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Supporting Information Table 1: Metal binding properties of polyligands

Polyligand	Metal	$\Delta \log \text{Me}^{\text{a}}$ $\Delta \log \{\text{Me}\}$	$\Delta \text{pMe}^{\text{b}}$ ΔpH	Surface Coverage ^c	References
Goethite	Cu^{2+}	0.6-0.7	1.6-1.9		(27)
Rutile	Cu^{2+}	0.6-0.7	1.4-1.6		(27)
Corundum	Cu^{2+}	0.6-0.7	1.3-1.6		(27)
am-Fe(OH) ₃	Cd^{2+}	0.7	2		(52)
Rutile	Cd^{2+}	0.6-0.7	1.1		(52)
Corundum	Cd^{2+}	0.7	1.4-1.6	high	(52)
Corundum	Cd^{2+}	1		low	(52)
am-Fe(OH) ₃	VO_2^+	0.8-0.9			(52)
Rutile	VO_2^+	0.8-0.9			(52)
Corundum	VO_2^+	0.8-0.9			(52)
am-Fe(OH) ₃	CrO_4^{2-}	0.8			(52)
Corundum	CrO_4^{2-}	0.9-1			(52)
Goethite	Cd^{2+}	1		low	(43)
Goethite	Zn^{2+}	0.5	1.5		(53)
am-Fe(OH) ₃	Zn^{2+}	0.55-0.7	1.5-1.7	high	(38, 54)
am-Fe(OH) ₃	Zn^{2+}	0.9-1		low	(38, 54)
am-Fe(OH) ₃	Hg^{2+}	1	2		(38, 54)
am-Fe(OH) ₃	Co^{2+}	1			(38, 54)
am-Fe(OH) ₃	Ca^{2+}	0.5		high	(38, 54)
am-Fe(OH) ₃	Ca^{2+}	0.9-1		low	(38, 54)
am-Fe(OH) ₃	SeO_4^{2-}	0.9-1	-1		(38, 54)
am-Fe(OH) ₃	Cd^{2+}	0.66	1.6-1.7	high	(55)
am-Fe(OH) ₃	Cd^{2+}	1		low	(55)
am-Fe(OH) ₃	Cu^{2+}	0.66		high	(55)
am-Fe(OH) ₃	Cu^{2+}	1		low	(55)
am-Fe(OH) ₃	Pb^{2+}	0.5			(55)
am-Fe(OH) ₃	Zn^{2+}	1			(55)
Hematite	Th^{4+}	1			(56)
Montmorillonite	Cu^{2+}	0.5			(27)
Bentonite	Cd^{2+}	0.8			(52)
Humic Acid	Cu^{2+}	0.4	0.9-1.0		(27)
Humic Acid	Cu^{2+}	0.4	1.5		(28)
Humic Acid	Cd^{2+}	0.6-0.7	0.9		(28)
Humic Acid	Ca^{2+}	0.4	0.25		(28)
Fulvic acid	Cu^{2+}	0.5	1.2-1.3		(57)
Sediment	Cu^{2+}	0.6	1		(27)
Hanford soil	Cu^{2+}	0.6	1		(27)
Hanford soil	Cd^{2+}	0.7-0.8			(52)

^aMe_b--bound metal, {Me}--solution activity ^b--for constant metal bound

^chigh coverage lower bound may range from <0.01 to 1% of total sites

Supporting Information Table 2--SCM copper binding fits (Table 4 of text)
TLM--SOCu⁺

Figure:						6a			
[S1OH] ^a	<u>6.81E-4</u>	5.43E-4	2.66E-4	<u>6.81E-4</u>	6.57E-4	5.26E-4	<u>6.00E-4</u>	<u>4.80E-4</u>	<u>4.00E-4</u>
[S2OH] ^b				1.16E-6	1.07E-6	1.07E-6	<u>8.00E-5</u>	<u>2.00E-4</u>	<u>2.80E-4</u>
[S3OH]			<u>4.10E-4</u>			<u>1.50E-4</u>	9.71E-7	1.00E-6	1.00E-6
logK1 _{Me}	2.59	2.76	3.06	2.41	2.45	2.54	2.24	2.07	1.93
logK2 _{Me} ^c				5.92	5.93	5.97	3.05	2.83	6.00
logK3 _{Me}							6.02	6.00	2.75
WSOS/DF	83.0	67.6	69.0	17.3	21.8	17.3	17.1	16.9	17.1

	Mod TL--SOCu ⁺			2.3/nm ²		DLM--SOCu ⁺		7/nm ²		
Figure:			6b							6c
[S1OH]	<u>6.64E-4</u>	9.90E-4	<u>6.64E-4</u>	1.41E-3	2.13E-4	<u>1.88E-4</u>	2.68E-4	<u>5.70E-4</u>	2.86E-4	<u>5.70E-4</u>
[S2OH]			5.28E-7	1.15E-6		6.72E-7	1.08E-6			9.66E-7
[S3OH]										
logK1 _{Me}	1.81	1.71	1.71	1.45	2.30	2.23	2.05	1.53	1.75	1.39
logK2 _{Me}			5.49	5.26		5.36	5.16			4.86
logK3 _{Me}										
WSOS/DF	79.7	68.0	50.0	11.5	140.6	110.7	110.7	159.3	171.9	111.8

TLM--S₂OCu⁺(·ClO₄⁻)

Figure:						6d		6f ^d		
[S1OH]	<u>6.81E-4</u>	3.89E-4	2.21E-4	<u>6.81E-4</u>	4.94E-4	2.78E-4	<u>5.80E-4</u>	<u>5.60E-4</u>	<u>5.30E-4</u>	<u>4.30E-4</u>
[S2OH]				2.28E-6	1.43E-6	1.37E-6	<u>1.00E-4</u>	<u>1.20E-4</u>	<u>1.50E-4</u>	<u>2.50E-4</u>
[S3OH]			<u>4.60E-4</u>			<u>4.00E-4</u>	1.02E-6	1.06E-6	1.13E-6	1.34E-6
logK1 _{Me}	2.12	2.37	2.72	1.89	2.08	2.40	1.39	1.32	1.20	0.59
logK2 _{Me}				5.16	5.36	5.45	2.83	2.76	2.66	2.44
logK3 _{Me}							5.62	5.60	5.56	5.46
logK1 _{Me..X}	2.55	2.81	3.15	2.32	2.51	2.83	1.83	1.75	1.63	1.03
logK2 _{Me..X}				5.59	5.80	5.89	3.26	3.19	3.10	2.87
logK3 _{Me..X}							6.05	6.03	6.00	5.90
WSOS/DF	136.9	87.3	86.8	22.3	15.7	14.5	11.1	11.0	11.1	13.2

Supporting Information Table 2, cont.

