

Supporting Information

Oxygen isotope indicators of selenate reaction with Fe(II) and Fe(III) hydroxides

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The Supporting Information consists of eleven pages that contain one table, six figures, and calculations referred to in the main manuscript.

Calculations for determining chloride green rust concentrations

Chloride green rust concentrations, on a mass basis as g l⁻¹ within experiments, were estimated using the measured total Fe concentration, measured Fe(II)/Fe(III) ratio, and an assumed molecular weight. It was not possible to definitively determine the number of H₂O molecules within the chemical formula (e.g. [Fe^{II}_{2.7}Fe^{III}(OH)_{7.4}][Cl•*n*H₂O]). For our purposes, we assumed *n*=2 for chloride green rust¹. Chloride green rust molecular weight was then calculated as:

$$MW_{GRCI} = \left(\frac{Fe(II)}{Fe(III)} \right) AW_{Fe} + \left(\frac{Fe(II)}{Fe(III)} 2 + 3 \right) MW_{OH} + AW_{Cl} + 2MW_{H_2O}$$

Where MW represents molecular weight, and AW represents atomic weight.

Chloride green rust mass concentrations (g l⁻¹) were then calculated as:

$$[GRCI] = \frac{mmolesFe}{liter} \times \frac{mmolGRCI}{\left(\frac{Fe(II)}{Fe(III)} + 1 \right) mmolFe} \times MW_{GRCI} \times \frac{g}{10^3 mg}$$

The molecular weight of GRCI was approximately 422 g mol⁻¹ for the first kinetic experiment (I), 352 g mol⁻¹ for the second kinetic experiment (IV), and 392 g mol⁻¹ for the batch reactor experiments (1-4) that varied GRCI concentration.

Calculations for the determining iowaite molecular weight and percent interlayer sites exchanged with selenate.

Approximately 16% of the interlayer anions were exchanged within iowaite during the kinetic experiment in Figure 1 of the manuscript. This number was determined by dividing the amount of selenate taken up (9.46 – 5.35 = 4.11 mM) by the amount of interlayer sites available (25.1 mM). The amount of interlayer sites was calculated using the iowaite concentration (8.0 g l⁻¹), an assumed molecular weight of 318.15 g mol⁻¹. The molecular weight assumed one water molecule present within the unit formula:



