SUPPLEMENTARY MATERIAL

related to

Interaction of corroding iron with seven bentonites in the alternative buffer materials field experiment (ABM2)

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S4 Mössbauer spectrometry data

Contents

S4-1 MX80 (Block #8)

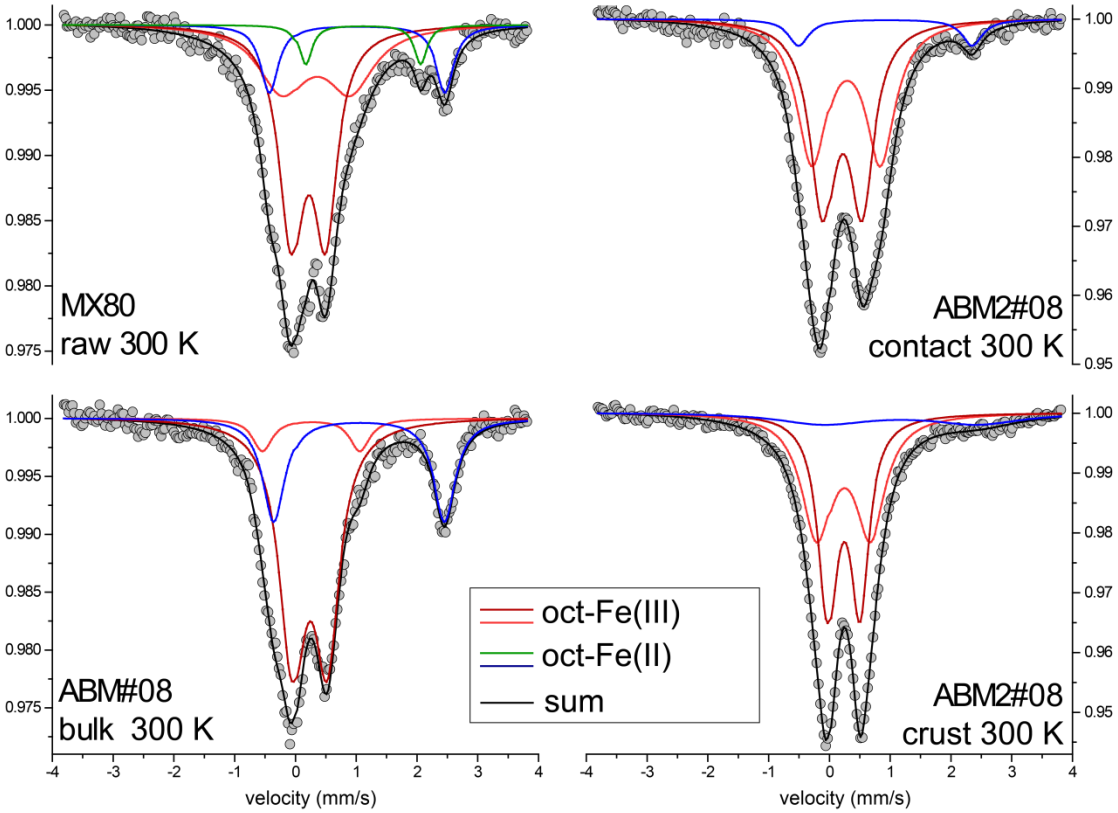

Fig. S4-1 Room temperature spectra of the raw MX80 bentonite used in ABM2 experiment and three samples from block ABM2#08 (hyperfine parameters displayed in Table S4-1)

Table S4-1 Refined values of Mössbauer parameters and doublet structural attributions for the raw MX80 sample and the samples from block ABM2#08

Hyperfine parameters				Attribution
I.S.	**F.W.H.M.**	**Q.S.**	**Area(%)**	
		raw		
0.46	0.95	1.10	32	HS-oct-Fe(III)
0.32	0.47	0.54	50	HS-oct-Fe(III)
1.13	0.35	2.85	13	HS-oct-Fe(II)
1.21	0.25	1.89	5	HS-oct-Fe(II)
		Bulk		
0.38	0.40	1.57	8	HS-oct-Fe(III)
0.35	0.50	0.55	66	HS-oct-Fe(III)
1.17	0.43	2.78	26	HS-oct-Fe(II)
		contact		
0.35	0.59	0.85	44	HS-oct-Fe(III)
0.35	0.37	0.51	44	HS-oct-Fe(III)
1.29	1.80	2.53	13	HS-oct-Fe(II)
		Crust		
0.40	0.59	1.10	46	HS-oct-Fe(III)
0.32	0.48	0.62	48	HS-oct-Fe(III)
1.04	0.41	2.82	6	HS-oct-Fe(II)

