A revised analysis of ferrihydrite at liquid helium temperature using Mössbauer spectroscopy

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Supplementary information

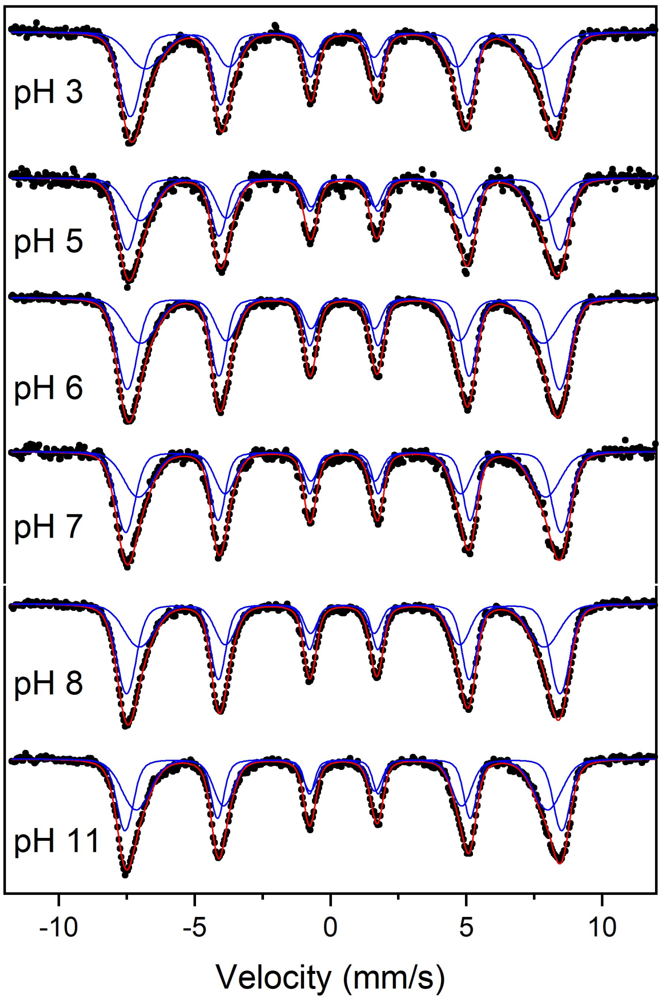

Figure S1 – Fitting results for samples collected at different pH during ferrihydrite synthesis, fitted with extended Voigt models (xVBF) and two sextets.

