5. DATA REPORT: DISSOLVED MANGANESE CONCENTRATIONS IN DEEP DRILL HOLES OFF NEW ZEALAND (ODP LEG 181)¹

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INTRODUCTION

During Leg 181, seven locations (Sites 1119–1125) were drilled off the eastern coast of New Zealand. Although the sites were primarily targeted to reconstruct the stratigraphy and paleoceanography of the region (Shipboard Scientific Party, 1999), they are particularly interesting from a geochemical perspective because, as clearly evidenced by shipboard pore water and gas analyses, recovered sediment cores span an exceptional range of chemical environments. Pore water alkalinity, NH_4^+ , SO_4^{2-} , and PO_4^{3-} concentrations, as well as headspace CH_4 concentrations, indicate significant differences in sediment redox conditions across the region (Shipboard Scientific Party, 1999). The distribution of solid and dissolved manganese plays an important role in geochemical interpretations of such sedimentary environments (e.g., Froelich et al., 1979; Thamdrup and Dalsgaard, 2000). Dissolved Mn^{2+} concentrations of pore waters at four sites (1119, 1122, 1123, and 1125) drilled during Leg 181 are presented in this report.

METHODS

Pore waters were squeezed from whole-round sediment intervals, acidified with HNO₃, and sealed in plastic tubes according to standard procedures aboard the *JOIDES Resolution*. The samples were shipped to James Cook University (JCU). After cutting each tube, precisely 1.00 mL of solution was removed with a pipette, placed into a plastic vial, and mixed with 8.90 mL of deionized water and 0.10 mL of 1% HNO₃

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spiked with 10 ppm rhodium for use as an internal standard. All samples were then analyzed for Mn concentrations by inductively coupled plasma-mass spectrometry (ICP-MS) at the JCU Advanced Analytical Centre (AAC). Prepared solutions were injected into a Varian Ultramass ICP-MS with a quadrupole mass analyzer. Manganese concentrations in solution were obtained through standard comparisons to a concentration curve. The curve was constructed by spiking the certified CASS-2 seawater standard with known concentrations of Mn and Ba. Four pore water samples from Leg 181 were prepared and analyzed a second time to assess precision. Repeated analyses of these true replicates are within 6% (Table T1).

RESULTS

Dissolved Mn^{2+} concentrations range between 0.1 and 26.5 μ M (Table T1; Fig. F1) and average 1.8, 3.3, 3.8, and 1.0 μ M at Sites 1119, 1122, 1123, and 1125, respectively. Thus, Mn^{2+} concentrations are relatively high at the deep sites (1122 and 1123) and relatively low at the shallow sites (1119 and 1125). This observation may reflect higher inputs of reducible solid Mn phases at the deeper locations. There is an overall positive correlation between dissolved Mn^{2+} and dissolved SO_4^{2-} concentrations (Fig. F1). Because SO_4^{2-} reduction increases alkalinity, it is probable that Mn^{2+} profiles are strongly influenced by authigenic carbonate precipitation and incorporation of Mn.

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F1. Dissolved Mn^{2+} and SO_4^{2-} concentrations, p. 4.



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Figure F1. Downcore profiles of dissolved Mn^{2+} and dissolved SO_4^{2-} concentrations at ODP Sites 1119, 1122, 1123, and 1125. Concentrations of dissolved SO_4^{2-} are reported in Leg 181 site chapters (Shipboard Scientific Party, 1999). mcd = meters composite depth.



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 Table T1. Manganese concentrations in pore waters Sites 1119, 1122, 1123, and 1125.

