1. Description of Synthesis Method

Green rust sulfate was synthesized in this study using a modified version of the co-precipitation method from Géhin et al. (2003) [1]. Separate solutions of $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot H_2O$ were synthesized, purged with N_2, and transferred to an anaerobic chamber. The $Fe_2(SO_4)_3 \cdot H_2O$ solution was added dropwise to the $FeSO_4 \cdot 7H_2O$ solution using a peristaltic pump, and the pH was maintained at a constant value of 7.0 by manual addition of 1M NaOH. During the synthesis, Fe (III) concentrations were low enough that side products such as ferrihydrite were not able to precipitate. In addition, since the overall Fe(II)/Fe(III) ratio was 2 after mixing of the two solutions, the suspension had a known [Fe(II)] primarily bound in the solid phase, preventing the products of side reactions between Cr(VI) and Fe^{2+} in the aqueous phase from forming. However, this synthesis method is only effective if the product is not aged for longer than 24 hours, as partial transformation of green rust to ferrihydrite occurs when there is no Fe^{2+} in solution to stabilize it.

2. XAS Methodology

All XAS experiments were carried out at the ANKA synchrotron facility in Eggenstein-Leopoldshafen, Germany. The storage ring at this facility operates at 2.50 GeV. The incident x-ray beam was scanned through the Cr and Fe K-edges (edge set at 5989 eV for metallic Cr and 7112 eV for metallic Fe) using a Si (111) crystal pair as a monochromator with a fixed-beam exit. An amount of each sample or reference standard calculated by the program XAFSMass [2] was mixed with cellulose powder, homogenized and pressed into a pellet. Each spectrum was collected in both transmission and fluorescence mode with an approximate energy range of -200 eV to 1000 eV for a total of two (reference compounds) or three scans (samples). Transmission spectra were collected using three ADC IC-Type ionization chambers with Kapton windows, and fluorescence spectra were collected using a Gresham 7-element Si (Li) detector. All spectra were calibrated with a Cr or Fe metal foil placed between ionization chambers 2 and 3.

Data reduction and analysis of the EXAFS spectra were performed using the Athena/Artemis software package (Ravel & Newville, 2005) [3]. The transmission spectra, which had less noise than the fluorescence spectra, were normalized using a third-order spline function to represent the background atomic absorption or fluorescence, and replicate scans of each reference compound and sample were merged. EXAFS linear combination fits were performed on the k^3-weighted χ (k) Fe spectra of each sample between 3 and 12 Å. For all Fe LCF fits, the total number of contributing reference standards was limited to four. All Fe reference compounds were synthesized according to the standard synthesis protocols in Cornell & Schwertmann (2008) [4].

The k^3-weighted χ (k) Cr EXAFS spectra were Fourier-transformed over a k-range of 3 to 10.5, bound by a Hanning window with a dk value of 1, to transform the spectra to R-space. Shell-fitting was performed using the Artemis software. Theoretical phase and amplitude functions were calculated using the embedded FEFF program from the crystal structure of lepidocrocite (Wyckoff, 1963) [5] in which half of the Fe was replace by Cr to account for the γ-MeOOH structure of Cr (III) hydroxide. S_0^2 was constrained to a value (0.7) determined by performing a similar fit on an EXAFS spectrum of eskolaite (Cr_2O_3), and E0 was constrained at -4.5. Fits were performed using three single-scattering paths: Cr-O (1.98 Å), edge-sharing Cr-Cr (3.05 Å) and single-corner sharing (3.98 Å). Other single- and multiple-scattering pathways were tested but ultimately excluded because they failed to improve the fit or produced unphysical parameter solutions. The coordination numbers of the first two shells were fixed after a preliminary fit excluding the third shell, and the edge-sharing and single corner-sharing Cr-Cr pathways were constrained to share the same Debye-Waller parameter value. A similar procedure was used by Charlet & Manceau (1992) [6].

3. Synthesis of Cr-bearing Reference Standards

In order to attempt linear combination fitting of the Cr EXAFS sample spectra, a series of Cr (III)-bearing reference standards was synthesized. The synthesis methods for standards that were detected during fitting are outlined below.

3.1 Cr (III)-bearing Ferrihydrite

The 2-line ferrihydrite synthesis method from Cornell & Schwertmann (2008) [4] was used here, with Cr substitution. A 0.15 M $Fe(NO_3)_3$, 0.05 M $Cr(NO_3)_3$ solution was prepared and the pH value was adjusted to 7.0 by dropwise addition of 1M NaOH. The product was purified by dialysis and air-dried, then stored as a solid.

3.2 Cr (III)-bearing Goethite

The synthesis method outlined in Cornell & Schwertmann (2008) [4] for synthesis of Cr-bearing goethite was used, with slight modifications. Instead of aging the product at 70°C for 111 days, the synthesis was terminated after 30 days due to time limitations. The poorly-crystalline portion of the solid was dissolved using 5M H_2SO_4, then filtered, air-dried and stored as a solid.

3.3 *Cr (III)-bearing Feroxyhyte*

For this synthesis, the Cornell & Schwertmann synthesis method for feroxyhyte was used, but 0.05 M $CrCl_3$ was added to the initial solution prior to H2O2 addition so that Cr (III) was incorporated into the final product.

4. Cr EXAFS Linear Combination Fits

Linear combination fits were also performed on the Cr EXAFS data, but were excluded from the manuscript. After normalizing the EXAFS spectra, linear combination fits incorporating a series of Cr(III)-bearing solids were performed using the ATHENA software. All fits were limited to a maximum of four reference standards. Fig. 1 shows the Cr EXAFS data and linear combination fits, as well as the reference standards used to construct the fits. The fit statistics are shown in Table 1. HMO refers to hydrous metal oxide, but is actually a Cr (III)-bearing ferrihydrite standard.