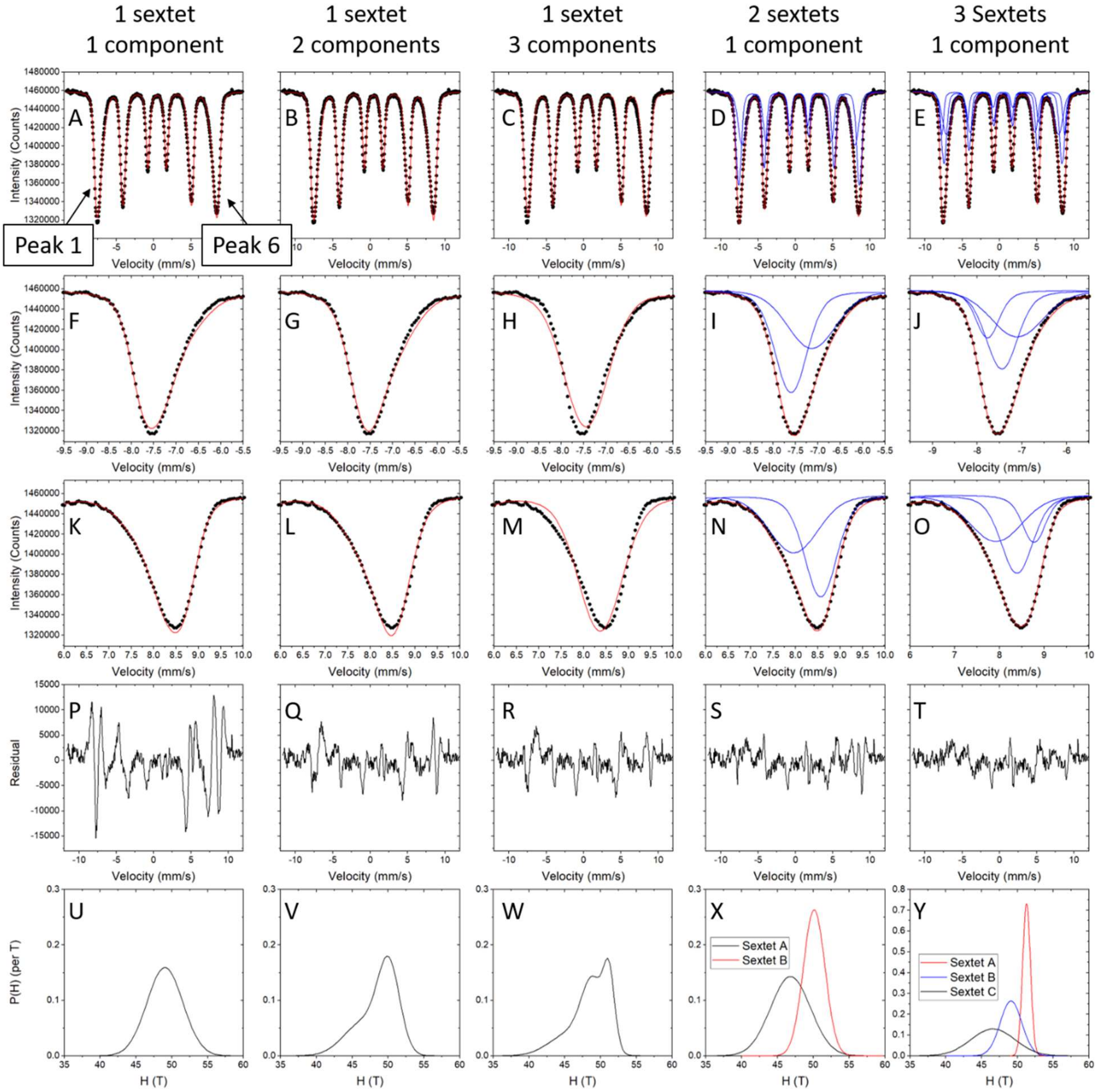

Figure S2 - Multicomponent fitting of 2-Line Fh with the xVBF model. A-E spectra showing full velocity range; F-J spectra focused on peak 1; K-O spectra focused on peak 6; P-T residual (difference between data and model fit); U-Y distribution of hyperfine field parameter.

