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# Supplementary Information for Environmental Science: Processes & Impacts

# Synergistic inhibition of green rust crystallization by coexisting arsenic and silica

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This Supplementary information contains: 16 pages, 7 figures and 5 tables.

## Text S1. Arsenic K-edge X-ray absorption spectroscopy (XAS)

#### Pellet preparation and protocol for preventing sample oxidation

Pellets were prepared in a glovebox at GFZ Potsdam by mixing powder samples with cellulose based on calculations using XAFSmass software.<sup>1</sup> Pellets were sealed inside 2 layers of single-sided 70-µm thick Kapton® polyimide tape, and then placed inside air-tight headspace crimp vials stored in an anaerobic jar, preventing oxidation during transport to the beamline. Sample vials were immediately transferred to the glovebox (Ar atmosphere, MBRAUN) upon arrival at the beamline.

#### Details of As K-edge XAS data collection

Arsenic K-edge XAS data were collected at BM23 of the European Synchrotron Radiation Facility (ESRF, Grenoble, France).<sup>2</sup> Spectra were recorded at 77 K both in transmission and fluorescence mode out to a reciprocal space value of 14 Å<sup>-1</sup>. For this, a cryostat was used with helium convection. Fluorescence data were collected using an Si vortex detector. The vertical dimension of the X-ray beam during data collection was 1 mm and the horizontal dimension was 2 mm. To prevent second-order harmonics, rejection mirrors were used. A Si(111) crystal pair with a fixed beam exit was used as a monochromator and the maximum in the first derivative of an Au foil was used to calibrate the beam at 11919 eV (Au L<sub>3</sub> edge). The XANES region was measured with 0.35 eV steps. About 4 to 6 scans were collected for each sample depending on data quality. Multiple scans were collected for each sample depending on data quality (at least 4 scans). Changes in line shape and peak position indicative of beam-induced redox reactions were examined and no beam damage was observed during spectra collection. Spectra were aligned, averaged, and background-subtracted using the SIXpack software.<sup>3</sup>

#### Shell-by-shell fitting routine

Shell-by-shell fits were performed from 1 to 4 Å in R+ $\Delta$ R-space using SIXPack software,<sup>3</sup> based on algorithms derived from IFEFFIT.<sup>4</sup> The fits included the interatomic distance (*R*), the coordination number (*CN*), the mean squared atomic displacement parameter ( $\sigma^2$ ), and the change in threshold energy ( $\Delta E_0$ ) for one sample. Phase and amplitude functions for single and multiple scattering paths were calculated using FEFF6<sup>5</sup> and included As-O, As-O-O and As-Fe paths derived from the structure of scorodite.<sup>6</sup> In preliminary fits, the *CN* and  $\sigma^2$  were found to be highly correlated, which produced high fit-derived standard errors in these fitting parameters. Therefore, following previous work,<sup>7,8</sup> we constrained  $\sigma^2$  to 0.01 and 0.009 in the second shell fits (As-Fe path) for FHY and GR<sub>SO4</sub>, respectively, to reduce the high correlations. Consistent with previous work,<sup>8,9</sup> the passive electron reduction parameter,  $S_0^2$ , in each fit was set to 1.0. The goodness-of-fit was assessed based on the R-factor, which is defined as the mean square difference between the fit and the data on a point-by-point basis: R-factor =  $\sum_i (data_i - fit_i)^2 / \sum_i (data_i)^2$ . An R-factor <0.05 is considered to reflect a reasonable fit.<sup>10</sup>

# F-test analysis for EXAFS

The validity of the addition of all scattering paths was evaluated using the F-test for EXAFS suggested by Downward et al.<sup>11</sup> This F-test, which has also been applied in many previous studies,<sup>12,13</sup> is used to assess whether the addition of an additional path (i.e. atomic correlation) statistically improved the fit. The EXAFS fitting data used for the F-test calculations and the test results can be found in Table S5. The confidence level  $\alpha$  denotes the probability of the new fit with the additional path is improved the previous EXAFS fit. In our analysis, we keep the same threshold proposed by Downward et al. that an  $\alpha$ -value greater than 67% improves the EXAFS fit.