TLM--SOCuOH

Figure:			6e		6g ^d	
[S1OH]	<u>6.81E-4</u>	1.89E-4	2.05E-4	<u>5.30E-4</u>	<u>5.50E-4</u>	<u>5.80E-4</u>
[S2OH]			2.05E-6	<u>1.50E-4</u>	<u>1.30E-4</u>	<u>1.00E-4</u>
[S3OH]			<u>4.80E-4</u>	<u>1.39E-6</u>	<u>1.20E-6</u>	9.58E-7
logK1 _{MeOH}	-6.61	-5.66	-6.10	-8.31	-8.15	-7.91
logK2 _{MeOH}			-3.29	-5.87	-5.78	-5.61
logK3 _{MeOH}				-3.06	-2.98	-2.85
WSOS/DF	513.0	133.3	37.7	13.6	12.7	16.3

Mod TL--SOCuOH

Figure:							
[S1OH]	<u>6.64E-4</u>	1.89E-4	1.75E-4	2.05E-4	<u>5.40E-4</u>	<u>5.30E-4</u>	<u>5.20E-4</u>
[S2OH]				2.05E-6	<u>1.20E-4</u>	<u>1.30E-4</u>	<u>1.40E-4</u>
[S3OH]			<u>4.80E-4</u>	<u>4.60E-4</u>	1.11E-6	1.20E-6	1.29E-6
logK1 _{MeOH}	-6.67	-5.72	-6.02	-6.17	-8.13	-8.21	-8.29
logK2 _{MeOH}				-3.36	-5.80	-5.85	-5.90
logK3 _{MeOH}					-3.01	-3.05	-3.09
WSOS/DF	504.0	130.9	138.1	37.8	13.2	12.8	13.0

2.3/nm²

DLM--SOCuOH

7/nm²

Figure:										
[S1OH]	1.89E-4	<u>1.88E-4</u>	2.30E-4	<u>5.70E-4</u>	1.82E-4	2.16E-4	2.04E-4	<u>3.70E-4</u>	4.20E-4	<u>4.70E-4</u>
[S2OH]		1.42E-6	<u>2.50E-6</u>			1.98E-6	2.06E-6	<u>2.00E-4</u>	<u>1.50E-4</u>	<u>1.00E-4</u>
[S3OH]							<u>3.50E-4</u>	1.98E-6	1.39E-6	9.54E-7
logK1 _{MeOH}	-5.61	-5.82	-6.07	-6.58	-5.73	-6.12	-6.16	-8.76	-8.28	-7.88
logK2 _{MeOH}		-2.91	-3.29			-3.26	-3.26	-6.15	-5.94	-5.67
logK3 _{MeOH}								-3.32	-3.12	-2.90
WSOS/DF	165.9	94.8	73.2	493.7	144.1	50.6	42.7	30.1	17.8	19.4

Supporting Information Table 2, cont.

TLM--(SO)₂Cu

Figure:							
[S1OH]	<u>6.81E-4</u>	4.63E-4	<u>6.81E-4</u>	5.47E-4	<u>3.50E-4</u>	<u>3.30E-4</u>	<u>3.00E-4</u>
[S2OH]			2.32E-6	1.46E-6	<u>3.30E-4</u>	<u>3.50E-4</u>	<u>3.80E-4</u>
[S3OH]					9.77E-7	1.01E-6	1.07E-6
logK1 _{biMe}	-4.10	-3.61	-4.35	-4.03	-4.98	-5.01	-5.08
logK2 _{biMe}			-1.07	-0.68	-3.53	-3.58	-3.63
logK3 _{biMe}					-0.27	-0.27	-0.26

Mod TL--(SO)₂Cu

Figure:							
[S1OH]	<u>6.64E-4</u>	4.66E-4	<u>6.64E-4</u>	5.31E-4	<u>3.50E-4</u>	<u>3.00E-4</u>	<u>3.00E-4</u>
[S2OH]			2.11E-6	1.45E-6	<u>3.10E-4</u>	<u>3.60E-4</u>	<u>3.60E-4</u>
[S3OH]				<u>1.40E-4</u>	9.57E-7	9.41E-7	1.04E-6
logK1 _{biMe}	-4.22	-3.76	-4.46	-4.17	-4.99	-3.59	-5.08
logK2 _{biMe}			-1.16	-0.83	-3.62	-4.97	-3.76
logK3 _{biMe}					-0.41	-0.30	-0.39
WSOS/DF	140.8	96.5	32.0	25.7	19.9	19.9	19.8

2.3/nm²DLM--(SO)₂Cu7/nm²

Figure:									
[S1OH]	<u>1.88E-4</u>	5.68E-4	<u>5.70E-4</u>	4.53E-4	<u>5.70E-4</u>	5.39E-4	<u>3.00E-4</u>	<u>2.50E-4</u>	<u>2.00E-4</u>
[S2OH]		1.62E-6			1.69E-6	1.50E-6	<u>2.70E-4</u>	<u>3.20E-4</u>	<u>3.70E-4</u>
[S3OH]							9.45E-7	9.97E-7	1.07E-7
logK1 _{biMe}	-2.26	-4.10	-4.03	-3.73	-4.25	-4.16	-4.56	-4.61	-4.66
logK2 _{biMe}		-0.75			-0.92	-0.82	-3.50	-3.65	-3.78
logK3 _{biMe}							-0.30	-0.25	-0.20
WSOS/DF	551.5	59.1	125.7	107.6	37.2	37.6	32.3	32.2	32.3

Supporting Information Table 2, cont.

TLM SOCu⁺ & SOCuOH

Figure:						
[S1OH] ^a	<u>3.50E-4</u>	<u>4.00E-4</u>	<u>4.50E-4</u>	<u>5.50E-4</u>	<u>5.50E-4</u>	<u>5.50E-4</u>
[S2OH] ^b	1.01E-6	1.04E-6	1.06E-6	<u>1.30E-4</u>	<u>1.30E-4</u>	<u>1.30E-4</u>
[S3OH]	<u>3.30E-4</u>	<u>2.80E-3</u>	<u>2.30E-3</u>	1.20E-6	1.20E-6	1.15E-6
logK1 _{Me}	2.73	2.67	2.61	-2.65	-0.67	0.27
logK2 _{Me}	5.99	5.98	5.97	-0.28	1.71	2.58
logK3 _{Me} ^c				2.52	4.51	5.40
logK1 _{MeOH}	-8.01	-8.34	-8.65	-8.15	-8.17	-8.23
logK2 _{MeOH}	-4.75	-5.03	-5.29	-5.78	-5.79	-5.92
logK3 _{MeOH}				-2.98	-3.00	-3.11
WSOS/DF	16.7	16.7	16.8	12.7	12.7	12.7

TLM SOCu⁺(·ClO₄⁻) & SOCuOH

Figure:	6h ^d						
[S1OH]	2.58E-4	2.64E-4	<u>5.00E-4</u>	<u>5.30E-4</u>	<u>5.40E-4</u>	<u>5.50E-4</u>	<u>6.00E-4</u>
[S2OH]		1.39E-6	<u>1.80E-4</u>	<u>1.50E-4</u>	<u>1.40E-4</u>	<u>1.30E-4</u>	<u>8.00E-5</u>
[S3OH]		<u>4.20E-4</u>	1.24E-6	1.16E-6	1.12E-6	1.06E-6	9.54E-7
logK1 _{Me}	2.50	2.41	0.59	0.53	0.54	0.60	1.42
logK2 _{Me}		5.44	2.56	2.60	2.63	2.56	2.93
logK3 _{Me}			5.47	5.46	5.47	5.47	5.65
logK1 _{Me..X}	2.93	2.84	1.02	0.96	0.98	1.04	1.86
logK2 _{Me..X}		5.87	2.99	3.04	3.06	2.99	3.37
logK3 _{Me..X}			5.91	5.90	5.90	5.91	6.09
logK1 _{MeOH}	-7.17	-7.92	-8.99	-8.66	-8.57	-8.49	-9.13
logK2 _{MeOH}		-4.89	-7.02	-6.58	-6.48	-6.54	-7.62
logK3 _{MeOH}			-4.11	-3.73	-3.64	-3.62	-4.90
WSOS/DF	73.9	14.7	9.2	7.7	7.5	7.6	10.8

Supporting Information Table 2, cont.