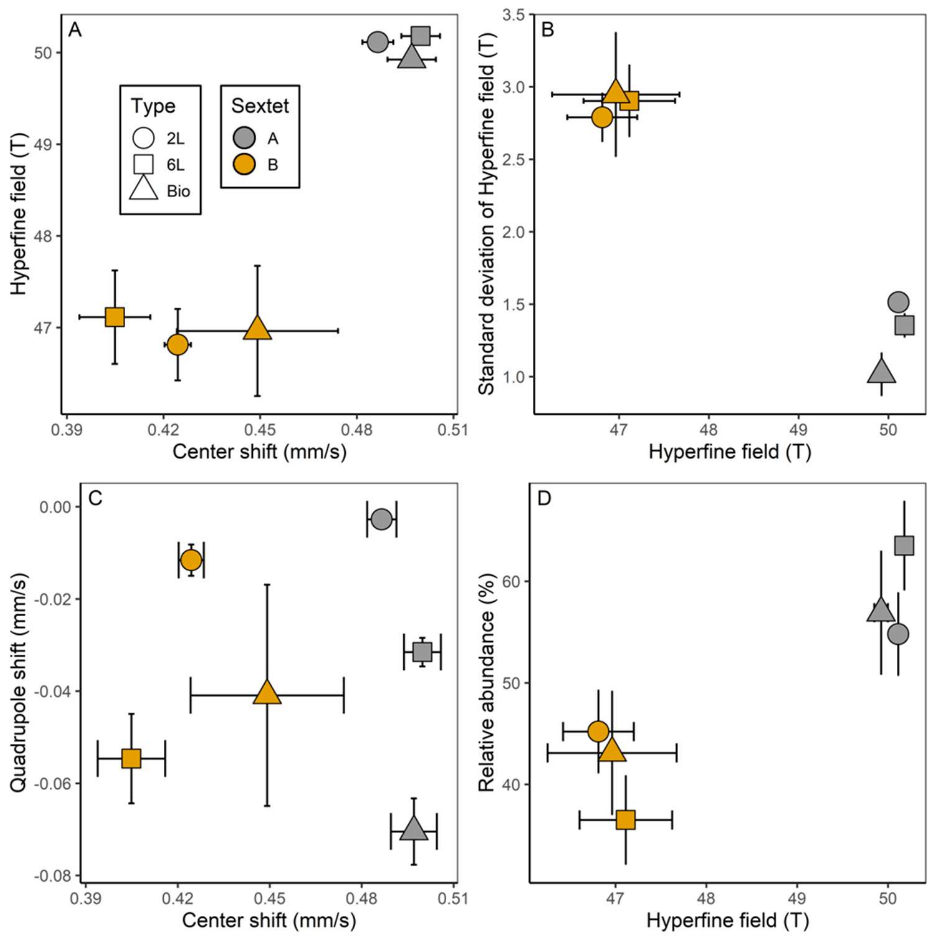

Figure S3 – Comparison of hyperfine parameters obtained through fitting 2-Line, 6-Line and biogenic Fh with a two-sextet xVBF model.

Table S1 – indicates which parameters were constrained and unconstrained during fitting in Recoil. Background – background, δ – Isomer shift, σ(δ) – standard deviation of δ, ε – quadrupole splitting, σ(ε)– standard deviation of ε, B_{hf} – hyperfine field, σ(B_{hf}) – standard deviation of B_{hf}, Area – relative area of each sextet, A1/A2 – ratio of the spectral areas of peak 1 to peak 3, A2/A3 – ratio of the spectral areas of peak 2 to peak 3, w3 – Half width half maximum (HWHM) of peaks 3 and 4, w1/w3 – ratio of HWHMs of peak 1 (and 6) to peak 3 (and 4), w2/w3 – ratio of HWHMs of peak 2 (and 5) to peak 3 (and 4), $δ_1$ – coupling parameters between δ and H, $ε_1$ - coupling parameters between ε and H, r(δ, ε) – correlation parameter between isomer shift distribution and quadrupole shift, r(δ, B_{hf}) – correlation parameter between isomer shift distribution and hyperfine field distribution, r(ε, B_{hf}) – correlation parameter between quadrupole shift distribution and hyperfine field distribution.

Model	**Unconstrained parameters**	**Constrained parameters**
LOR	Background; δ; ε; B_{hf}; w3; Area	A1/A2 = 3; A2/A3 = 2; w1/w3 = 1; w2/w3 = 1
VBF	Background; δ; ε; B_{hf}; σ(B_{hf}); Area	Lorentzian HWHM=0.125 mm/s; $δ_1$; $ε_1$; A1/A3 = 3; A2/A3 = 2
xVBF	Background; δ; σ(δ); ε; σ(ε); B_{hf}; σ(B_{hf}); Area;	Lorentzian HWHM=0.125 mm/s; A1/A3 =3; A2/A3 = 2; r(δ, ε)=0; r(δ, B_{hf})=0; r(ε,B_{hf})=0

Table S2 - Hyperfine parameters obtained for fitting different types of Fh with a 2 site, xVBF model. , δ– isomer shift (mm/s), σ(δ) – standard deviation of the isomer shift, ε – quadrupole shift (mm/s), σ(ε) – standard deviation of the quadrupole shift, B_{hf} – hyperfine magnetic field (T), σ(B_{hf}) – standard deviation of hyperfine magnetic field (T), w – linewidth of the Lorentzian (mm/s), R.A.- relative abundance (%), red. (reduced) χ^2– goodness of fit.