# Additional As(III) bonding geometries for GR<sub>SO4</sub>

Fitting the second neighbor contribution using an As-Fe path considering other bonding geometries (i.e., monodentate mononuclear (<sup>1</sup>*V*), edge-sharing (<sup>2</sup>*E*); see Fig. S7) resulted in unrealistic fits (negative *CN* values). Adding a second As-Fe path in addition to in addition to the bidentate binuclear inner-sphere (<sup>2</sup>*C*) complex with either <sup>1</sup>*V* or <sup>2</sup>*E* geometries were also not supported by the fit. Moreover, an additional As-As path corresponding to As(III) oligomers (*CN*<sub>As-As</sub> ≈ 1-3, *R*<sub>As-As</sub> ≈ 3.3 Å), previously observed for GR<sub>CI</sub> and GR<sub>CO3</sub>,<sup>14,15</sup> were also added to the As-Fe path with <sup>2</sup>*C* complex. However, this yielded unreasonable fitting parameters, supporting recent studies wherein the presence of such As(III) oligomers were also not observed.<sup>16-18</sup>

## Text S2. Fourier transform infrared (FTIR) spectroscopy

#### Protocol for preventing sample oxidation

Dry powder samples were placed inside 2-mL glass vial and then put in crimp capped glass vials to prevent oxidation during transport. Sample vials were opened just before each spectrum was collected.

#### Phase identification of unconverted ferrihydrite precursor

Identification of ferrihydrite (FHY) by XRD is often very difficult due to its nanocrystalline nature. In this work, this problem is compounded by the intense basal reflections of  $GR_{SO4}$  (00/) from preferential orientation effects. However, the FTIR spectra of FHY synthesized under normal atmospheric conditions exhibit characteristic bands at 1460 and 1350 cm<sup>-1</sup>, which comes from the asymmetric and symmetric stretching mode of adsorbed carbonate [ $v(CO_3)$ ] from  $CO_{2(g)}$  dissolution.<sup>19,20</sup> The presence of these characteristic bands can therefore indicate the presence of untransformed FHY precursor in the reacted solids.

#### Speciation and local bonding environment of mineral-bound Si

The vibrations associated with Si can be found in the region of interest between 1250 and 950 cm<sup>-1</sup>. We considered three possible mineral-bound Si species based from the previous works of Swedlund et al.<sup>21</sup> and Goberna-Ferrón et al.<sup>22</sup>: (i) monomers (i.e. inner-sphere surface complexes; 890-980 cm<sup>-1</sup>); (ii) oligomers (1000-1150 cm<sup>-1</sup>); and (iii) polymers (>1150 cm<sup>-1</sup>). We cross-checked these peak assignments with our synthetic Si-bearing ferrihydrites (i.e. adsorbed and coprecipitated<sup>23</sup>). We deconvoluted the IR band for both adsorbed and co-precipitated Si (Fig. S2) using a mixture of Gaussian and Lorentzian function (G:L ratio  $\ge$  0.7), ensuring that we use the fewest number of components possible. The details of component bands are presented in Table S2, including the band assignment for Si species.

With our samples, however, this FTIR region also coincides with the strong bands assigned to the (splitted) sulfate stretching region  $[v_3(SO_4)]$  at 1098 cm<sup>-1</sup> arising from the interlayer SO<sub>4</sub><sup>2-</sup> of GR. Using the IR spectra of a pure GR<sub>SO4</sub> (reference phase), we have assigned the following bands for  $v_3(SO_4)$ : 1131, 1101, 1075 and 1043 (Fig. S3, Table S4). Thus, for the deconvolution routine, we fitted the sample FTIR spectrum first with the 4 component bands of  $v_3(SO_4)$  from GR<sub>SO4</sub>, ensuring that the band shape parameters (i.e. height and area ratios) are kept similar to the reference spectra (see Table S4). We then added the minimum number of component bands attributed to Si species to prevent overfitting the dataset. Finally, we checked and adjusted the band shape parameters (i.e., FWHM, G:L ratio) of the  $v_3(SO_4)$  component bands to verify if the values have drifted from the desired height and area ratios. Using procedure, we were able to selectively assign the specific component bands associated with Si species in our experimental samples (see Fig. S4 for example fitting).

