

**Supplemental Material for**  
**Polycrystallinity of green rust minerals and their synthetic analogs:**  
**Implications for particle formation and reactivity in complex systems**

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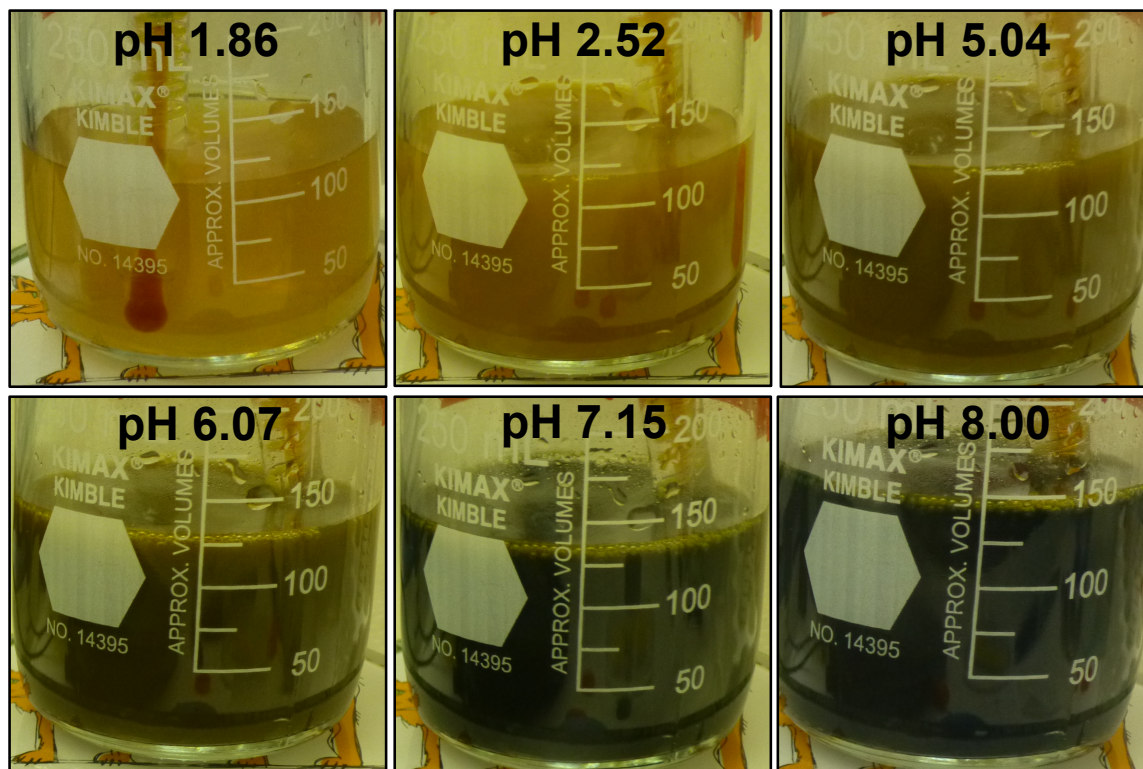
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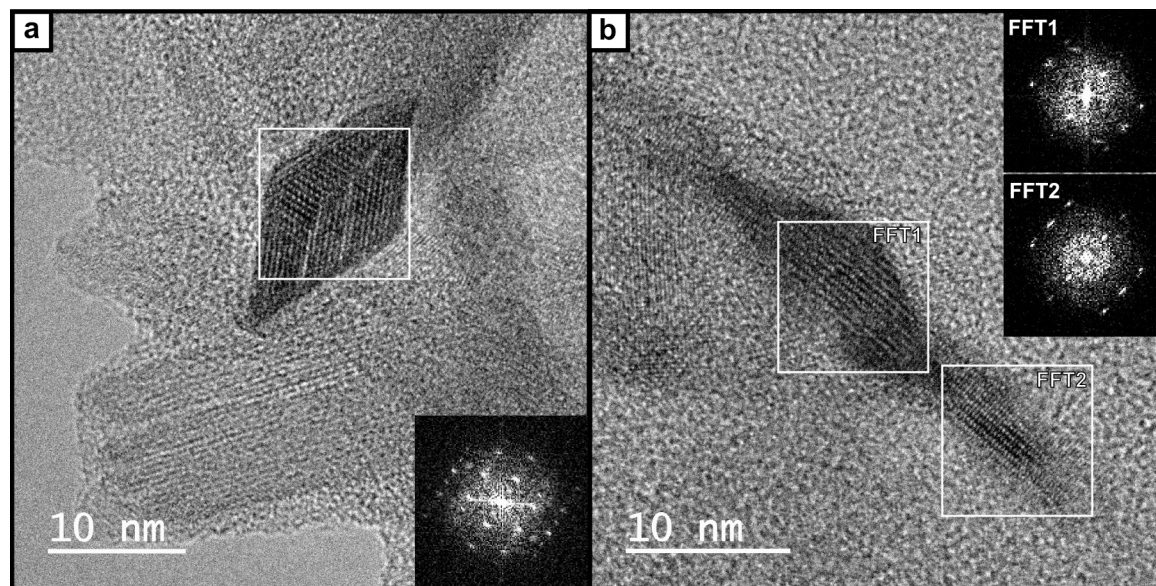