Mod TL SOCu⁺ & SOCuOH

Figure:	6i ^d						
[S1OH]	<u>6.64E-4</u>	2.88E-4	<u>6.64E-4</u>	<u>2.73E-4</u>	<u>5.00E-4</u>	<u>5.20E-4</u>	<u>5.30E-4</u>
[S2OH]			9.21E-7	1.06E-6	<u>1.60E-4</u>	<u>1.40E-4</u>	<u>1.30E-4</u>
[S3OH]				<u>4.00E-4</u>	1.19E-6	1.13E-6	1.08E-6
logK1 _{Me}	1.76	1.85	1.58	1.90	-0.25	-0.24	-0.21
logK2 _{Me}			5.14	5.02	1.94	1.95	1.97
logK3 _{Me}					4.81	4.78	4.79
logK1 _{MeOH}	-8.39	-7.30	-8.19	-7.17	-8.58	-8.43	-8.35
logK2 _{MeOH}			-4.63	-4.05	-6.40	-6.24	-6.18
logK3 _{MeOH}					-3.53	-3.41	-3.36
WSOS/DF	65.3		18.8	15.1	7.4	6.8	7.0

2.3/nm²DLM SOCu⁺ & SOCuOH7/nm²

Figure:				6j ^d					
[S1OH]	<u>1.88E-4</u>	<u>1.88E-4</u>	<u>2.16E-4</u>	<u>5.70E-4</u>	2.14E-4	2.08E-4	<u>5.70E-4</u>	2.16E-4	<u>4.40E-4</u>
[S2OH]		1.68E-6	1.92E-6				1.81E-6	1.88E-6	<u>1.30E-4</u>
[S3OH]						<u>3.60E-4</u>		<u>3.50E-4</u>	1.18E-6
logK1 _{Me}	2.50	1.79	1.76	1.50	1.63	1.87	1.25	1.32	-0.63
logK2 _{Me}		4.61	4.60				4.47	4.16	1.52
logK3 _{Me}									4.30
logK1 _{MeOH}	2.50	1.79	1.76	1.50	1.63	1.87	1.25	1.32	-0.63
logK2 _{MeOH}		4.61	4.60				4.47	4.16	1.52
logK3 _{MeOH}									4.30
WSOS/DF	94.9	34.6	26.6	146.7	99.4	107.1	72.0	26.1	6.2

^asite concentration, moles/g goethite; underlined, italicized values were fixed, not fit^bif blank there are no sites in this class^cif blank, site class does not bind copper^dFigures included in Supporting Information

Regressions of pH5&6; 0.(0)1N data; 207 data points

Acid base parameters shown in Table 2 of main text

FITEQL Error terms--(Absolute:CuT--1.0E-7); (Relative: CuT--0.01; Cu_f--.046; H_f, Na_f, ClO_{4f}--.023); T--total, f--freeFor bidentate reactions use (SxO)₂Cu for total [SxOH] >1.00E-4M; use (S1O)Cu(SxO) for total [SxOH]<1.0E-4M, i.e., assumes a low density site is more likely to be located adjacent to a high density site than to another low density site