Sample	pH	Fh	Sextet	δ *mm/s*	±	σ(δ) *mm/s*	ε *mm/s*	±	σ(ε) *mm/s*	B_{hf} *T*	±	σ(B_{hf}) *T*	±	R.A. *%*	±	red. χ^2
Biogenic Fh	7	Bio	A	0.497	0.008	0.070	-0.070	0.007	0.070	49.92	0.08	1.02	0.15	56.9	6.1	0.60
Biogenic Fh	7	Bio	B	0.449	0.025	0.140	-0.041	0.024	0.140	46.96	0.71	2.95	0.43	43.1	6.1	0.60
pH 3	3	2L	A	0.487	0.011	0.114	-0.011	0.007	0.114	48.64	0.13	1.80	0.26	60.0	16.0	0.60
pH 3	3	2L	B	0.449	0.020	0.150	-0.017	0.019	0.150	44.93	2.00	3.30	0.86	40.0	16.0	0.60
pH 5	4.9	2L	A	0.489	0.024	0.125	-0.014	0.013	0.125	49.35	0.24	1.46	0.58	53.0	29.0	0.62
pH 5	4.9	2L	B	0.450	0.024	0.124	-0.023	0.022	0.124	46.14	2.60	2.87	1.10	47.0	29.0	0.62
pH 6	6.1	2L	A	0.488	0.008	0.011	-0.009	0.004	0.011	49.37	0.08	1.72	0.15	57.4	9.3	0.96
pH 6	6.1	2L	B	0.440	0.010	0.134	-0.017	0.009	0.134	45.94	1.00	3.08	0.42	42.6	9.3	0.96
pH 7	7.15	2L	A	0.489	0.019	0.100	-0.013	0.088	0.100	49.73	0.19	1.61	0.30	55.0	21.0	0.64
pH 7	7.15	2L	B	0.441	0.020	0.066	-0.017	0.017	0.176	46.48	0.20	2.81	0.90	45.0	21.0	0.64
pH 8	8.24	2L	A	0.481	0.088	0.108	-0.009	0.004	0.108	49.49	0.08	1.61	0.15	58.2	9.9	0.89
pH 8	8.24	2L	B	0.430	0.011	0.124	-0.014	0.009	0.124	46.23	1.00	2.95	0.43	41.8	9.9	0.89
pH 11	11.68	2L	A	0.484	0.008	0.091	-0.009	0.006	0.091	49.85	0.08	1.32	0.15	46.7	7.3	1.00
pH 11	11.68	2L	B	0.434	0.010	0.130	-0.014	0.009	0.130	46.98	0.58	2.69	0.27	53.3	7.3	1.00

Table S3 - Hyperfine parameters obtained for fitting 2-Line Fh using multicomponent (2 or 3) models (c.f. Figure S2). δ– isomer shift (mm/s), σ(δ) – standard deviation of the isomer shift, ε – quadrupole shift (mm/s), σ(ε) – standard deviation of the quadrupole shift, B_{hf} – hyperfine magnetic field (T), σ(B_{hf}) – standard deviation of hyperfine magnetic field (T), w – linewidth of the Lorentzian (mm/s), R.A.- relative abundance (%), red. (reduced) χ^2– goodness of fit.

Model	Sample	N_{sx}	N_{comp}	Sextet	Component	δ *mm/s*	±	σ(δ) *mm/s*	ε *mm/s*	±	σ(ε) *mm/s*	B_{hf} *T*	±	σ(B_{hf}) *T*	±	w *mm/s*	±	R.A. *%*	±	red. χ^2
xVBF	2L	1	2	A		0.469	0.001	0.128	-0.001	0.001	0.128	48.62		2.74				100.0		4.82
					1							*46.68*	*0.72*	*2.78*	*0.30*			*42.1*		
					2							*50.10*	*0.07*	*1.52*	*0.11*			*57.0*	*10.0*	
xVBF	2L	1	3	A		0.470	0.001	0.129	-0.001	0.001	0.129	48.55		2.78				100.0		4.23
					1							*45.90*	*2.90*	*2.94*	*0.87*			*29.8*		
					2							*48.90*	*2.00*	*1.60*	*1.50*			*46.0*	*80.0*	
					3							*51.18*	*0.61*	*0.78*	*0.83*			*24.0*	*52.0*	