I.S. = Isomer shift value relative to that of the α-Fe at 300 K.
F.W.H.M = Full width of line at half of its maximum intensity.
Q.S. = Quadrupolar splitting

S4-2 Ibecoseal (Block #11)

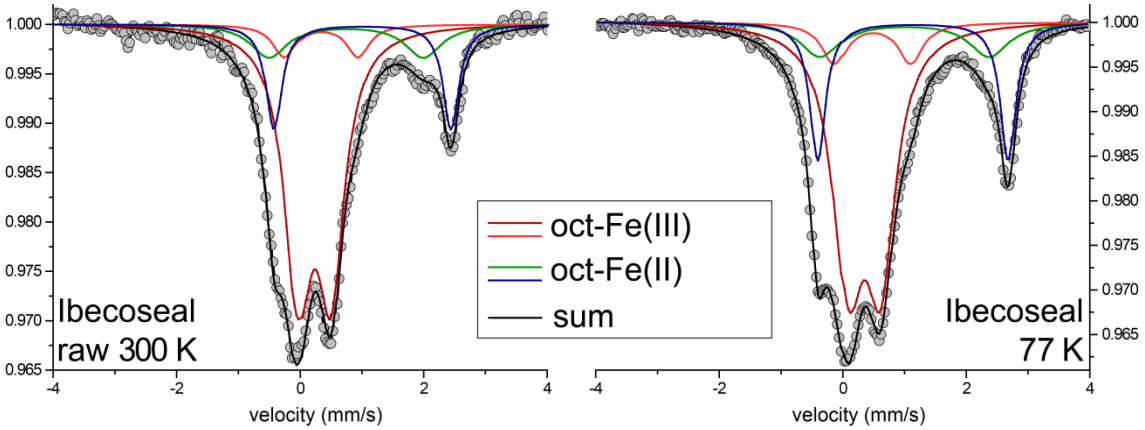

Fig. S4-2 Room temperature and 77 K Mössbauer spectra of the raw Ibecoseal bentonite used in ABM2 experiment (hyperfine parameters displayed in Table S4-2)

Table S4-2 Refined values of Mössbauer parameters and doublet structural attributions for the raw Ibecoseal sample.

Hyperfine parameters				Attribution
I.S.	**F.W.H.M.**	**Q.S.**	**Area(%)**	
		300 K		
0.47	0.57	0.52	60	HS-oct-Fe(III)
0.61	0.48	1.21	9	HS-oct-Fe(III)
1.13	0.77	2.71	12	HS-oct-Fe(II)
1.27	0.31	3.05	19	HS-oct-Fe(II)
		77 K		
0.35	0.52	0.52	64	HS-oct-Fe(III)
0.46	0.44	1.17	7	HS-oct-Fe(III)
0.87	0.71	2.47	12	HS-oct-Fe(II)
1.13	0.32	2.83	17	HS-oct-Fe(II)

I.S. = Isomer shift value relative to that of the α-Fe at 300 K.
F.W.H.M = Full width of line at half of its maximum intensity.
Q.S. = Quadrupolar splitting