Fig. SI 1a

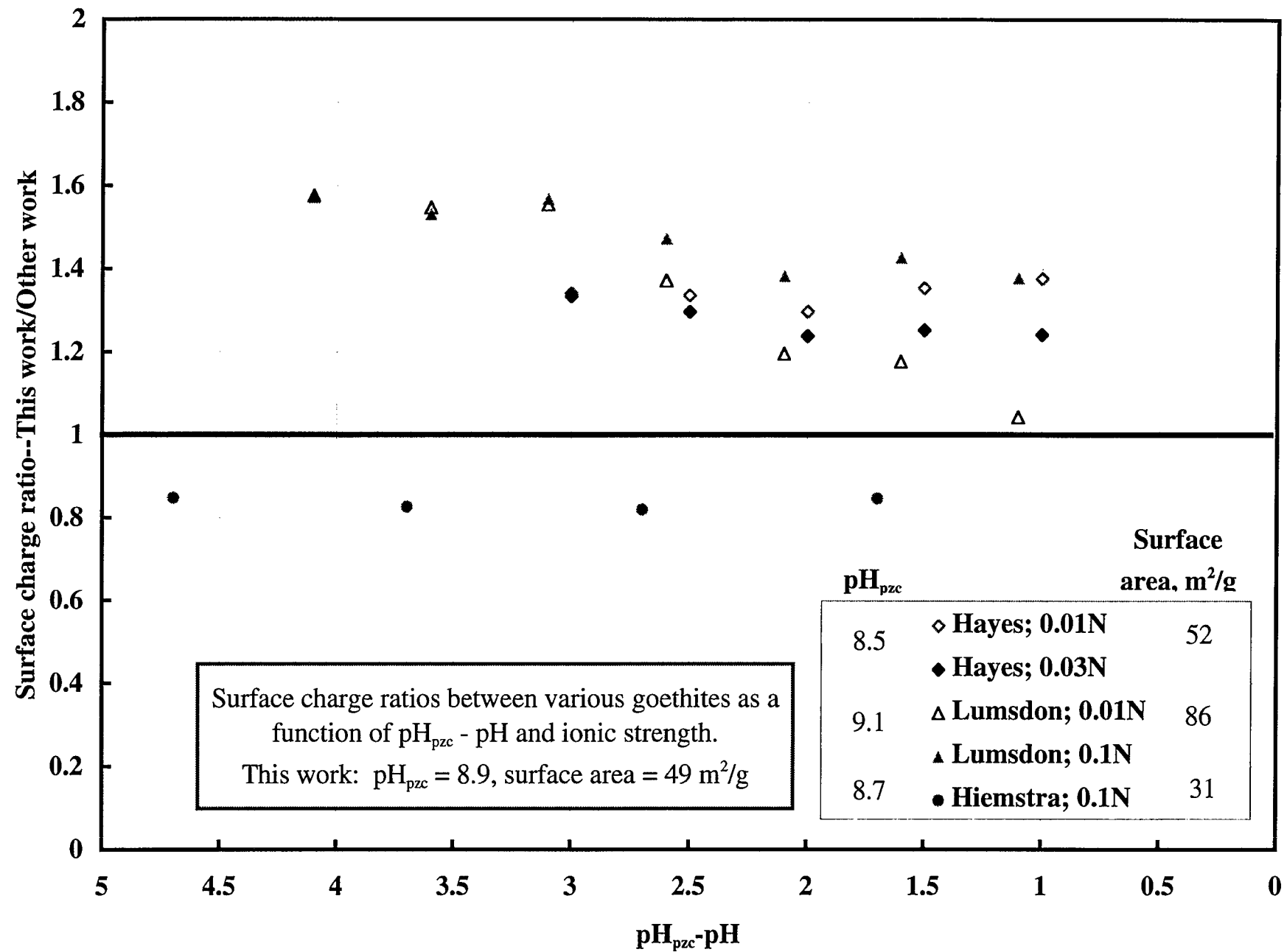


Fig. SI 1b

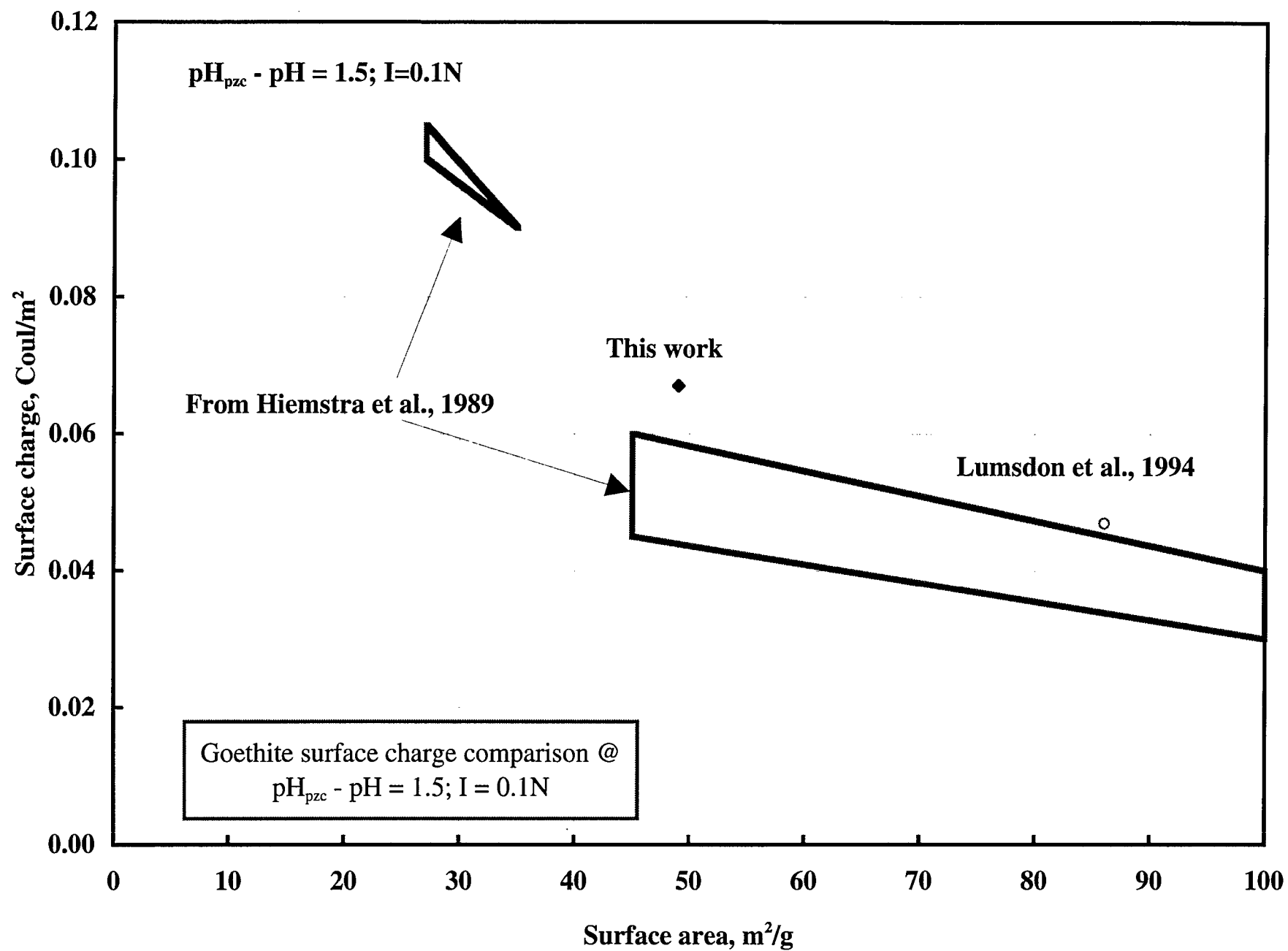