Table SI-1. Experimental conditions and measured analyte concentrations.^a

Expt. No.	Time min	[SeO ₄ ²⁻] mM	$\delta^{18}\text{O}$ ‰	[Se(0)] mM	[Fe(II)] _{TOT} ^b mM	[Fe(III)] _{TOT} ^c mM	Fe(II)/ Fe(III) Ratio	[Cl ⁻] mM
<i>Chloride Green Rust Experiments</i>								
I	0	9.69	-8.41 ± 0.22	nm ^d	46.10±0.97	17.05±1.22	2.70	1.04
	0.5	5.50	-7.26 ± 0.08	nm	46.50±1.05	nm	nm	9.16
	30	5.98	-1.36 ± 0.58	nm	26.71±0.94	29.03±3.15	0.92	9.71
	90	5.90	3.33 ± 0.02	nm	19.02±0.24	35.64±0.80	0.53	9.72
	330	5.42	5.82 ± 0.12	nm	16.34±0.69	41.67±2.32	0.39	9.62
IV	0	8.93	-8.01±0.15	0	44.95±0.52	23.32±1.57	1.93	0.22
	0.5	2.97	-4.98±0.18	0	48.10±1.26	26.08±2.49	1.84	14.38
	30	1.81	1.74±0.47	2.75	36.63±1.71	35.66±2.18	1.03	14.44
	90	1.56	13.54±0.28	5.38	22.21±0.12	45.41±1.11	0.50	14.57
	330	1.05	22.87±0.30	6.84	14.70±0.48	51.35±6.12	0.29	14.55
	1440	0.94	27.39±0.67	6.30	9.38±0.54	54.72±5.88	0.17	17.68
1	0	9.07	-8.41 ± 0.16	0	5.40±6.55 ^e	2.27±5.93 ^e	2.38	1.04
	330	7.40	-6.57 ± 0.21	0.66	3.33±0.09	6.01±0.10	0.55	24.43
2	0	9.07	-8.41 ± 0.16	0	10.81±6.55	4.53±5.93	2.39	1.04
	330	6.94	-4.02 ± 0.07	1.27	6.94±0.04	6.19±2.40	1.12	50.15
3	0	9.07	-8.41 ± 0.16	0	21.61±6.55	9.06±5.93	2.39	1.04
	330	5.35	1.43 ± 0.15	2.37	7.90±0.05	11.62±1.66	0.68	97.84
4	0	9.07	-8.41 ± 0.16	0	37.82±6.55	15.86±5.93	2.38	1.04
	330	4.30	8.08 ± 0.21	3.89	16.23±1.27	32.11±2.29	0.51	187.42
<i>Ferrous Hydroxide Experiments</i>								
III	0	10.15	-8.55 ± 0.15	nm	nm	nm	nm	48.49
	0.5	7.56	-8.44 ± 0.71	nm	40.98±0.41	1.93±0.72	21.23	58.35
	30	7.68	-7.45 ± 0.66	nm	38.99±0.69	5.10±0.78	7.65	59.82
	90	6.75	-6.13 ± 0.17	nm	29.28±1.33	9.05±1.40	3.24	59.76
	330	5.75	4.32 ± 0.38	nm	27.88±0.62	14.40±0.62	1.94	62.54