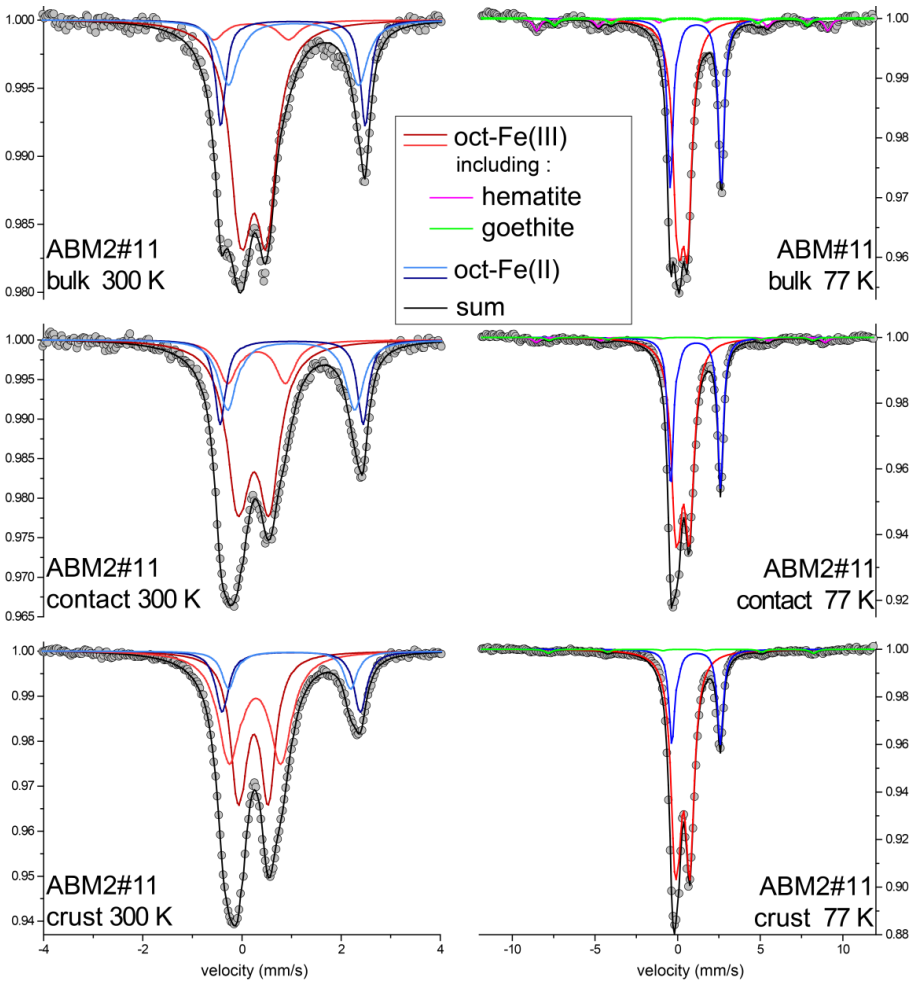

Fig. S4-3 Room temperature and 77 K Mössbauer spectra of a series of 3 samples from block ABM2#11. The hyperfine parameters are displayed in

Table S4-3.

Table S4-3 Refined values of Mössbauer parameters and doublet structural attributions for the sample collected on block ABM2#11 (Ibecoseal)

Hyperfine parameters					Attribution
I.S.	**F.W.H.M.**	**Q.S./2ε**	**B_{hf}**	**Area(%)**	
		Bulk			
		300 K			
0.35	0.50	0.49		60	HS-oct-Fe(III)
0.31	0.50	1.47		6	
1.15	0.24	2.88		16	HS-oct-Fe(II)
1.16	0.45	2.59		18	
		77 K			
0.46	0.64	0.52		57	HS-oct-Fe(III)
1.26	0.42	2.99		34	HS-oct-Fe(II)
0.47	0.50	-0.04	54.4	6	hematite
0.48	0.50	-0.22	47.2	3	goethite
		Contact			
		300 K			
0.34	0.37	0.57		37	HS-oct-Fe(III)
0.38	0.55	1.01		41	

1.11	0.32	2.75		14	HS-oct-Fe(II)
1.08	0.33	2.43		9	
		77 K			
0.46	0.64	0.78		74	HS-oct-Fe(III)
1.28	0.43	2.83		24	HS-oct-Fe(II)
0.48	0.5	-0.22	49.5	2	goethite
		Crust			
		300 K			
0.35	0.53	0.60		53	HS-oct-Fe(III)
0.41	0.27	1.13		13	
1.12	0.27	2.85		15	HS-oct-Fe(II)
1.11	0.43	2.53		20	
		77 K			
0.47	0.68	0.72		63	HS-oct-Fe(III)
1.25	0.41	2.92		33	HS-oct-Fe(II)
0.46	0.5	-0.22	54.0	3	hematite
0.48	0.5	-0.22	49.2	2	goethite

I.S. = Isomer shift value relative to that of the α-Fe at 300 K. ($mm \cdot s^{-1}$)
F.W.H.M = Full width of line at half of its maximum intensity. ($mm \cdot s^{-1}$)
Q.S./2ε = Quadrupolar splitting
B_{hf} = Magnetic hyperfine field (T)

S4-3 MX80/quartz (Block #25)