Fig. SI 2a

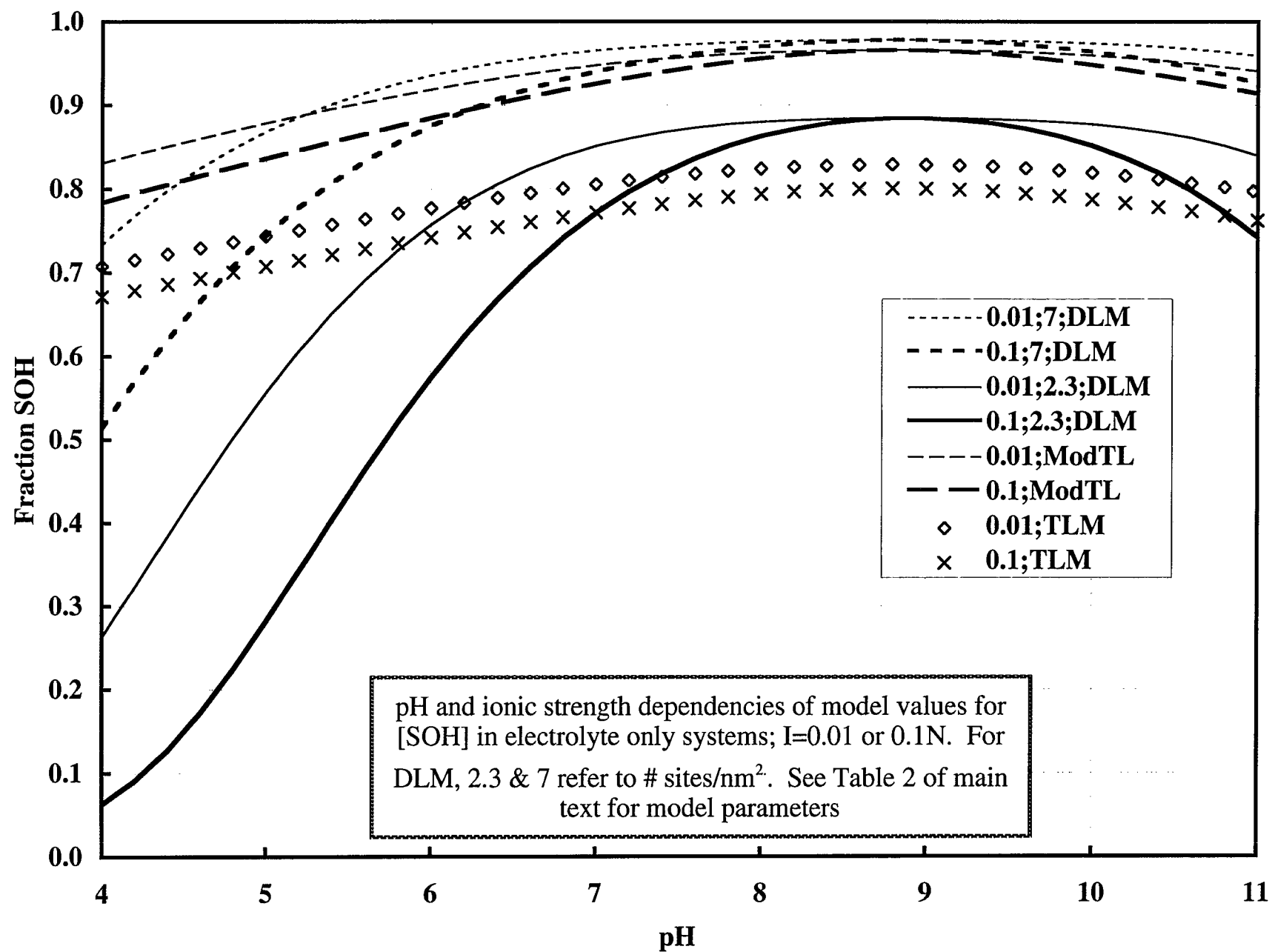


Fig. SI 2b

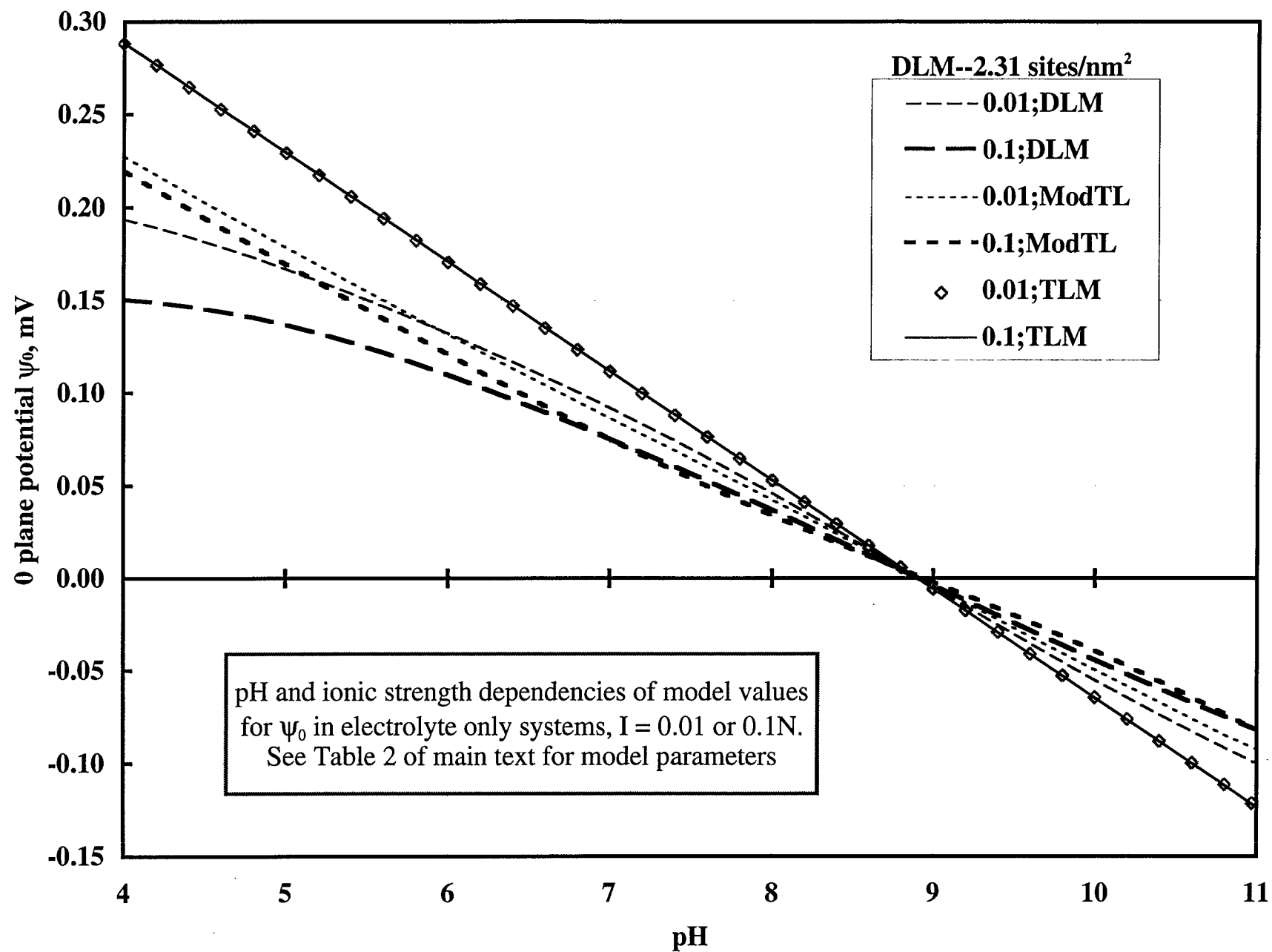