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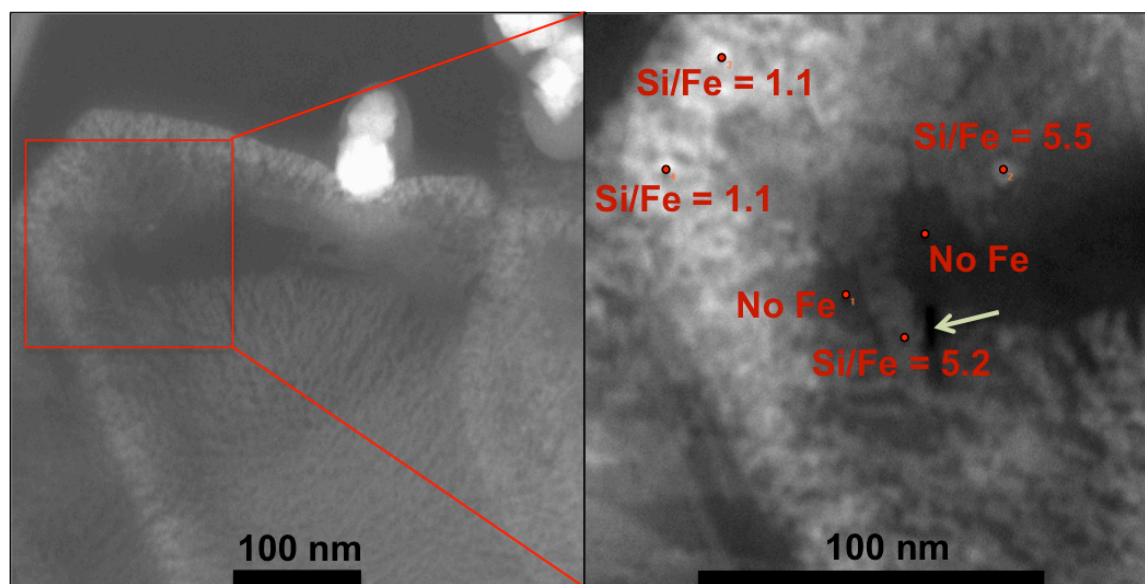
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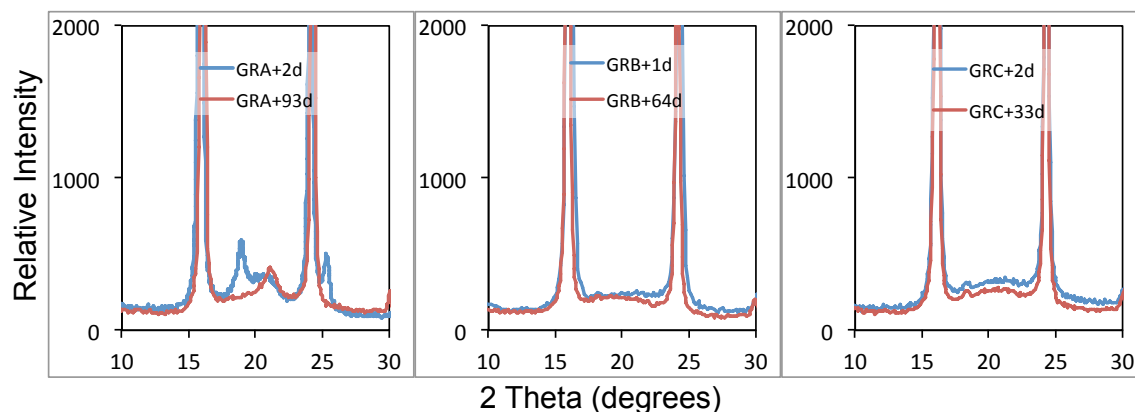
**Figure S1.** Color changes during the slow titration of NaOH into Fe(II)-Fe(III) solution during synthesis GR-A.