IV	0	9.10	-8.12±0.20	0	54.38±0.21	2.71±1.14	20.09	0.11
	0.5	6.87	-6.59±0.46	0	54.13±0.43	4.57±1.30	11.85	7.18
	30	5.94	-5.20±0.30	1.09	50.88±0.81	8.80±1.10	5.78	6.85
	90	6.00	-5.37±0.18	2.23	51.53±0.35	8.08±0.90	6.38	6.82
	330	3.67	8.12±0.45	6.62	32.97±0.33	23.39±1.35	1.41	7.16
	1440	2.57	16.30±0.39	13.06 ^f	30.18±0.76	29.14±3.13	1.04	6.95
1	0	9.91	-8.41 ± 0.16	0	0.59±1.56 ^e	0.13±0.50 ^e	4.54	10.01
	330	9.24	-7.95 ± 0.20	0.01	0.42±0.06	0.19±0.10	2.21	8.15

2	0	9.91	-8.41 ± 0.16	0	9.66 ± 1.56	2.17 ± 0.50	4.45	10.01
	330	8.82	-6.50 ± 0.39	0.72	3.81 ± 0.45	7.73 ± 0.22	0.49	11.78
3	0	9.91	-8.41 ± 0.16	0	23.31 ± 1.56	5.24 ± 0.50	4.45	10.01
	330	7.22	-1.60 ± 0.39	2.09	13.01 ± 0.23	15.34 ± 0.23	0.85	29.58
4	0	9.91	-8.41 ± 0.16	0	38.91 ± 1.56	8.75 ± 0.50	4.45	10.01
	330	5.63	3.53 ± 0.61	3.41	27.44 ± 0.74	20.53 ± 0.84	1.34	51.22
<i>Iowaite Experiments</i>								
II	0	9.46	-8.41 ± 0.22	nm	nm	nm	nm	3.30
	0.5	5.89	-8.49 ± 0.13	nm	nm	nm	nm	8.10
	30	5.08	-8.26 ± 0.29	nm	nm	nm	nm	7.48
	90	5.30	-8.14 ± 0.26	nm	nm	nm	nm	7.66
	330	5.35	-8.55 ± 0.15	nm	nm	nm	nm	8.05
1	0	9.95	-8.51 ± 0.22	nm	nm	nm	nm	1.01
	330	9.10	-8.43 ± 0.58	nm	nm	nm	nm	0.68
2	0	9.95	-8.51 ± 0.22	nm	nm	nm	nm	1.01
	330	5.91	-7.91 ± 0.06	nm	nm	nm	nm	4.01
3	0	9.95	-8.51 ± 0.22	nm	nm	nm	nm	1.01
	330	4.54	-7.34 ± 0.11	nm	nm	nm	nm	5.53
4	0	9.95	-8.51 ± 0.22	nm	nm	nm	nm	1.01
	330	4.19	-7.14 ± 0.40	nm	nm	nm	nm	6.29
<i>Iowaite Tracer Experiment</i>								
1	0	9.93	-8.05 ± 0.17	nm	nm	nm	nm	3.20
	1	7.04	-7.56 ± 0.16	nm	nm	nm	nm	9.02
	450	6.70	-7.98 ± 0.13	nm	nm	nm	nm	9.25
	450	16.90	-11.04 ± 0.20	nm	nm	nm	nm	10.01
	451	15.94	nm	nm	nm	nm	nm	10.29
	455	16.14	-11.16 ± 0.35	nm	nm	nm	nm	10.23
	1380	14.85	-11.18 ± 0.37	nm	nm	nm	nm	9.99