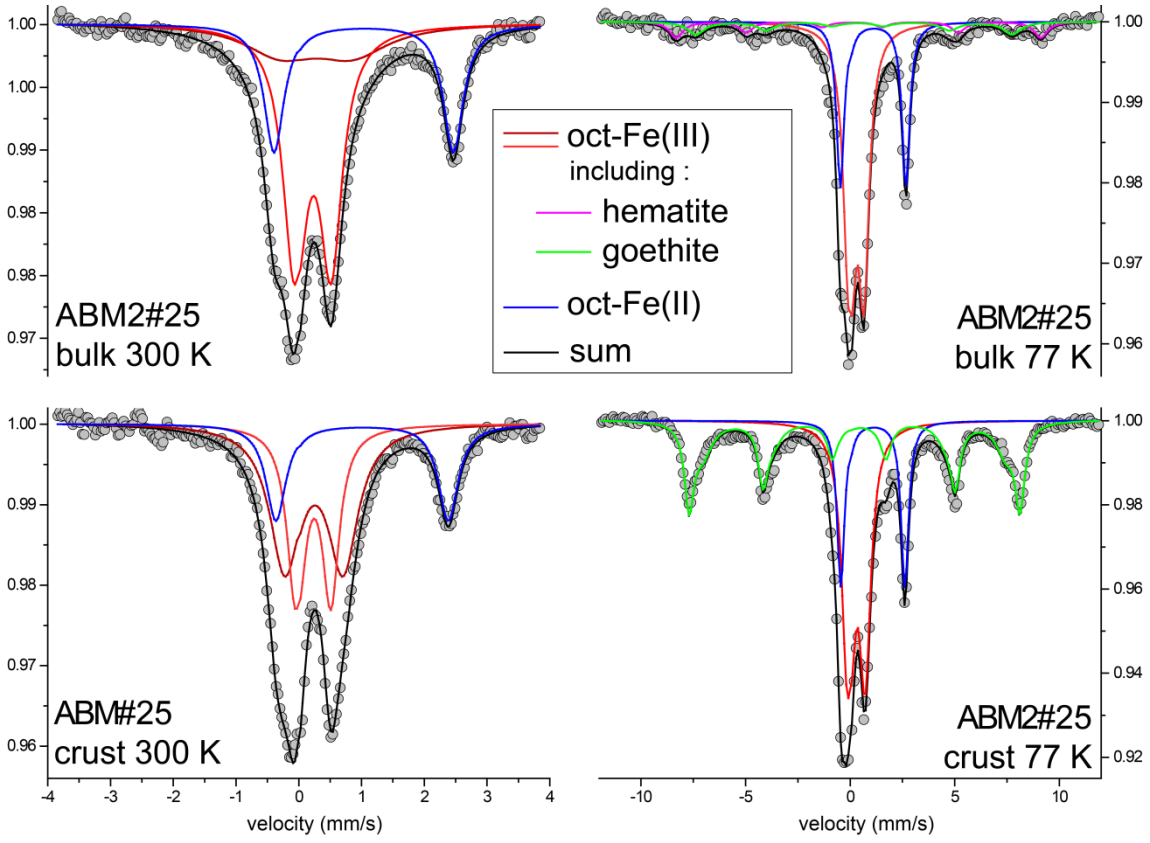

Fig. S4-4 Mössbauer spectra of the bulk and crust samples of block ABM2#25 (hyperfine parameters displayed in Table S4-4).

Table S4-4 Refined values of Mössbauer parameters and doublet structural attributions for the bulk and crust samples collected on block ABM2#25 (MX80+quartz).

Hyperfine parameters					Attribution
I.S.	**F.W.H.M.**	**Q.S./2ε**	***B*hf**	**Area(%)**	
		Bulk			
		300 K			
0.41	1.40	1.12		22	HS-oct-Fe(III)
0.35	0.43	0.56		52	
1.16	0.39	2.83		26	HS-oct-Fe(II)
		77 K			
0.46	0.61	0.62		55	HS-oct-Fe(III)
1.25	0.45	3.04		27	HS-oct-Fe(II)
0.41	0.80	0.30	53.8	9	hematite
0.54	1.04	-0.18	46.7	9	goethite
		Crust			
		300 K			
0.37	0.58	0.90		47	HS-oct-Fe(III)
0.35	0.33	0.53		32	
1.14	0.38	2.72		21	HS-oct-Fe(II)
		77 K			
0.46	0.65	0.75		40	HS-oct-Fe(III)
1.25	0.44	2.97		19	HS-oct-Fe(II)
0.48	0.53	-0.22	48.8	22	hematite
0.49	1.16	-0.26	44.8	19	goethite

I.S. = Isomer shift value relative to that of the α-Fe at 300 K. ($mm \cdot s^{-1}$)
F.W.H.M = Full width of line at half of its maximum intensity. ($mm \cdot s^{-1}$)
Q.S./2ε = Quadrupolar splitting
B_{hf} = Magnetic hyperfine field (T)