**Figure S2.** Additional examples of putative green rust nanorod cross-sections from GR-D. (a) Cross-section that is very similar to the one in Figure 8, with an FFT pattern (inset) that matches exactly with the simulated pattern of sulfate green rust (Simon et al. 2003) oriented along the [100] zone axis. (b) Cross-section with FFT patterns of two regions, which are missing half of the reflections including the (001) reflection.

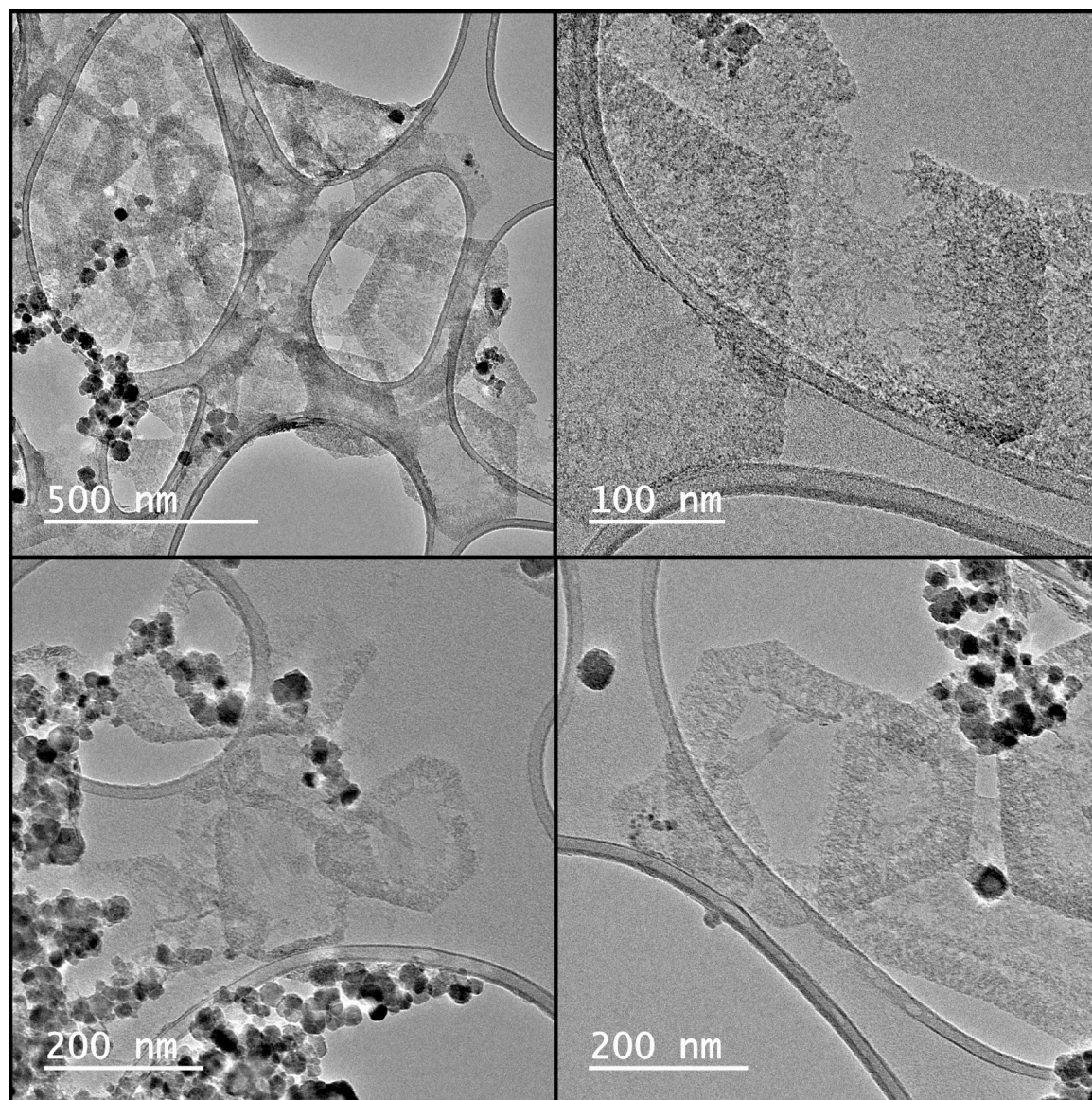


**Figure S3.** Scanning transmission electron microscopy (STEM) high angle annular dark field (HAADF) images of part of a platelet in GR-B (aged 54 days). Bright areas correspond to higher average Z in addition to higher diffraction contrast, i.e. the “dendritic” patterns also observed with TEM in bright field mode. Si/Fe are atomic ratios based on the energy-dispersive