^aExperimental conditions: All experiments numbered 1 were kinetic experiments conducted in glass jars with 100 ml suspension with 1 mM NaCl at pH 8.0. All experiments numbered 1-4 were conducted in 50 ml Falcon centrifuge tubes containing 40 ml suspension with 1 mM NaCl at pH 8.0.

^bFe(II) concentration measured in an unfiltered sample of reactor suspension (containing both solid and dissolved Fe(II), if any). Dissolved Fe(II) was always less than ~1.2 mM.

^cFe(III) concentration measured in an unfiltered sample of reactor suspension (containing both solid and dissolved Fe(III), if any). Dissolved Fe(III) measurements were always below detection limits.

^dnm = not measured.

^eStandard deviations on initial Fe(II) and Fe(III) measurements for batch reactors 1-4 for GRCl and Fe(OH)₂ are the same within each experiment because measurements were taken once for batch #4 which was then diluted for batch #1-3.

^fThis value of Se(0) mass is higher than what a selenate mass balance would predict (6.5 mM). The sample became discolored during processing with sulfide solution, and we presume a contaminant, such as an iron oxide, reacted with sulfide and formed an interfering species.

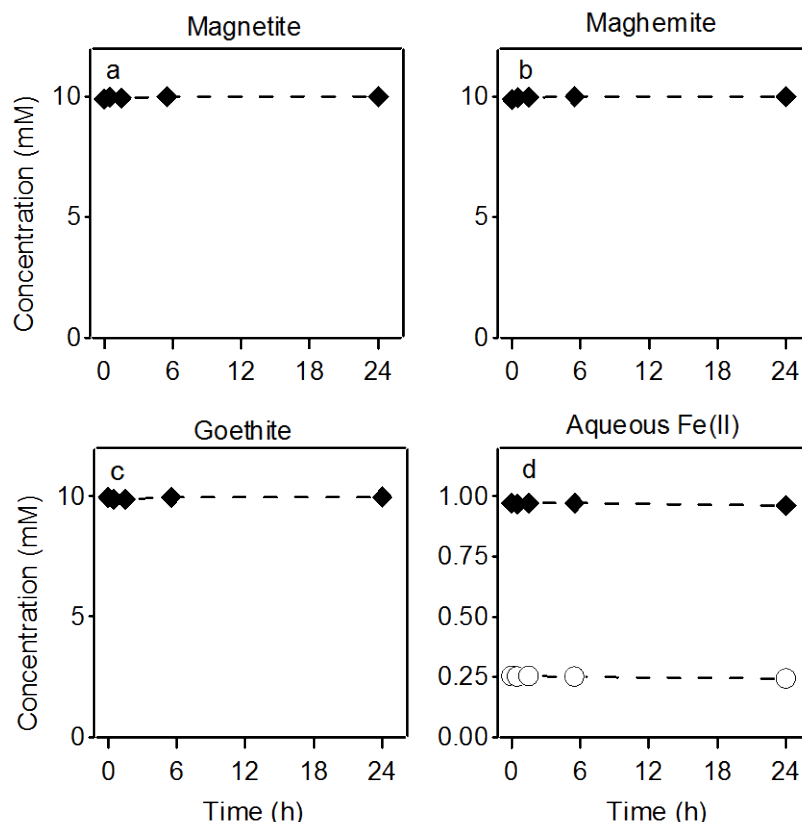


Figure SI-1. Control reactors containing either (a) 4.63 g L⁻¹ magnetite, (b) 4.79 g L⁻¹ maghemite, (c) 5.34 g L⁻¹ goethite, or (d) 0.25 mM aqueous Fe(II). Filled diamonds are selenate concentrations, and open circles are aqueous Fe(II) concentrations. All batch reactors contained 1 mM NaCl at pH 8.0. Magnetite and maghemite concentrations were chosen to represent similar total Fe concentrations (~60 mM) within green rust kinetic experiments. Initial selenate concentrations were chosen as 10 mM for (a) and (b) to represent the same initial concentrations in green rust kinetic experiments, but was chosen as 1 mM for (c) in order to observe any subtle potential removal caused by aqueous Fe(II) (none occurred). The initial aqueous Fe(II) concentration was chosen as 0.25 mM because aqueous Fe(II) concentrations remained below 1 mM at all time points in all experiments, and 0.25 mM is well below the solubility limit of Fe(II) at pH 8.0 (~1.0 mM). Magnetite was synthesized by combining 120 ml of 180 mM FeCl₂•4H₂O and 360 mM FeCl₃•6H₂O, 120 ml of 2.14 M NaOH, and 160 ml of water at 40°C while vigorously stirring for 2 h.² The black solids were washed with deoxygenated deionized water via centrifugation, dried in the glove box, sieved (150 micron), and stored in the glove box until use. A sample of magnetite was converted to maghemite by heating to 190°C for 36 hours and noting a color change from black to brown.³ Goethite was prepared by heating a 60 mM FeCl₃•6H₂O solution at pH 12.0 at 65°C for four days.⁴ No selenate removal was observed for all three control reactors.