Fig. 6f

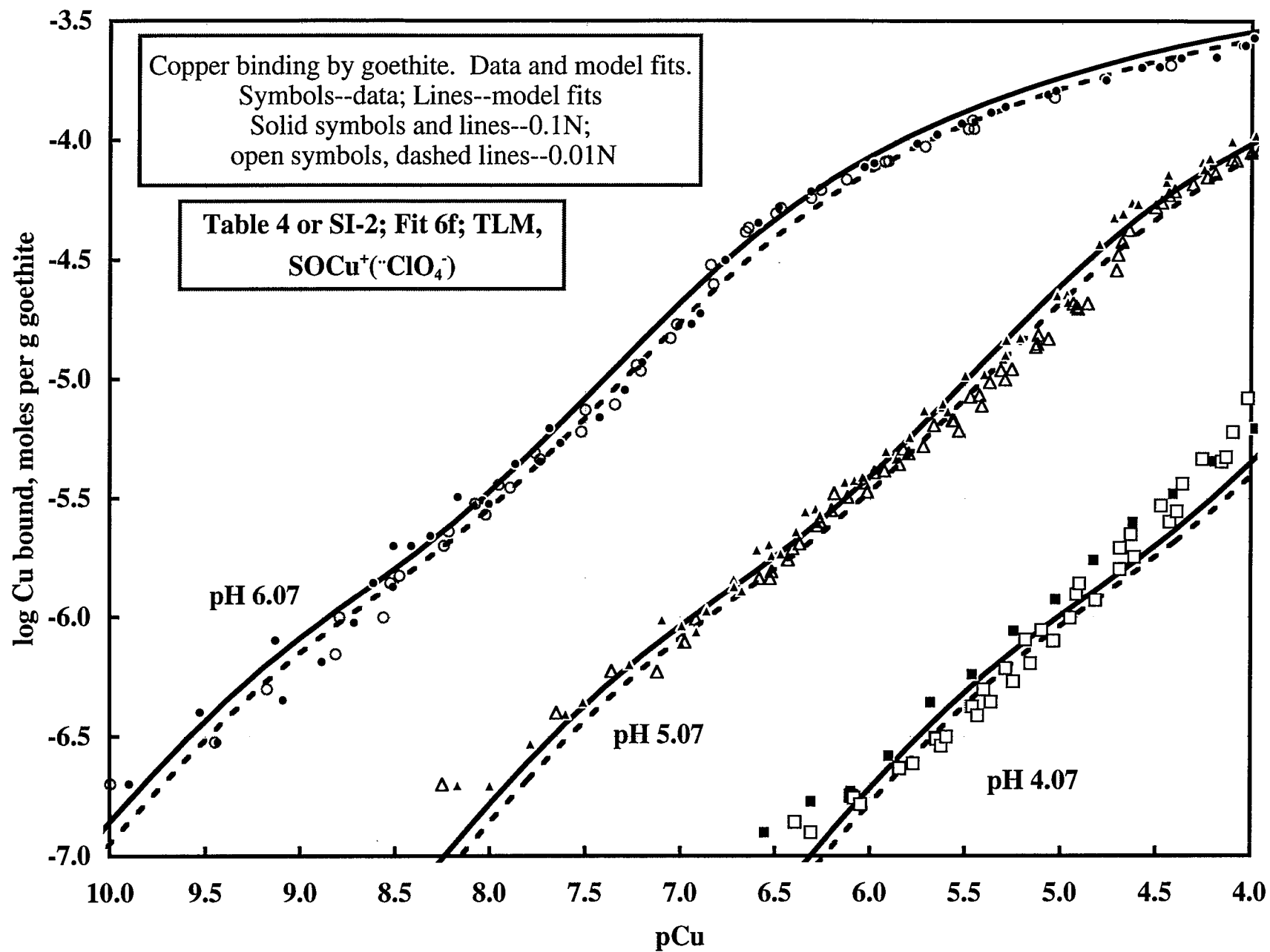


Fig. 6g

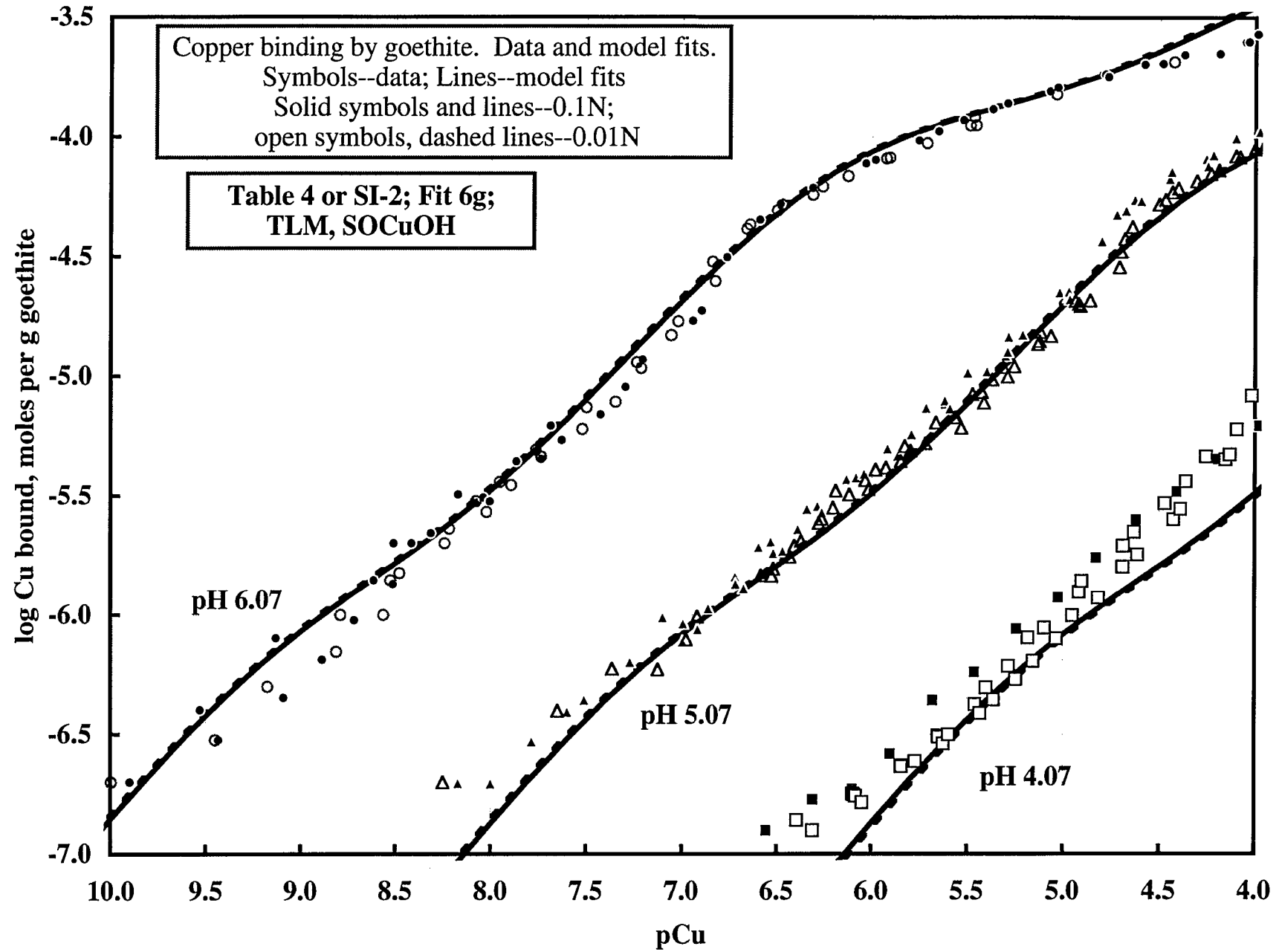