# **S3. Supplementary Figures and Tables**

Fe phase precursor	рН	Initial [Fe(III) <sub>solid</sub> ] (mM)	Fe <sup>2+</sup> (aq)/ Fe(III) <sub>solid</sub>	As/Fe <sub>solid</sub>	Si/Fe <sub>solid</sub>	As oxidation state	Mineral end- product	Reference
As only LP	6.6	6	0.5	0.008	-	+3	MGT	Wang et
				0.040	-	+5 +3 +5		al
FHY	8.0	4	3	0.012	-	+3 +5	GR <sub>SO4</sub> MGT	Perez et al. <sup>25</sup>
Si only								
LP	7.0	15	0.2	-	0.08	-	LP	Schulz et
Si–FHY	7.0	15	0.2	-	0.05	-	LP, GOE	al. <sup>26</sup>
FHY	8.0	4	3	-	0.08	-	GR <sub>SO4</sub> , MGT	This work
As + Si FHY	8.0	4	3	0.012	0.12	+3 +5	GR <sub>SO4</sub> GR <sub>SO4</sub>	This work

**Table S1.** Studies on the Fe<sup>2+</sup>-induced transformation of As– and/or Si–bearing Fe(III) mineral phases under anoxic and circum-neutral pH conditions.

Note: FHY – ferrihydrite, GOE – goethite,  $GR_{Cl}$  – green rust chloride,  $GR_{SO4}$  – green rust sulfate, LP – lepidocrocite, MGT – magnetite, Si–FHY – Si-coprecipitated ferrihydrite.



**Fig. S1** Changes in the dissolved (a) As and (b) Si concentrations in the supernatant after preequilibration with FHY at pH 8 for 24 h.

**Table S2.** ICP-OES data for quality control solutions (QC) that were prepared from single element standard solutions (Merck, CertiPur) to achieve chemical compositions similar to the experimental sample solutions. The mean results of *n* replicate analyses are given together with the standard deviation (SD) and relative standard deviation (RSD) (SD represents 68% of the population, 2SD represents 95% of the population). The measured deviation from the reference value is a quantitative estimation of accuracy.

	As (mg L <sup>-1</sup> )	Fe (mg L <sup>-1</sup> )	S (mg L <sup>-1</sup> )
Wavelength (nm)	193.696	261.382	181.972
Instrumental limits			
Limit of detection (LoD)	0.015	0.171	0.233
Limit of quantification (LoQ)	0.044	0.373	0.521
Quality control			
QC verify $(n = 9)$	0.574	6.301	6.298
SD	0.010	0.061	0.020
RSD	1.67%	1.94%	0.32%
2RSD	3.34%	1.94%	0.65%
Reference value	0.579	6.284	6.222
Uncertainty	0.003	0.063	0.008
Measured deviation from reference value	0.86%	0.26%	1.22%



**Fig. S2** Deconvoluted FTIR spectra of synthetic Si-bearing ferrihydrites (reference phases): (a) adsorbed Si ( $C_0 = 1 \text{ mM}$ ) and (b) coprecipitated Si (molar Si/Fe = 0.75) in the range between 1200 to 800 cm<sup>-1</sup> showing the different Si species.

No.	Band position (cm <sup>-1</sup> )	Band height (a.u.)	FWHH (cm <sup>-1</sup> )	G:L ratio	Integrated area (a.u.)	Band assignment	Relative contribution	
Si-ad	sorbed FHY							
1	831	0.004	23	0.74	0.11			
2	853	0.007	37	0.81	0.32	Manamaria Ci	400/	
3	905	0.038	74	1.00	3.02	Monomeric Si	40%	
4	955	0.037	62	1.00	2.47			
5	1004	0.049	65	1.00	3.41			
6	1046	0.023	55	0.83	1.48	Oligomeric	E 40/	
7	1087	0.022	63	0.88	1.55	Si	54%	
8	1135	0.010	48	0.81	0.57			
Si-co	precipitated FHY							
1	853	0.033	65	0.70	2.61			
2	895	0.095	83	0.84	8.98	Monomeric Si	57%	
3	948	0.083	80	0.87	7.45			
4	1001	0.086	79	0.92	7.43			
5	1046	0.032	66	0.83	2.41	Oligomorio Ci	400/	
6	1087	0.035	73	0.90	2.87	Oligometic Si	42%	
7	1139	0.019	59	0.85	1.24			
8	1171	0.007	44	0.80	0.36	Polymeric Si	1%	

**Table S3.** Details of the deconvolution of FTIR spectra of Si-bearing ferrihydrites in the spectral range between 1200 to 800 cm<sup>-1</sup>.

Note: FWHH denote full width at half height, and G:L ratio refer to the Gaussian/Lorentzian ratio used for the fitting.



**Fig. S3** Deconvoluted FTIR spectrum of synthetic  $GR_{SO4}$  (reference phase) in the range between 1200 to 950 cm<sup>-1</sup>.