	Weights					
Sample	Feroxyhyte	HMO*	Goethite	Sum	R-factor	X^2
S1 24h	0.34	0.371	0.25	0.961	0.0113	0.115
S1 7d	0.272	0.538	0.229	1.039	0.0142	0.2083
S2 24h	0.204	0.486	0.3	0.99	0.0116	0.125
S2 7d	0.184	0.554	0.23	0.986	0.0197	0.2491
S3 24h	0.244	0.626	0.131	1.001	0.0112	0.121
S3 7d	0.032	0.593	0.396	1.021	0.0181	0.2575
S4 24h	0.311	0.7	0.016	1.027	0.012	0.137
S4 7d	0.125	0.681	0.152	0.958	0.0059	0.0711
S5 24h	0.162	0.695	0.141	0.998	0.0078	0.0829
S5 7d	0.077	0.684	0.241	1.002	0.0063	0.0843
S6 24h	0.145	0.661	0.192	0.998	0.0086	0.0917
S6 7d	0.117	0.745	0.11	0.972	0.0072	0.0889

Table 1 Cr linear combination fit results and fit statistics. Samples fit to Cr reference standards synthesized using methods outlines by Cornell and Schwertmann (2008). Fits were constrained to no more than three standards. *HMO refers to hydrous metal oxide. Actual standard was Cr (III)-substituted ferrihydrite.

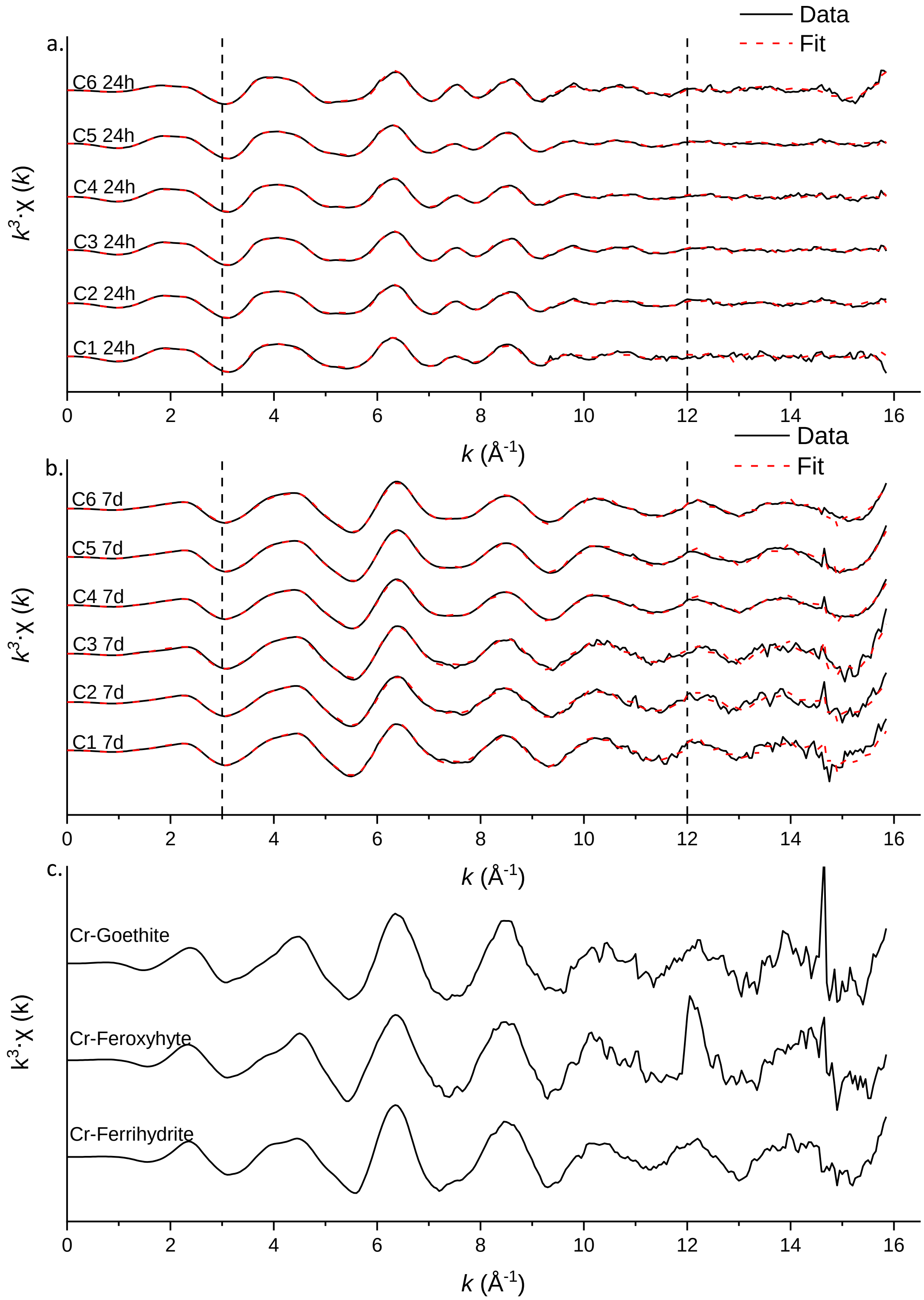

Figure 1 Cr k^3- weighted EXAFS spectra of samples aged for 24 hours (a) and 7 days (b). Fits are linear combinations of Cr-bearing reference standards (c).

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