X-ray spectroscopy (EDS) analysis of areas approximately 1 nm in diameter, calculated using the thin-film approximation in the TIA software (FEI). Arrow points to a hole burned away by the electron beam during an EDS line scan.



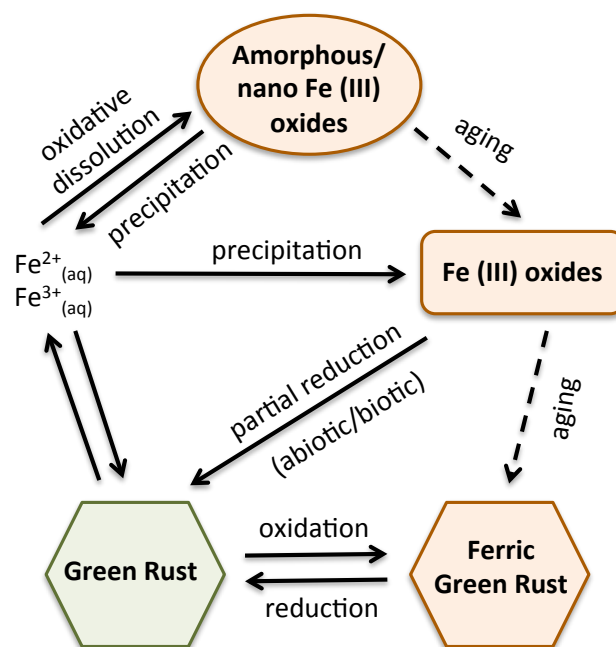
**Figure S4.** Enlarged area (10-30°) of XRD spectra (Figure 4) for GR-A, GR-B, and GR-C showing the weak broad peak centered around 20° that could indicate amorphous silica.





**Figure S5.** Low-magnification images of green rust platelets synthesized in GR-B and aged for 90 days, that are undergoing disintegration. Notice that for the most part, the rims remain intact while the center is removed first.





**Figure S6.** Formation and transformation of green rust in relation to partially and fully oxidized iron species. Figure modified from (Antony et al. 2008).