Fig. 6h

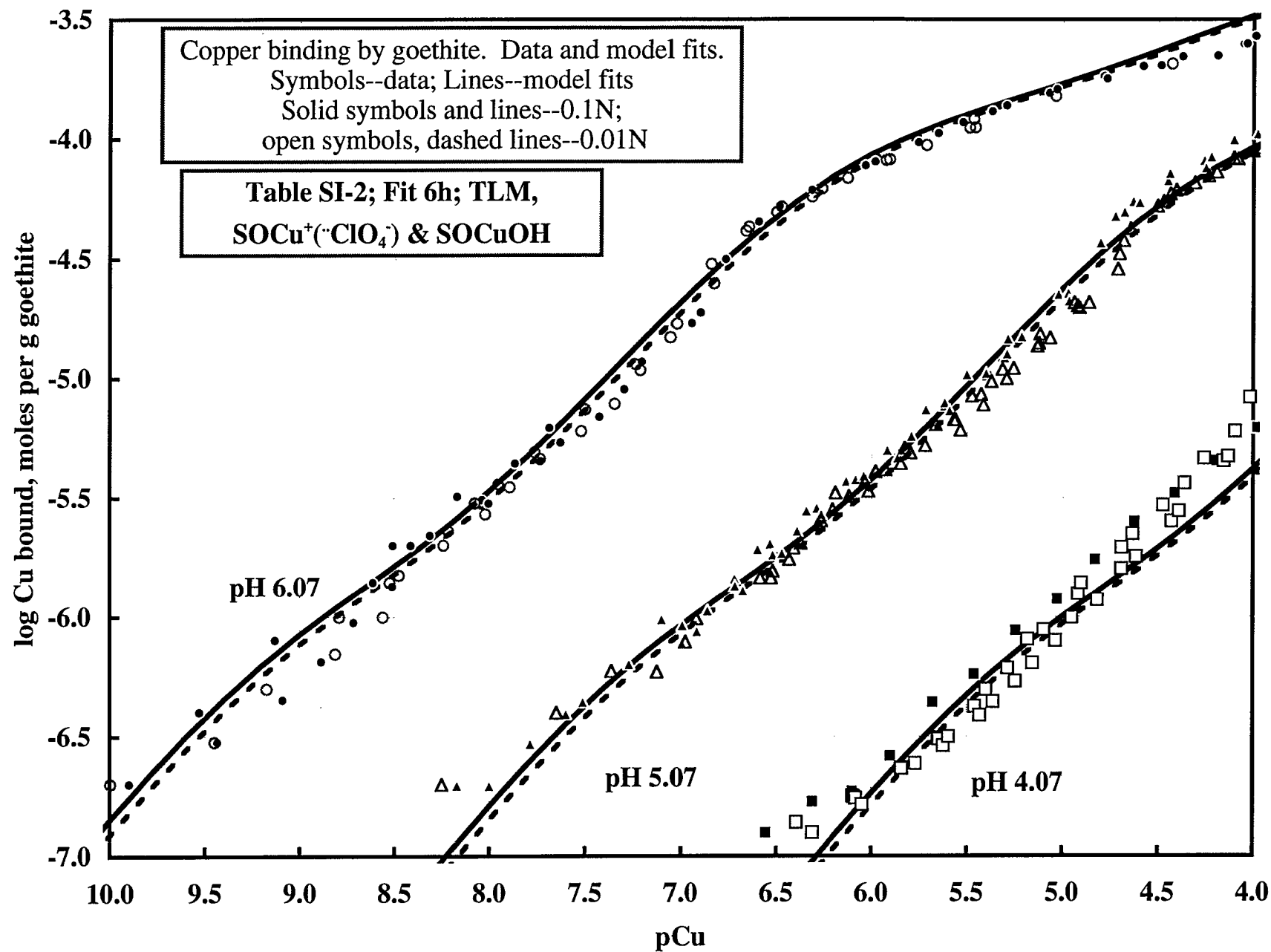


Fig. 6i

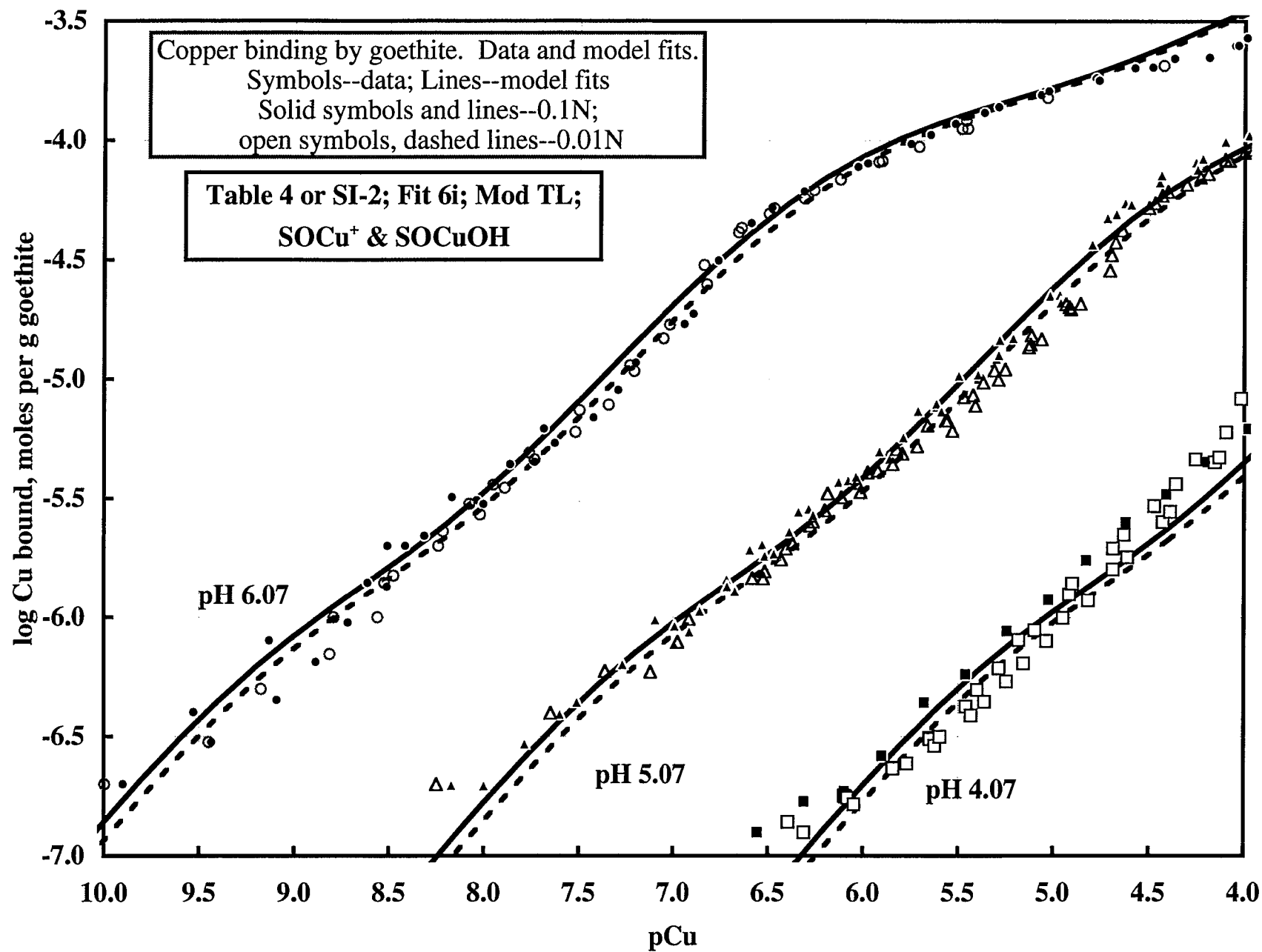