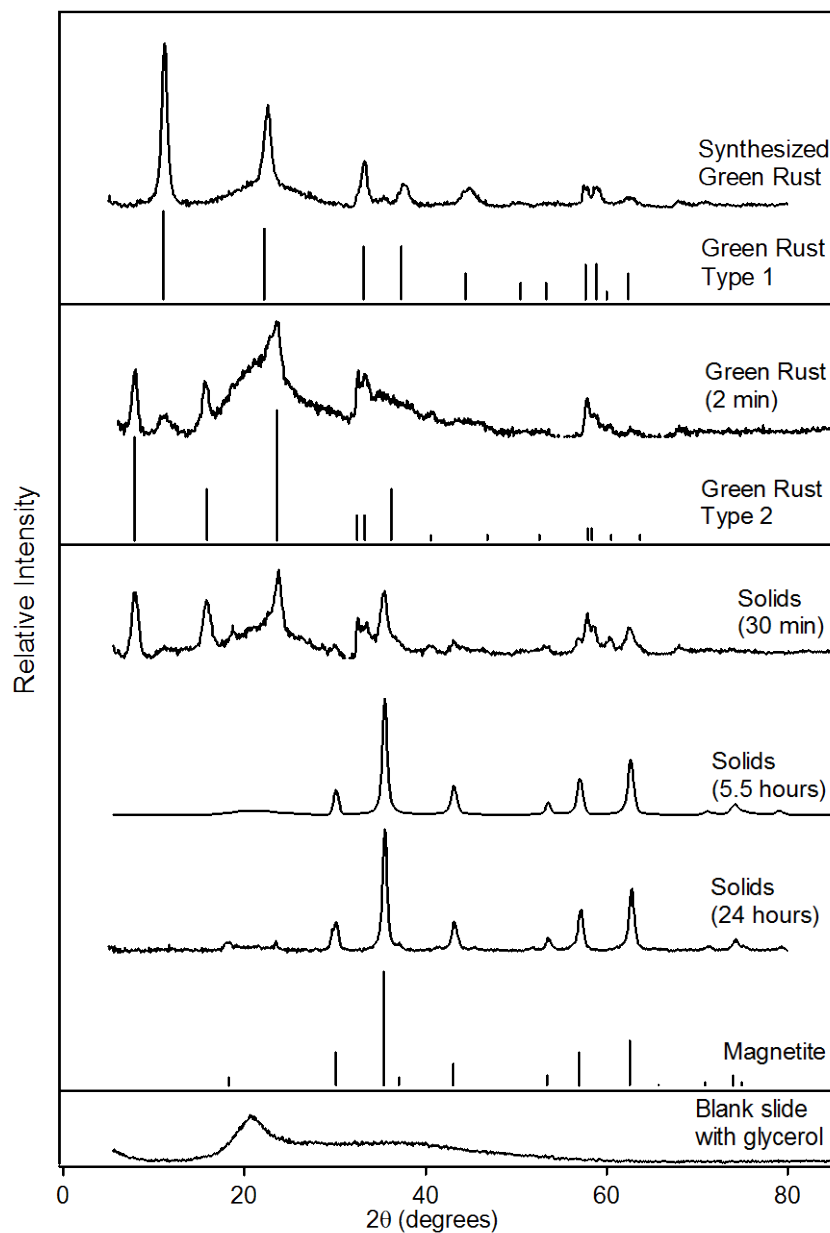


Figure SI-2. X-ray diffraction patterns of the synthesized chloride green rust, filtered solids after 2 minutes, 30 minutes, 5.5 hours, or 24 hours exposure to selenate, and glycerol. Solution conditions for reactions were 10 mM sodium selenate, 1 mM sodium chloride, and pH 8.0. The reference patterns provided are for green rust type 1 (chloride green rust, ICDD powder diffraction file number 00-040-0127), green rust type 2 (sulfate green rust, 00-014-0041), and magnetite (00-019-0629). The amorphous mound shape between ~18-22 degrees in some patterns is attributed to the glycerol coating.

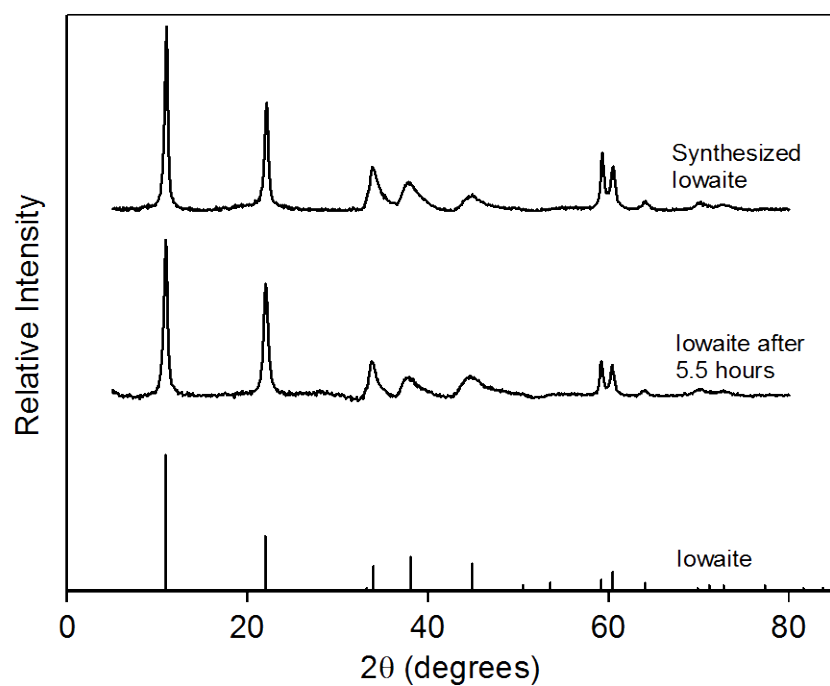


Figure SI-3. XRD patterns of the synthesized iowaite and iowaite after 5.5 hours exposure to 10 mM sodium selenate, 1 mM sodium chloride at pH 8.0. The reference pattern is iowaite (01-073-8407).