**Table S1. The d-spacings (in Angstroms) for pseudo-hexagonal platelets found in outflow water and terrace sediment.**

Reference Data <sup>a</sup>					Outflow water i.e. Figures 1-2		Terrace Sediment i.e. Figure 3	
GR-SO <sub>4</sub>		GR-Na <sub>2</sub> SO <sub>4</sub>		hematite	SAED	FFT	SAED	FFT
d	hkl	d	hkl	d	d	d	d	d
11.01	001	10.98	001					
		7.37						
5.51	002	5.49	002					
4.78	100	4.78	110					
					4.45			
4.39	101	4.38	111					
		3.91	021					
					3.86			
3.67	003	3.66	003	3.68	3.73			
					3.55			
					3.37-3.41			
2.91	103	3.07	120				2.94	
2.76, 2.75	110,004	2.75	030,004					
2.68	-1-11	2.67	031	2.69				
		2.60	014		2.57-2.62			
2.47	-1-12	2.46	032	2.51	2.45-2.52	2.54	2.49	2.52-2.61
2.34,2.39	201,200							
2.21	-1-13,005	2.20	033,005	2.20			2.22	
2.00	105,203				2.29			
1.95	-1-14	1.94	034		1.92			
1.81,1.84	210,006	1.80,1.83	140,006	1.84				
1.72	-1-15	1.72	035	1.69				
1.60,1.62	300,213	1.59	330	1.60			1.61	
1.58	301	1.57	331,007					
1.53	302	1.53	332		1.54			1.51
1.49	107	1.49	117	1.49	1.48-1.5		1.48	
1.46	303	1.46	333	1.45	1.43	1.46	1.46	
		1.37	060,334					
		1.36	061	1.35				
		1.33	062		1.28			
		1.29	063,335				1.25	

Note: Figure numbers are given for reference, but the d-spacing values (in Å) are representative of multiple areas. Grey highlighted cells represent the values that appear in a hexagonal pattern when the crystal is oriented along the [001] zone axis. Minus signs preceding numbers represent overbars.

<sup>a</sup>Reference data sources: GR-SO<sub>4</sub> (Simon et al. 2003), GR-Na<sub>2</sub>SO<sub>4</sub> (Christiansen et al. 2009), hematite (ICDD PDF card 00-001-1053 (Hanawalt et al. 1938))

**Table S2. The d-spacing data (in Angstroms) for synthetic green rust materials, from XRD, SAED and FFT.**

Reference Data <sup>a</sup>				GR-A pH8 + 2 days <sup>b</sup>				GR-B + 54 days			
GR-Na <sub>2</sub> SO <sub>4</sub>		goethite	magnetite	i.e. Figure 5				i.e. Figure 6			
d	hkl	d	d	XRD d	SAED d (np's)	SAED d (platelets)	FFT	XRD d	SAED d (np's)	SAED d (platelets)	FFT
10.98	001			11.32				11.07			
7.37									7.52		
5.49	002	4.98		5.57				5.50			
4.78	110		4.85						4.78		
				4.68							
4.38	111			4.30							
		4.19									
3.91	021										
3.66	003			3.69				3.66			
				3.51							
							3.32 <sup>c</sup>				
3.07	120		2.97					2.96	2.94		3.03
2.75	030,004			2.76				2.75			
2.67	031	2.69		2.69				2.68			
2.60	014		2.53	2.55		2.53	2.54-2.57	2.53	2.50	2.55	2.54-2.57
2.46	032	2.45,2.49		2.47				2.46			
			2.42						2.39		
2.20	033,005	2.19		2.21,2.24	2.21			2.20			
			2.10	2.00,2.04				2.08	2.08		
1.94	034			1.95	1.93			1.94	1.91	1.87	
1.80, 1.83	140, 006			1.83				1.81,1.83			
1.72	035		1.72	1.72	1.71			1.72	1.70		
1.59	330	1.66	1.62					1.61	1.59		
1.57	331,007	1.56		1.58				1.57			
1.53	332				1.53						
1.49	117		1.49			1.47				1.49	
1.46	333				1.44				1.46		
1.37	060,334		1.42								
1.36	061	1.36									
1.33	062								1.31		
1.29	063,335										

Note: D-spacings are divided based on whether they were from sharp spots (nanoparticles) or broad spots (platelets). Grey highlighted cells represent the values that appear in a hexagonal pattern when the crystal is oriented along the [001] zone axis.

<sup>a</sup>Reference data sources: GR-Na<sub>2</sub>SO<sub>4</sub> (Christiansen et al. 2009), goethite (ICDD PDF card 01-074-2195 (Szytula et al. 1968)), magnetite (PDF card 00-019-0629 (Swanson et al. 1967)).