Table S4.	Details of the	deconvolution of	f FTIR	spectra	of synthetic	GR <sub>SO4</sub>	(duplicate	samples)	in the
spectral ra	nge between	1200 to 950 cm <sup>-7</sup>	۱ <u>.</u>						

No.	Band position	Band height	3and height FWHH		Integrated	Band height	Area
	(cm <sup>-1</sup> )	(a.u.)	(cm <sup>-1</sup> )	0.2.10.00	area (a.u.)	ratio*	ratio*
GR <sub>SO4</sub> –	- Sample 1						
1	1043	0.063	51	0.78	3.8	0.22	0.37
2	1075	0.161	41	0.82	7.6	0.56	0.75
3	1101	0.288	31	0.86	10.2	1.00	1.00
4	1131	0.067	27	0.75	2.1	0.23	0.21
GR <sub>SO4</sub> –	Sample 2						
1	1042	0.061	54	0.75	3.9	0.22	0.38
2	1076	0.162	43	0.79	8.1	0.57	0.80
3	1101	0.282	31	0.81	10.2	1.00	1.00
4	1131	0.066	27	0.74	2.1	0.23	0.20

Note: FWHH denote full width at half height and G:L ratio refer to the Gaussian/Lorentzian ratio used for the fitting.



**Fig. S4** Deconvoluted FTIR spectra of (a) Si, (b) As(III)+Si and (c) As(V)+Si bearing solids after 24 h of reaction in the range between 1200 to 950 cm<sup>-1</sup>. (d) Superimposed FTIR spectra of the As/Sibearing solids, highlighting the difference between each spectra.



**Fig. S5** FTIR spectra of solids collected at different elapsed times during the Fe<sup>2+</sup>-induced transformation of the various FHY systems: (a) Si–FHY, (b) As(III)+Si–FHY and (c) As(V)+Si–FHY. (d) Spectra of synthetic reference phases FHY, Si-bearing hydrous ferric oxide (HFO) and GR<sub>SO4</sub> are shown for comparison. Note: '\*' denotes symmetric and antisymmetric stretching band v(CO<sub>3</sub>) from adsorbed CO<sub>2</sub>-impurity in FHY<sup>19,20</sup> and ' $\bigstar$ ' refers to OH deformation of GR<sub>SO4</sub>.<sup>27</sup>



**Fig. S6** Changes in the concentration of dissolved (a)  $Fe^{2+}$  and (b)  $SO_4^{2-}$  during the  $Fe^{2+}$ -induced transformation of FHY in the presence of Si and either As(III) or As(V).



**Fig. S7** Possible bonding geometries for As(III) and As(V) inner-sphere surface complexes at the GR particle edges:  ${}^{2}C$  – bidentate binuclear geometry (double corner sharing,  $R_{As-Fe} \approx 3.4$  Å),  ${}^{1}V$  – monodentate mononuclear geometry (single corner sharing,  $R_{As-Fe} \approx 3.5$  Å),  ${}^{2}E$  – bidentate mononuclear geometry (edge-sharing,  $R_{As-Fe} \approx 3.0$  Å). As(III) oligomers (As<sup>III</sup><sub>x</sub>O<sub>2x+1</sub>) were also considered based on previous studies of Wang et al.<sup>14</sup> and Ona-Nguema et al.<sup>15</sup>

Fit	Atomic pairs	CN	<i>R</i> (Å)	σ² (Ų)	$\Delta E_0$ (eV)	$\chi^2$	$\chi v^2$	R-factor	NIDP	NVARYS	DF	Confidence level α (%)
As(III)+Si–FHY, 168 h												
As-MS only	As-O	3.4 (0.4)	1.78 (0.01)	0.004 (0.001)	9.7 (1.6)	699	56	0.0306	16.5	4	12.5	
	As-O-O	6	1.82(R <sub>As-O</sub> ) = 3.24	σ² (As-O)								
Addition of As-Fe ( <sup>2</sup> C)	As-O	3.5 (0.3)	1.78 (0.01)	0.004 (0.001)	9.5 (1.5)	504	48	0.0220	16.5	6	10.5	82.2%
	As-O-O	6	1.82(R <sub>As-O</sub> ) = 3.24	σ² (As-O)								
	As-Fe	1.0 (0.5)	3.39 (0.03)	0.009								
As(V)+Si–FHY, 168 h												
As-MS only	As-O	4.3 (0.5)	1.70 (0.01)	0.003 (0.001)	4.8 (1.8)	1355	108	0.0249	16.5	4	12.5	
	As-O-O	12	1.82(R <sub>As-O</sub> ) = 3.09	σ² (As-O)								
Addition of As-Fe ( <sup>2</sup> C)	As-O	4.3 (0.4)	1.69 (0.01)	0.003 (0.001)	4.5 (1.5)	864	82	0.0159	16.5	6	10.5	90.6%
	As-O-O	12	1.82(R <sub>As-O</sub> ) = 3.08	σ² (As-O)								
	As-Fe	1.4 (0.6)	3.36 (0.03)	0.009								

Table S5. Summary of the F-test analysis of the additional scattering paths used in the As K-edge EXAFS fitting.