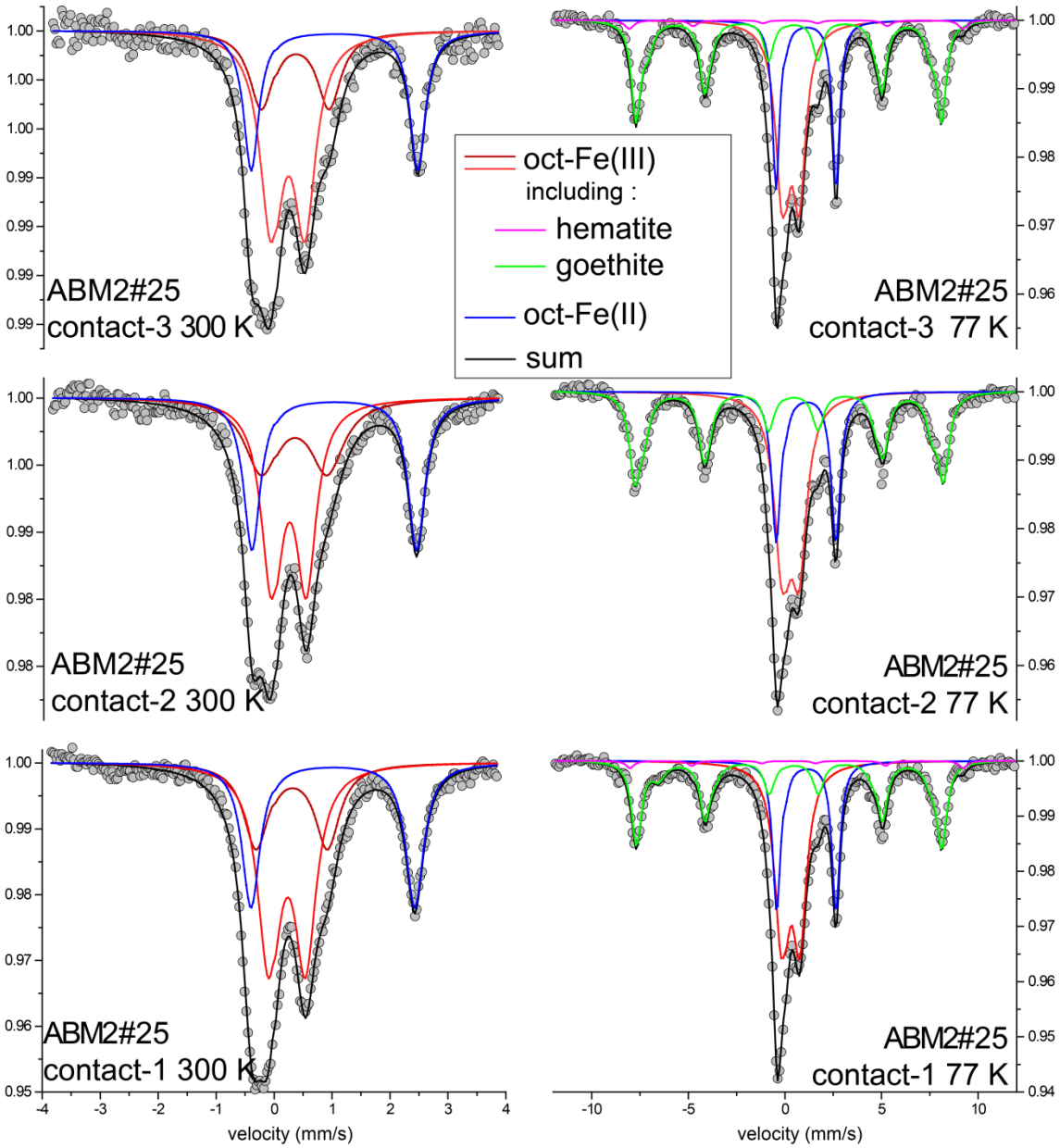

Fig. S4-5 Mössbauer spectra of the crust samples from ABM2#25. The hyperfine parameters are displayed in

Table S4-5.

Table S4-5 Refined values of Mössbauer parameters and doublet structural attributions for the three contact sample collected on block ABM2#25 (MX80+quartz). Parameters indicated in italic account for an inconsistent fit (regarding fit at 77K and evolution of parameters). These data are preliminary.