Core, section, interval (cm)	Depth (mbsf)	Depth (mcd)	Mn (µM)	Core, section, interval (cm)	Depth (mbsf)	Depth (mcd)	Mn (µM)
101 11100				1011 4 140 150*	· ·		1.1
181-1119B- 1H-2 145-150	2 95	NA	10	10H-4, 140–150* 11H-4 140–150	97 50	103 58	1.1
2H-4, 145–150	10.65	NA	1.8	12H-4, 140–150	107.00	113.66	1.3
3H-4, 145–150	20.15	NA	2.4	13H-4, 140–150	116.50	124.26	1.1
4H-4, 145–150	29.65	NA	1.9	14H-4, 140–150	126.00	134.70	0.8
5H-4, 135–140	39.05	NA	1.0	15H-4, 140–150	135.50	145.66	1.1
6H-4, 145–150	48.65	NA	1.5	16H-4, 140–150	145.00	156.64	0.9
7H-4, 135–140	58.05	NA	2.2	17H-4, 140–150	154.50	158.14	1.1
8H-4, 140–155	67.60	NA	6.9	181-1123B-			
9H-4, 135-140	//.05	NA NA	1./	17H-4, 140–150	151.80	163.74	0.8
10H-4, 140-150	00.00 96.10	INA NA	0.7	20X-4, 140–150	178.20	190.20	1.1
14H-4, 140–150	124 70	NA	0.5	23X-3, 140–150	205.60	217.54	2.2
17H-4, 140–150	153.10	NA	1.1	26X-2, 140–150	232.90	244.84	0.9
				29X-4, 140–150	264.70	276.64	1.3
181-1122A-	5 00	12 70	5 (32X-4, 140-150	293.60	305.54	1.5
1H-4, 140-150	5.90	15./0	3.0	35X-4, 140-150	322.40	334.34	1.8
211-4, 140-150 4H-4 140-150	34 20	42.05	3.9 1 7	307-4, 140-130 11X-4 140 150	380.00	302.94	0.0
5H-5 130-140	45 10	53 44	2.0	47X-2 135-150	434.65	446 59	0.9
6H-4, 140–150	53.20	59.66	1.6	50X-4, 135–150	466.25	478.19	1.4
7H-4, 140–150	62.70	68.86	1.9	52X-3, 135–150	483.65	495.59	1.5
11X-1, 140–150	96.40	102.98	1.3	101 11220			
12X-2, 140–150	107.60	114.18	1.8	101-1123C-	404.25	502 67	2.0
13X-2, 140–150	117.20	123.78	4.5	197-4, 135-130 228-4 135 150	494.33 532.85	532 57	2.0
181-1122C-				227-4, 133-130	552.05	552.57	2.7
9H-4, 140–150	67.40	70.44	1.5	181-1125A-			
10H-4, 140–150	76.90	79.54	1.1	1H-2, 145–150	2.95	2.95	2.9
12H-4, 140–150	92.80	95.44	1.5	3H-4, 145-150	19.75	19.64	1.9
13H-4, 140–150	100.80	103.44	0.9	51-4, 145-150	38 75	19.04	1.0
16X-3, 140–150	122.00	124.64	2.3	7H-4 140-150	57 70	67.88	1.2
19X-1, 140–150	147.90	150.54	3.8	9H-4, 140–150	76.70	88.62	1.0
22X-1, 130–140	176.60	179.24	2.0	11H-4, 140–150	95.70	109.28	0.8
26X-2, 90–100	216.40	219.04	1.6	13H-2, 145–155	111.75	127.98	1.0
29X-3, 140-150	247.30	249.94	1.8	15H-4, 145–155	133.75	151.73	0.7
328-1, 140-150	2/2./0	2/3.34	2.4	17H-4, 145–155	152.75	171.50	0.3
388-2 140-150	303.90	334 44	3.7 4 0	19H-4, 143–153	171.73	194.53	1.0
42X-2, 140–150	370.40	373.04	1.2	21H-4, 140–150	190.70	216.56	0.3
45X-2, 140–150	399.50	402.14	1.3	181-1125B-			
48X-4, 140–150	431.40	434.04	1.3	21X-4, 140–150	194.70	221.76	0.5
51X-4, 140–150	460.30	462.94	4.2	23X-4, 140–150	212.70	243.77	0.3
54X-3, 140–150	487.40	490.04	26.5	27X-4, 140–150	251.10	282.17	0.1
57X-2, 140–150	514.80	517.44	5.4	29X-4, 140–150	270.30	301.37	2.6
61X-3, 140–150	554.80	557.44	2.1	31X-2, 140–150	286.60	317.67	0.4
65X-2, 140–150	591.80	594.44	2.8	31X-2, 140-150*	286.60	317.67	0.4
181-1123A-				337-4, 140-130 357 4 140 150	200.90	258 87	0.5
1H-1, 140–150	1.40	1.40	9.4	37X-3 140-150	345 50	376 57	0.4
1H-3, 135–145	4.35	4.35	14.6	39X-4, 140–150	366.30	397.37	1.1
2H-1, 140–150	7.50	5.70	16.3	41X-4, 140–150	385.60	416.67	0.7
2H-3, 140–150	10.50	8.70	13.8	43X-3, 140–150	403.40	434.47	0.7
2H-5, 140–150	13.50	11.70	11.5	45X-3, 135–150	422.65	453.72	1.0
3H-3 140-130	17.00	10./0	13.ð	47X-4, 135–150	443.35	474.42	1.3
3H-5, 140-130 3H-5, 120-130	20.00	22 56	0.5 7 1	49X-4, 135–150	462.25	493.32	0.4
4H-1, 140–150	26.50	24.06	5.2	52X-4, 135–150	490.75	521.82	1.0
4H-3, 140–150	29.50	27.06	5.2				
4H-3, 140–150*			5.1	Notes: mcd = me	eters con	nposite de	pth (Ship-
4H-5, 140–150	32.50	30.06	3.6	board Scienti	fic Party,	1999). N	NA = not
5H-1, 140–150	36.00	35.86	2.5	applicable. * =	= Core, s	ection, inte	erval (cm)
5H-3, 140–150	39.00	38.86	2.5	value was dup	licated.		. /
5H-5, 140–150	42.00	41.86	2.4	· · · · - F			
6H-1, 140–150	45.50	48.06	2.8				
6H-3, 140–150	48.50	51.06	2.3				
6H-5, 140–150	51.50	54.06	2.9				
70-4, 140-150 8H_4 140 150	59.50 60.00	02.20 72.20	2.0 2.2				
9H-4 140-150	78 50	72.00 82.88	2.2 1.8				
211-7, 170-130	/0.50	02.00	1.0				

10H-4, 140–150 88.00 93.88

1.2