Note: CN, coordination number; *R*, interatomic distance;  $\sigma^2$ , mean-squared atomic displacement;  $\Delta E_0$ , change in threshold energy;  $\chi^2$ , chi-square;  $\chi_v^2$ , reduced chi-square; N<sub>IDP</sub>, number of independent points; N<sub>VARYS</sub>, number of variables; DF, degrees of freedom; and Confidence level  $\alpha$ , statistical validity that the added scattering path improved the fit, calculated by the F-test for EXAFS.<sup>11</sup> The passive electron reduction factor ( $S_0^2$ ) was fixed at 1.0. The multiple scattering As-O-O path was constrained geometrically to the single scattering As-O path ( $R_{As-O-O} = 1.82 \times R_{As-O}$ ). All fits were carried out from 1 to 3.5 Å in  $R+\Delta R$  - space.

# References

- 1. K. Klementiev and R. Chernikov, XAFSmass: A program for calculating the optimal mass of XAFS samples, J. Phys. Conf. Ser., 2016, **712**, 012008.
- O. Mathon, A. Beteva, J. Borrel, D. Bugnazet, S. Gatla, R. Hino, I. Kantor, T. Mairs, M. Munoz, S. Pasternak, F. Perrin and S. Pascarelli, The time-resolved and extreme conditions XAS (TEXAS) facility at the European Synchrotron Radiation Facility: The general-purpose EXAFS bending-magnet beamline BM23, J. Synchr. Radiat., 2015, 22, 1548-1554.
- 3. S. M. Webb, SIXpack: a graphical user interface for XAS analysis using IFEFFIT, Phys. Scr., 2005, **T115**, 1011-1014.
- 4. M. Newville, IFEFFIT: Interactive XAFS analysis and FEFF fitting, J. Synchr. Radiat., 2001, **8**, 322-324.
- 5. J. J. Rehr, R. C. Albers and S. I. Zabinsky, High-order multiple-scattering calculations of X-rayabsorption fine structure, Phys. Rev. Lett., 1992, **69**, 3397-3400.
- K. Kitahama, R. Kiriyama and Y. Baba, Refinement of the crystal structure of scorodite, Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry, 1975, **31**, 322-324.
- C. M. van Genuchten, S. E. Addy, J. Pena and A. J. Gadgil, Removing arsenic from synthetic groundwater with iron electrocoagulation: an Fe and As K-edge EXAFS study, Environ. Sci. Technol., 2012, 46, 986-994.
- C. Mikutta, J. Frommer, A. Voegelin, R. Kaegi and R. Kretzschmar, Effect of citrate on the local Fe coordination in ferrihydrite, arsenate binding, and ternary arsenate complex formation, Geochim. Cosmochim. Acta, 2010, **74**, 5574-5592.
- D. Paktunc, J. Dutrizac and V. Gertsman, Synthesis and phase transformations involving scorodite, ferric arsenate and arsenical ferrihydrite: Implications for arsenic mobility, Geochim. Cosmochim. Acta, 2008, **72**, 2649-2672.
- S. D. Kelly, D. Hesterberg and B. Ravel, in Methods of Soil Analysis Part 5 Mineralogical methods, eds. A. L. Ulery and L. R. Drees, Soil Science Society of America, Madison, WI, 2008.
- L. Downward, C. H. Booth, W. W. Lukens and F. Bridges, A Variation of the F-Test for Determining Statistical Relevance of Particular Parameters in EXAFS Fits, AIP Conference Proceedings, 2007, 882, 129-131.
- P. Bots, S. Shaw, G. T. W. Law, T. A. Marshall, J. F. W. Mosselmans and K. Morris, Controls on the Fate and Speciation of Np(V) During Iron (Oxyhydr)oxide Crystallization, Environ. Sci. Technol., 2016, **50**, 3382-3390.
- T. A. Marshall, K. Morris, G. T. W. Law, F. R. Livens, J. F. W. Mosselmans, P. Bots and S. Shaw, Incorporation of Uranium into Hematite during Crystallization from Ferrihydrite, Environ. Sci. Technol., 2014, 48, 3724-3731.

