performing the measurements at ESRF.



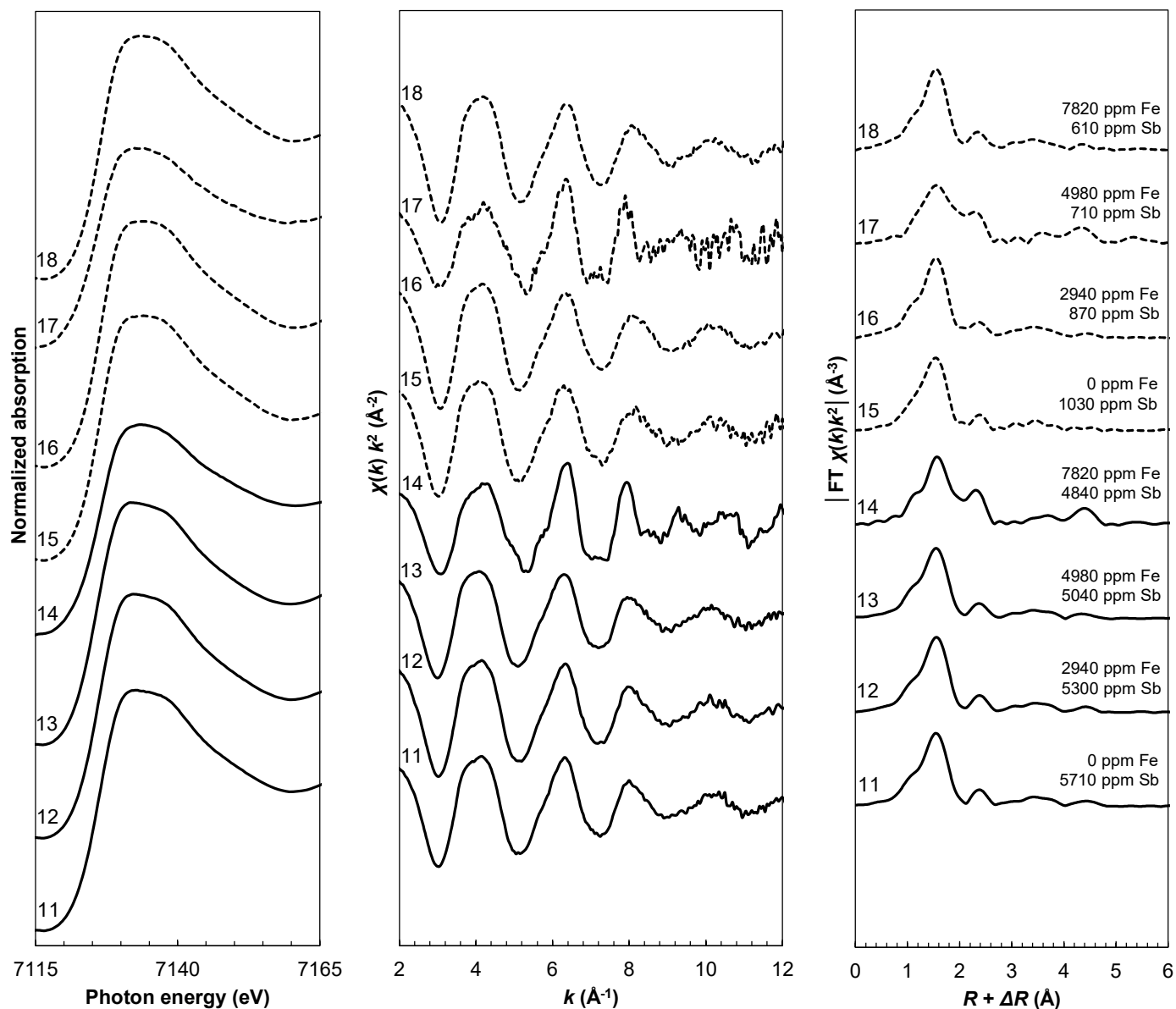
**Figure 1:** Experimental  $k^2$ -weighted Sb K-edge EXAFS spectra and their corresponding FT magnitudes of NOM samples loaded with Sr and Sb(V). Dashed lines = references (XANES), solid lines = NOM reacted with Sb(V) at pH 3, dotted lines = NOM reacted with Sb(V) at pH 5.



**Figure 2:** Experimental  $k^2$ -weighted Sb K-edge EXAFS spectra and their corresponding FT magnitudes of NOM samples loaded with Fe(III) and Sb(V). Dashed lines = references (XANES), solid lines = NOM reacted with Sb(V) at pH 3, dotted lines = NOM reacted with Sb(V) at pH 5.



**Figure 3:** Experimental  $k^2$ -weighted Sr K-edge EXAFS spectra and their corresponding FT magnitudes for NOM samples, loaded with Sr and Sb(V). Solid lines = NOM reacted with Sb(V) at pH 3, dotted lines = NOM reacted with Sb(V) at pH 5.



**Figure 4:** Experimental  $k^2$ -weighted Fe K-edge EXAFS spectra and their corresponding FT magnitudes of NOM samples loaded with Fe(III) and Sb(V). Solid lines = NOM reacted with Sb(V) at pH 3, dotted lines = NOM reacted with Sb(V) at pH 5.