Hyperfine parameters					Attribution
I.S.	**F.W.H.M.**	**Q.S./2ε**	**B_{hf}**	**Area(%)**	
		Contact-3			
		300 K			
0.46	0.29	1.14		22	HS-oct-Fe(III)

Hyperfine parameters					Attribution
I.S.	**F.W.H.M.**	**Q.S./2ε**	***B*hf**	**Area(%)**	
0.33	0.45	0.56		51	
1.14	0.32	2.84		27	HS-oct-Fe(II)
		77 K			
0.46	0.81	0.80		37	HS-oct-Fe(III)
1.26	0.45	3.01		21	HS-oct-Fe(II)
0.59	0.56	0.30	53.3	3	hematite
0.48	0.57	-0.23	48.8	30	goethite
0.48	0.69	-0.19	45.1	9	goethite
		Contact-2			
		300 K			
0.45	*0.70*	*1.11*		*28*	HS-oct-Fe(III)
0.35	*0.42*	*0.57*		*42*	
1.14	*0.35*	*2.81*		*30*	HS-oct-Fe(II)
		77 K			
0.45	0.96	0.79		38	HS-oct-Fe(III)
1.26	0.58	2.99		22	HS-oct-Fe(II)
0.5	0.66	-0.23	49.4	28	hematite
0.44	0.73	-0.23	46.1	12	goethite
		Contact-1			
		300 K			
0.35	0.63	0.61		37	HS-oct-Fe(III)
0.35	0.63	1.25		14	
1.14	0.52	2.71		23	HS-oct-Fe(II)
0.27	1.11	-0.31	31.9	16	goethite
0.27	1.11	-0.31	22.8	10	goethite
		77 K			
0.46	0.86	0.86		40	HS-oct-Fe(III)
1.27	0.50	2.97		21	HS-oct-Fe(II)
0.58	0.50	0.40	53.3	2	hematite
0.50	0.62	-0.24	48.8	29	goethite
0.50	0.83	-0.24	43.4	7	goethite

I.S. = Isomer shift value relative to that of the α-Fe at 300 K. (mm·s^{-1})
F.W.H.M = Full width of line at half of its maximum intensity. (mm·s^{-1})
Q.S./2ε = Quadrupolar splitting
B_{hf} = Magnetic hyperfine field (T)

S4-4 Deponit (Block #26)

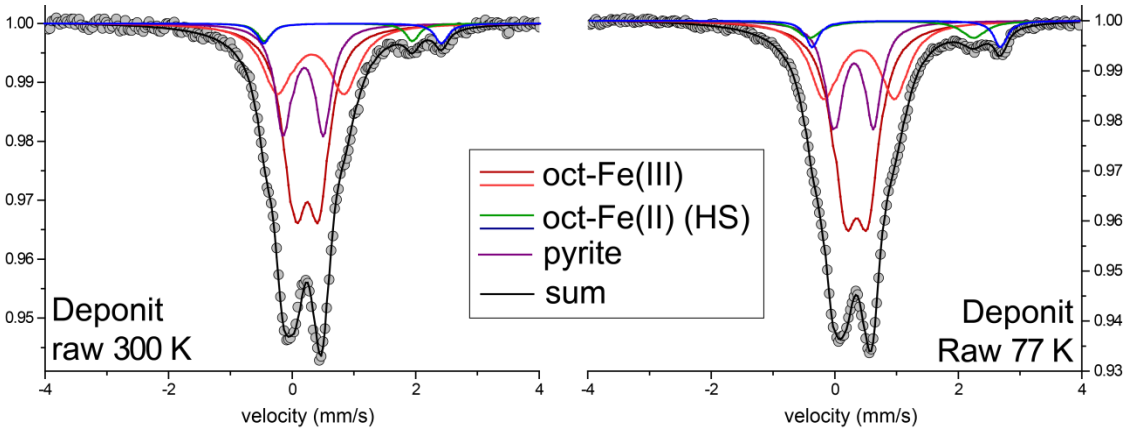

Fig. S4-6 Room temperature and 77 K Mössbauer spectra of the raw Deponit bentonite used in ABM2 experiment.

Table S4-6 Refined values of Mössbauer parameters and doublet structural attributions for the raw Deponit sample.

Hyperfine parameters				Attribution
I.S.	**F.W.H.M.**	**Q.S.**	**Area(%)**	
		300 K		
0.35	0.42	0.37	45	HS-oct-Fe(III)
0.42	0.59	1.05	26	HS-oct-Fe(III)
0.30	0.32	0.62	22	Pyrite
0.87	0.27	2.36	3	HS-oct-Fe(II)
1.10	0.27	2.84	4	HS-oct-Fe(II)
		77 K		
0.46	0.45	0.36	45	HS-oct-Fe(III)
0.52	0.56	1.11	26	HS-oct-Fe(III)
0.42	0.32	0.62	20	Pyrite
1.04	0.48	2.63	5	HS-oct-Fe(II)
1.28	0.27	3.02	4	HS-oct-Fe(II)

I.S. = Isomer shift value relative to that of the α-Fe at 300 K.
F.W.H.M = Full width of line at half of its maximum intensity.
Q.S. = Quadrupolar splitting