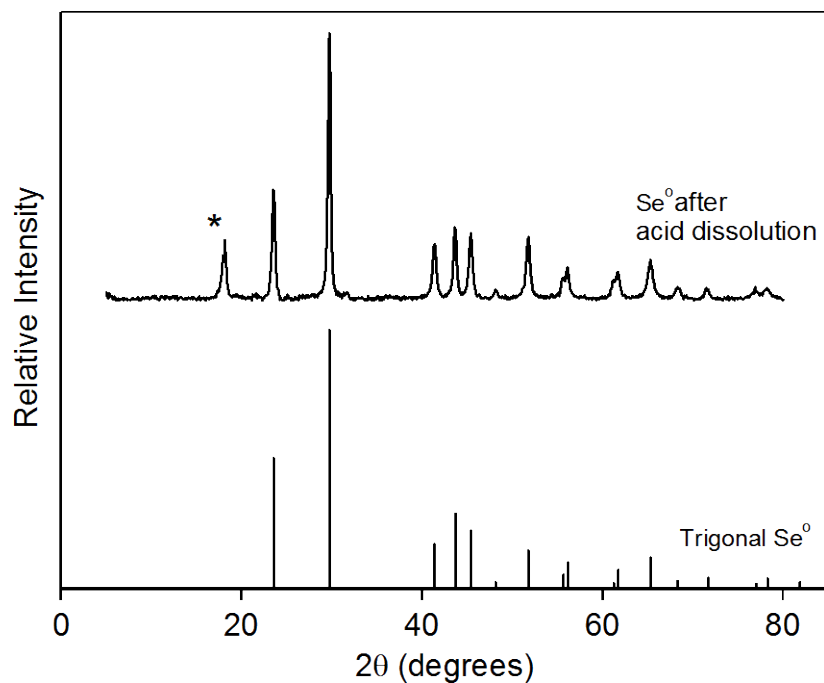


Figure SI-4. XRD pattern of the elemental selenium produced by reduction of selenate by chloride green rust. Solution conditions were 10 mM sodium selenate, 1 mM sodium chloride at pH 8.0. Red solids were collected after dissolution of iron oxides in 1.0 M HCl. The reflection marked with the asterisk is unidentified and could possibly be attributed to goethite or another allotrope of elemental selenium.