- 14. Y. Wang, G. Morin, G. Ona-Nguema, F. Juillot, F. Guyot, G. Calas and G. E. Brown, Evidence for different surface speciation of arsenite and arsenate on green rust: an EXAFS and XANES study, Environ. Sci. Technol., 2010, **44**, 109-115.
- 15. G. Ona-Nguema, G. Morin, Y. H. Wang, N. Menguy, F. Juillot, L. Olivi, G. Aquilanti, M. Abdelmoula, C. Ruby, J. R. Bargar, F. Guyot, G. Calas and G. E. Brown, Arsenite sequestration at the surface of nano-Fe(OH)(2), ferrous-carbonate hydroxide, and green-rust after bioreduction of arsenic-sorbed lepidocrocite by Shewanella putrefaciens, Geochim. Cosmochim. Acta, 2009, 73, 1359-1381.
- 16. S. R. S. Bandaru, C. M. van Genuchten, A. Kumar, S. Glade, D. Hernandez, M. Nahata and A. Gadgil, Rapid and Efficient Arsenic Removal by Iron Electrocoagulation Enabled with in Situ Generation of Hydrogen Peroxide, Environ. Sci. Technol., 2020, 54, 6094-6103.
- C. M. van Genuchten, T. Behrends, S. L. S. Stipp and K. Dideriksen, Achieving arsenic concentrations of <1 µg/L by Fe(0) electrolysis: The exceptional performance of magnetite, Water Res., 2020, 168, 115170.
- J. P. H. Perez, H. M. Freeman, A. P. Brown, C. M. van Genuchten, K. Dideriksen, M. S'Ari, D. J. Tobler and L. G. Benning, Direct visualization of arsenic binding on green rust sulfate, Environ. Sci. Technol., 2020, 54, 3297-3305.
- M. Ristić, E. De Grave, S. Musić, S. Popović and Z. Orehovec, Transformation of low crystalline ferrihydrite to α-Fe2O3 in the solid state, Journal of Molecular Structure, 2007, 834-836, 454-460.
- 20. D. B. Hausner, N. Bhandari, A.-M. Pierre-Louis, J. D. Kubicki and D. R. Strongin, Ferrihydrite reactivity toward carbon dioxide, J. Colloid Interface Sci., 2009, **337**, 492-500.
- P. J. Swedlund, G. M. Miskelly and A. J. McQuillan, Silicic Acid Adsorption and Oligomerization at the Ferrihydrite–Water Interface: Interpretation of ATR-IR Spectra Based on a Model Surface Structure, Langmuir, 2010, 26, 3394-3401.
- 22. S. Goberna-Ferrón, M. P. Asta, B. Zareeipolgardani, S. Bureau, N. Findling, L. Simonelli, J.-M. Greneche, L. Charlet and A. Fernández-Martínez, Influence of Silica Coatings on Magnetite-Catalyzed Selenium Reduction, Environ. Sci. Technol., 2021, 55, 3021-3031.
- 23. A. Voegelin, R. Kaegi, J. Frommer, D. Vantelon and S. J. Hug, Effect of phosphate, silicate, and Ca on Fe(III)-precipitates formed in aerated Fe(II)- and As(III)-containing water studied by X-ray absorption spectroscopy, Geochim. Cosmochim. Acta, 2010, 74, 164-186.
- 24. Y. Wang, G. Morin, G. Ona-Nguema and G. E. Brown, Jr., Arsenic(III) and arsenic(V) speciation during transformation of lepidocrocite to magnetite, Environ. Sci. Technol., 2014, **48**, 14282-14290.
- 25. J. P. H. Perez, D. J. Tobler, H. M. Freeman, A. P. Brown, N. S. Hondow, C. M. van Genuchten and L. G. Benning, Arsenic species delay structural ordering during green rust sulfate crystallization from ferrihydrite, Environ. Sci.: Nano, 2021, 8, 2950-2963.

- 26. K. Schulz, L. K. ThomasArrigo, R. Kaegi and R. Kretzschmar, Stabilization of ferrihydrite and lepidocrocite by silicate during Fe(II)-catalyzed mineral transformation: Impact on particle morphology and silicate distribution, Environ. Sci. Technol., 2022, 56, 5929-5938.
- S. Peulon, L. Legrand, H. Antony and A. Chausse, Electrochemical deposition of thin films of green rusts 1 and 2 on inert gold substrate, Electrochemistry Communications, 2003, 5, 208-213.