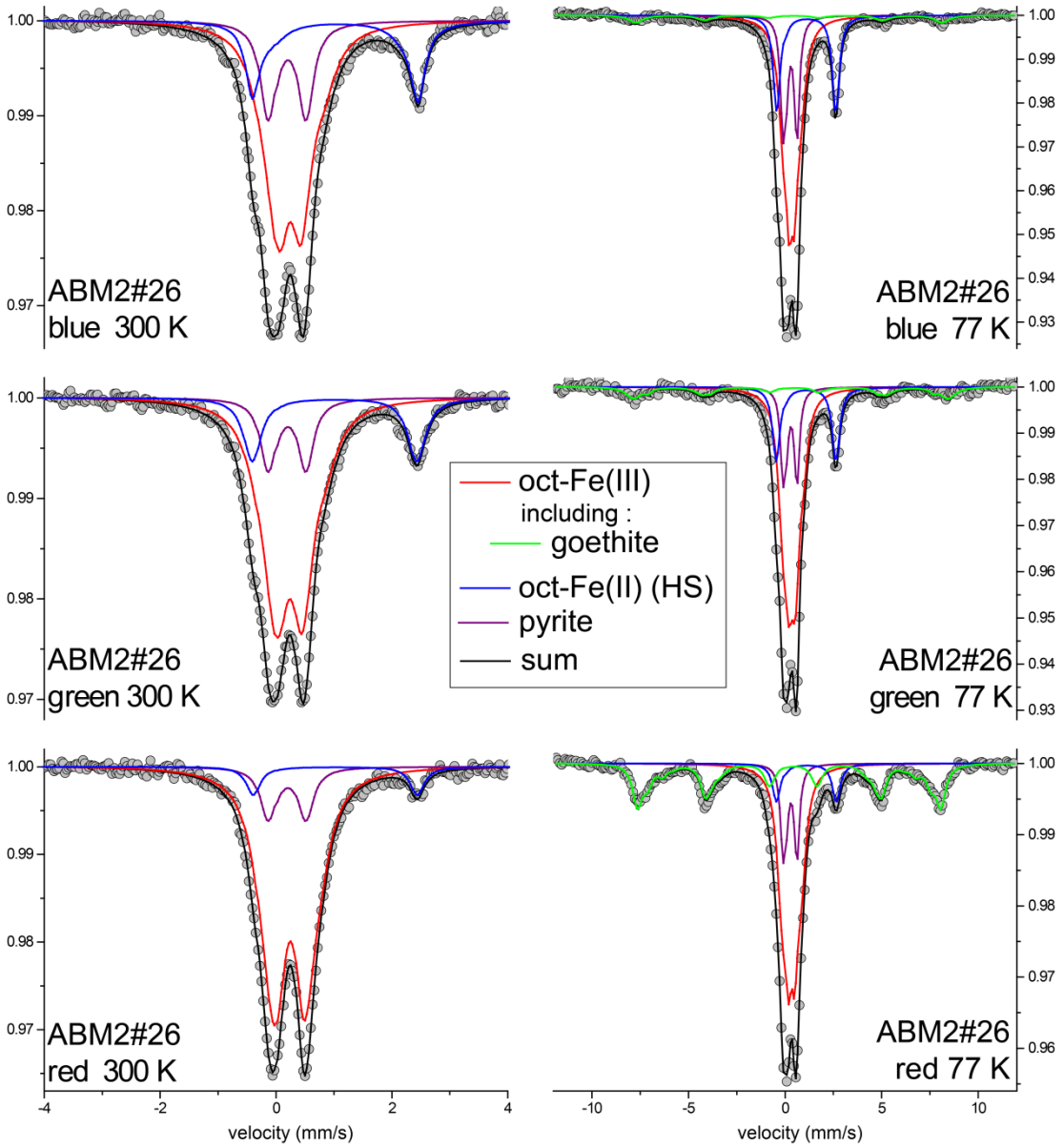

Fig. S4-7 Room temperature and 77 K Mössbauer spectra of a series of 3 samples from block ABM2#26. The hyperfine parameters are displayed in Table S4-7.