<sup>b</sup>After sample reached pH 8, XRD data was from 2 days aged, while TEM data was taken from the fresh sample.

<sup>c</sup>Not a spot in the typical hexagonal pattern.



**Table S2. The d-spacings data, continued.**

Reference Data <sup>a</sup>				GR-C + 2 days			GR-D		
GR-Na <sub>2</sub> SO <sub>4</sub>		goethite	magnetite	i.e. Figure 7			i.e. Figure 8		
d	hkl	d	d	XRD d	SAED d (np's)	SAED d (plate)	XRD d	SAED d (nanorods)	FFT
10.98	001			11.05			11.16		10.0-10.4
7.37									
					6.02				
5.49	002	4.97		5.50			5.55		
4.78	110		4.85		4.81				4.70, 4.89
									4.53-4.63
4.38	111								
		4.17			4.15				
3.91	021							3.87	
3.66	003			3.66			3.69		
					3.54				
3.07	120		2.97	2.98	2.97		3.17		
2.75	030,004						2.77		
2.67	031	2.69		2.67			2.69	2.67	
2.60	014		2.53	2.53	2.53	2.53		2.51	2.54-2.57
2.46	032	2.45,2.49		2.46			2.48		
			2.42		2.41				2.35
2.20	033,005	2.19		2.20			2.21	2.19	2.20,2.25
			2.10	2.08	2.09				
1.94	034			1.95			1.96	1.88	
1.80,1.83	140,006			1.83	1.86				
1.72	035		1.72	1.71	1.71		1.72	1.69	
1.59	330	1.66	1.62	1.62	1.61		1.59		
1.57	331,007	1.56					1.58	1.57	
1.53	332						1.53		
1.49	117		1.49		1.48	1.47		1.48	
1.46	333							1.45	
1.37	060,334		1.42						
1.36	061	1.36							
1.33	062				1.31				
1.29	063,335								

<sup>a</sup>Reference data sources: GR-Na<sub>2</sub>SO<sub>4</sub> (Christiansen et al. 2009), goethite (ICDD PDF card 01-074-2195 (Szytula et al. 1968)), magnetite (ICDD PDF card 00-019-0629 (Swanson et al. 1967)).

**Table S3. Crystallite sizes calculated from XRD peak broadening and  $K = 1$ .**

GR-SO <sub>4</sub> (h,k,l)	GR-A, 93 days		GR-B, 64 days		GR-C, 33 days		GR-D, 0 days	
	d (Å)	size (nm)	d (Å)	size (nm)	d (Å)	size (nm)	d (Å)	size (nm)
(001)	11.12	23	11.32	23	11.07	23	11.16	14
(002)	5.51	24	5.56	24	5.50	25	5.55	15
(101)	4.20	9						
(003)	3.66	26	3.69	26	3.66	27	3.69	14
			2.76	48	2.75	40	2.77	16
(111)	2.67	9	2.66	4	2.68	38	2.69	26
(112)	2.46	35	2.47	27	2.46	29	2.48	20
(005)	2.20	27	2.21	25	2.20	24	2.21	17
(114)	1.94	30	1.95	24	1.94	34	1.96	17
(006)	1.83	32	1.83	28	1.83	28		
					1.81	19		
(115) <sup>a</sup>	1.72	31	1.72	22	1.72	23	1.72	12
(205) <sup>a</sup>	1.62	37	1.62	17	1.61	21		
(300)	1.59	46					1.59	17
(007)	1.57	26			1.57	63	1.58	15
							1.53	28
<b>All peaks</b>								
Avg		24		25		28		17
Stdev		9		12		7		5
<b>(001), (002), (003) peaks</b>								
Avg		24		24		25		14
Stdev		1.7		1.6		1.9		0.7

Note: XRD spectra used were from aged samples (with aging time indicated). Only GR-SO<sub>4</sub> peaks are shown (Simon et al. 2003). Averages (Avg) and standard deviations (Stdev) are also shown.

<sup>a</sup>Shares a peak position with magnetite

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