Fig. 6j

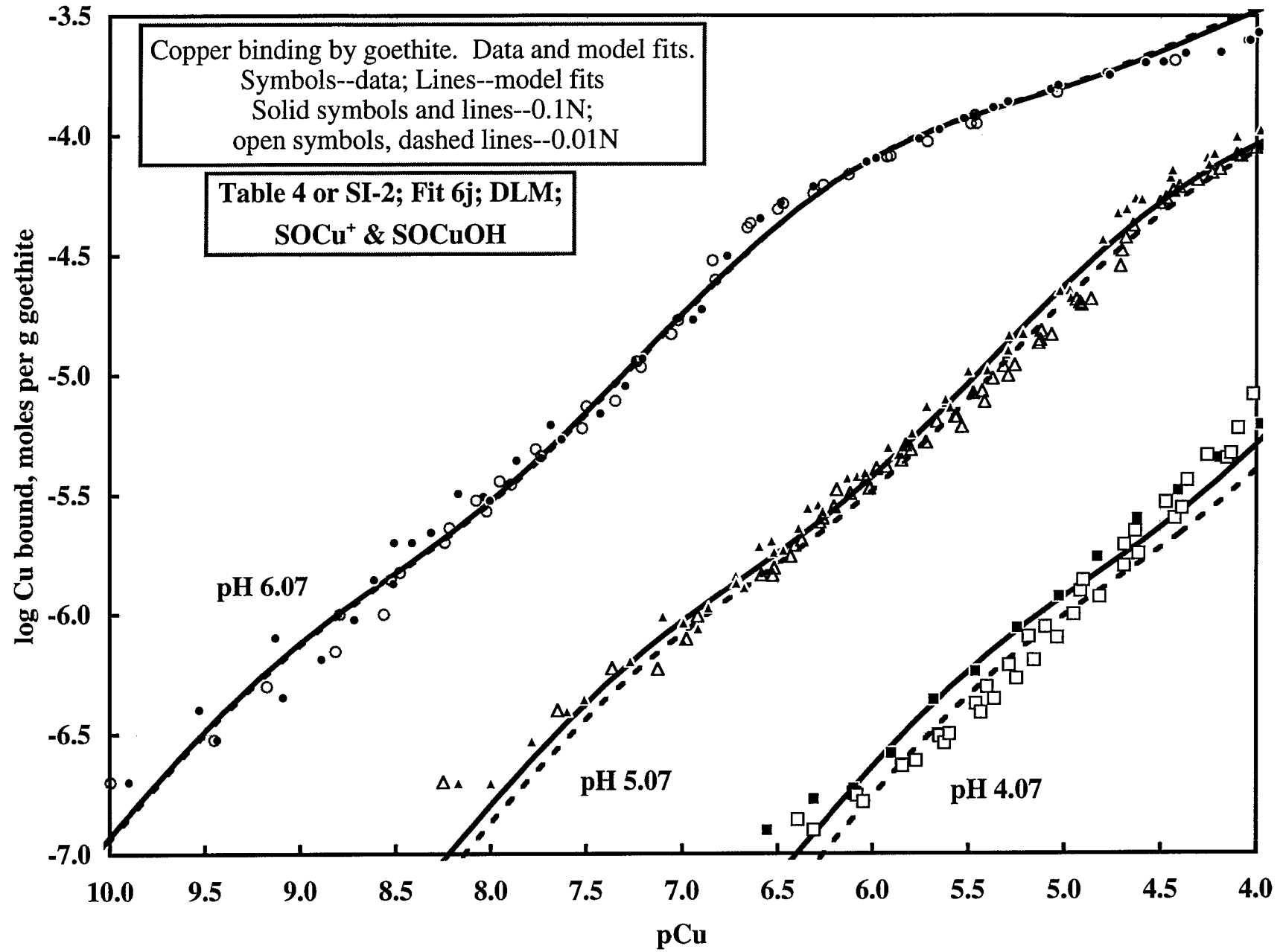


Fig. 7b

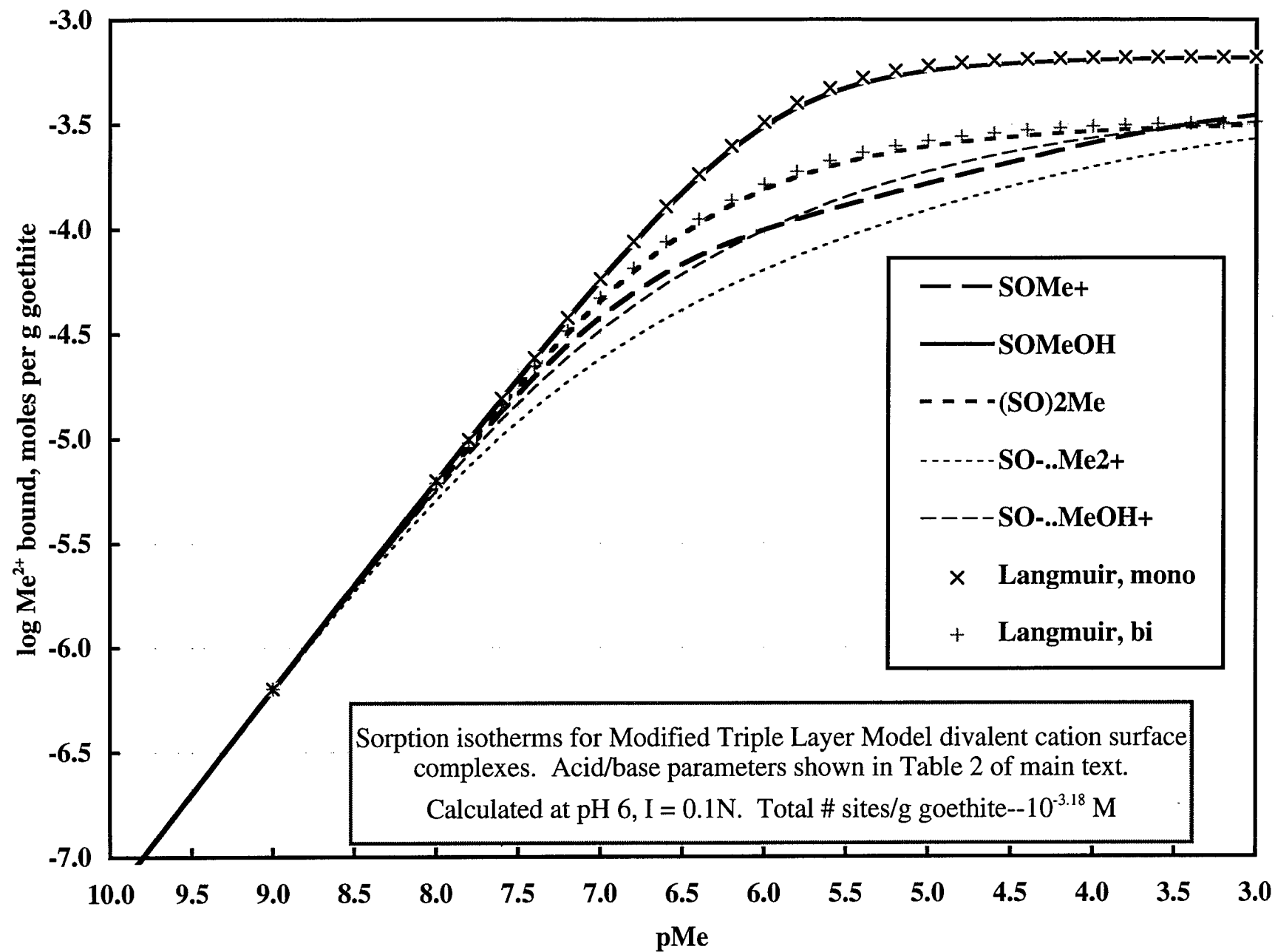


Fig.7c