Table S4-7 Refined values of Mössbauer parameters and doublet structural attributions for the ample collected on block ABM2#26 (Deponit)

Hyperfine parameters					Attribution
I.S.	**F.W.H.M.**	**Q.S./2ε**	***B*hf**	**Area(%)**	
		Red			
		300 K			
0.35	0.38	0.48		51	HS-oct-Fe(III)
0.36	0.55	0.90		31	
0.31	0.32	0.62		12	pyrite
1.14	0.30	2.80		6	HS-oct-Fe(II)
		77 K			
0.45	0.41	0.31		22	HS-oct-Fe(III)
0.48	0.62	0.93		24	HS-oct-Fe(III)
0.42	0.32	0.62		12	pyrite

Hyperfine parameters					Attribution
I.S.	**F.W.H.M.**	**Q.S./2ε**	***B*hf**	**Area(%)**	
1.26	0.50	3.00		8	HS-oct-Fe(II)
<0.48>		<-.22>	<46.1>	35	goethite
0.48	0.60	-0.22	48.5	(20)	(goethite)
0.48	0.60	-0.22	45.3	(9)	(goethite)
0.48	0.60	-0.22	40.5	(5)	(goethite)
0.48	0.60	-0.22	37	(2)	(goethite)
		Green			
		300 K			
0.34	0.45	0.43	55%	37	HS-oct-Fe(III)
0.39	0.56	1.11	14%	41	
0.31	0.32	0.62	15%	14	HS-oct-Fe(II)
1.13	0.37	2.81	16%	9	
		77 K			
0.46	0.64	0.78		74	HS-oct-Fe(III)
1.28	0.43	2.83		24	HS-oct-Fe(II)
0.48	0.50	-0.22	49.5	2	goethite
		Blue			
		300 K			
0.35	0.53	0.60		53	HS-oct-Fe(III)
0.41	0.27	1.13		13	
1.12	0.27	2.85		15	HS-oct-Fe(II)
1.11	0.43	2.53		20	
		77 K			
0.47	0.68	0.72		63	HS-oct-Fe(III)
1.25	0.41	2.92		33	HS-oct-Fe(III)
0.46	0.50	-0.22	54.0	3	hematite
0.48	0.50	-0.22	49.2	2	goethite

I.S. = Isomer shift value relative to that of the α-Fe at 300 K. ($mm \cdot s^{-1}$)
F.W.H.M = Full width of line at half of its maximum intensity. ($mm \cdot s^{-1}$)
Q.S./2ε = Quadrupolar splitting
B_{hf} = Magnetic hyperfine field (T)

S4-5 Fe distribution inferred from Mössbauer data

Table S4-8 Fe distribution inferred from Mössbauer data

block #	material	sample type	Distance interface	Absolute content								
				total Fe[a]	(species distribution)							
					HS-para-Fe(II)[b]	HS-para-Fe(III)[c]	mag-Fe(III)[d]					pyrite
							total mag[e]	goethite		hematite		
								large[f]	medium[g]	large[f]	medium[g]	
			(mm)	(mmolFe·kg^{-1})								
#08	MX80	raw	raw	490	88	402						
		crust	<0.3									
		contact	0.3-5	610	77	533						
		bulk	>45	485	127	357						
#11	Ibecoseal	raw	raw	476	148	328			n.d.		n.d.	
		crust	<0.3	2128	500	1581	47		47			
		contact	0.3-5	856	278	542	36		14		22	
		bulk	>45	512	174	291	47		17		30	
#12	Ikosorb	raw	raw	321								
		crust	<0.3	1420	128	1150	142		114		28	
		contact	0.3-5	436	44	306	87		61		26	
		heart	15-25	353	74	251	28		14		14	
		bulk	>45	290	29	226	35		9		26	
#13	Kunigel	raw	raw	232								
		crust		290								
#25	MX80+30%qtz		raw	343	62	281						
		crust	<0.3	1989	378	796	816		816			
		contact 1	1.5	1658	348	663	630		597		33	
		contact 2	3	604	133	230	242		242			
		contact 3	4.5	552	116	204	232		215		17	
		bulk	45	378	102	208	68		34		34	
#26	Deponit CAN		raw	581	54	410	0		0			117
		red crust	<0.3	798								
		salt	27	623								
		red	n.a.	1231	95	562	425		425			149
		green	n.a.	694	119	381	97		97			105
		blue	n.a.	752	164	383	53		53			152
#27	MX80		raw	490	88	402						
		crust	<0.3	645	97	548						
		salt	7	576	63	294	219		219			
		bulk	25	533								

Table S4-9 (cont.)

[a] Determined by XRF (raw materials) and SEM/EDX by EDX contact/bulk samples

[b] Paramagnetic Fe(II) (~total Fe(II) content)

[c] Paramagnetic Fe(III) (Paramagnetic Fe(III) (= total Fe – paramagnetic Fe(II) – magnetically ordered Fe(III))

[d] Magnetically ordered Fe(III)

[e] Fe(III) in species magnetically ordered at 77 K (i.e. includes medium- and large-sized species)

[f] Fe(III) in species magnetically ordered at 300 K

[g] Difference between contents at 77 K and at 300 K