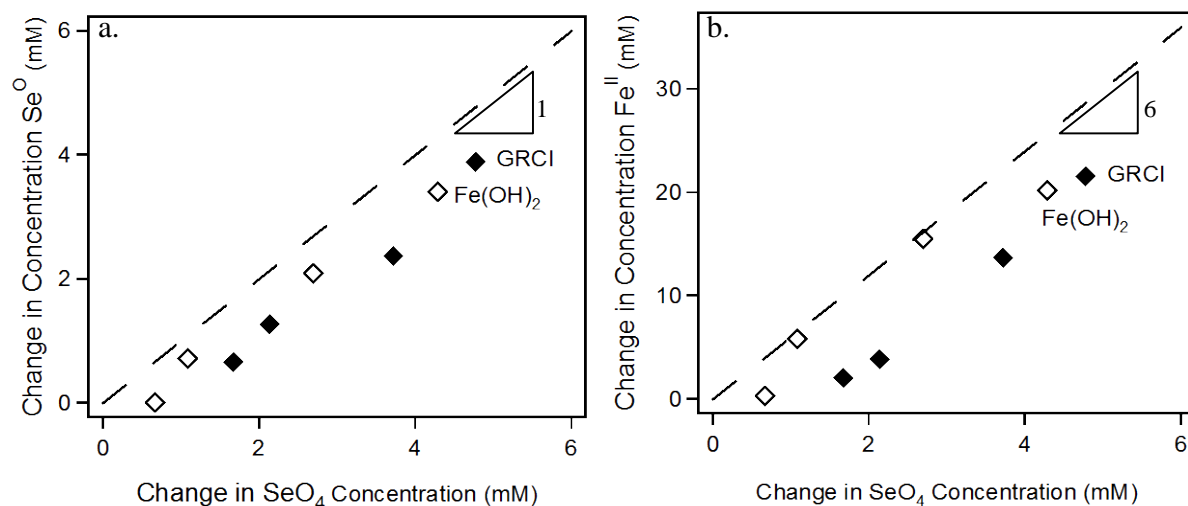


Figure SI-5. Relationship between (a) selenium formation and selenate consumption and (b) total Fe(II) consumption and selenate consumption within batch reactors containing varying amounts of either chloride green rust (filled diamonds) or ferrous hydroxide (white diamonds). Dashed lines represent ideal stoichiometric relationships indicated in equation 2. Solution conditions are given in Table SI-1 (experiments listed as 1-4 for each mineral).

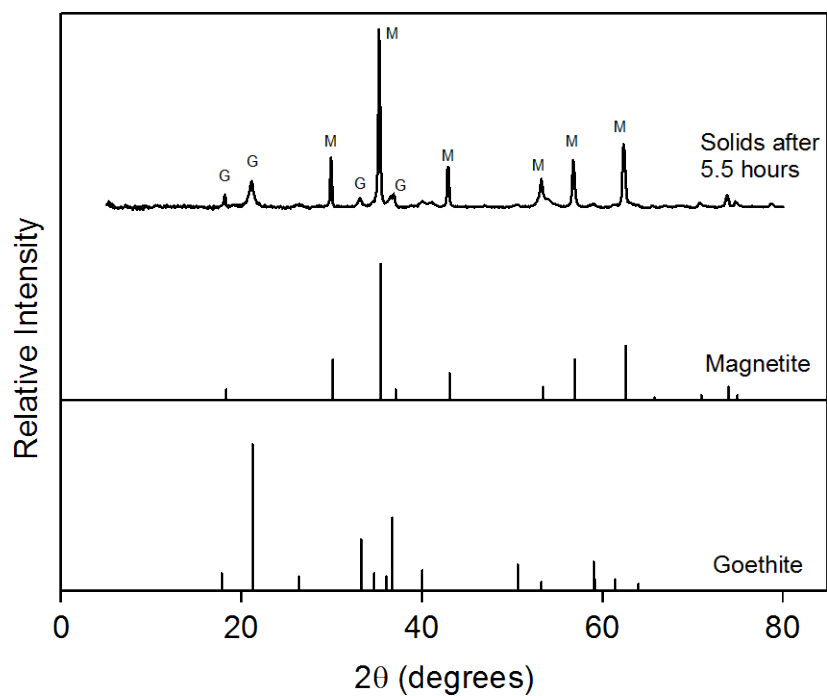


Figure SI-6. XRD pattern of solids obtained after ferrous hydroxide was exposed to 10 mM selenate at pH 8.0 after 5.5 hours reaction. Reference patterns are magnetite (00-019-0629) and goethite (00-029-0713).

Literature Cited for Citations within the Supporting Information

(1) Génin, J.R. and Ruby, C. Anion and cation distributions in Fe(II–III) hydroxysalt green rusts from XRD and Mössbauer analysis (carbonate, chloride, sulphate, ...); the “fougerite” mineral. *Solid State Sciences* **2004**, 6, 705-718.

- (2) Sayar, F.; Güven, G.; Pişkin, E. Magnetically loaded poly(methyl methacrylate-co-acrylic acid) nano-particles. *Nano Lett.* **2006**, 8, 1965-1970.
- (3) Cornell, R.M. and Schwertmann, U. *The Iron Oxides: Structure, Properties, Reactions, Occurences and Uses*. Wiley-VCH Verlag GmbH: Weinheim, 2003.
- (4) Schwertmann, U. and Cornell, R.M. *Iron Oxides in the Laboratory: Preparation and Characterization*. Wiley-VCH Verlag GmbH: Weinheim, 2000.