Tiedemann, R., Mix, A.C., Richter, C., and Ruddiman, W.F. (Eds.)
Proceedings of the Ocean Drilling Program, Scientific Results Volume 202

10. Data Report: Major and Trace Element Data For Leg 202 Sites 1233 and 1234[1]

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INTRODUCTION

The exchange of waters between the Pacific and the Southern Oceans occurs along the eastern boundary of the South Pacific. Because water masses of the Antarctic provide a connection among the world's ocean basins, these water masses maintain the ability to influence changes in ocean circulation and climate (Lynch-Stieglitz et al., 1996). One of the primary goals of Ocean Drilling Program (ODP) Leg 202 was to exploit the sediments underlying the southeast Pacific continental margin to ascertain how changes in past ocean circulation (i.e., water mass distributions) have affected global carbon, heat, and nutrient balances.

In the southeast Pacific, oxygen-rich Antarctic Intermediate Water (AAIW) combines with (low oxygen) North Pacific Intermediate Water to produce a steep water column–dissolved oxygen gradient between depths of ~0.5 and 1 km. Shallower in the water column, the classical oxygen minimum zone (OMZ) impinges along the continental margin. These different water masses thus produce a "double" OMZ, with low-oxygen waters straddling the oxygen-rich AAIW. Given this distribution, changes in the intensity of water mass source functions through time should leave behind a depth transect of changing proxy distributions in response to changing bottom water oxygen concentrations.

Sediments at Site 1233 are bathed by AAIW at a water depth of 838 m, whereas Pacific Central Water bathes the overlying waters at Site 1234. Site 1234 is located north of Site 1233 at 1015-m water depth. Because of rapid erosion of the high Andes, terrigenous sedimentation rates at these sites are in the range of 1–2 m/k.y.

[1]McManus, J., 2006. Data report: major and trace element data for Leg 202 Sites 1233 and 1234. *In* Tiedemann, R., Mix, A.C., Richter, C., and Ruddiman, W.F. (Eds.), *Proc. ODP, Sci. Results,* 202: College Station, TX (Ocean Drilling Program), 1–9. doi:10.2973/odp.proc.sr.202.202.2006
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Initial receipt: 6 September 2004
Acceptance: 7 July 2006
Web publication: 3 November 2006
Ms 202SR-202

To assess changes in the reducing nature of these sediments through time, a number of geochemical indicators were determined. The solubility of uranium, molybdenum, cadmium, and vanadium decreases under the reducing conditions common along the continental margin seafloor; thus changes in their distribution may signify changes in the reducing character of the surface sediment. A number of other, primarily ancillary, elements were also measured. Most of these elements are used to assess terrigenous inputs.

METHODS

Samples from Sites 1233 and 1234 were analyzed for a suite of major (K, Ca, Mg, Fe, and Ti) and minor (Mn, Cu, Ba, U, Cd, Mo, and V) elements. Samples were dried, ground, and stored in glass vials. Approximately 50 mg of sediment was used for analyses. To the dried sediment, 2 mL of 30% H_2O_2 was initially added. The sample was then placed (covered) in an oven at 60°C overnight. The following day the sample was removed from the oven and evaporated on a hotplate. Concentrated HF (1 mL) was then added to the sample, which was then placed (covered) in an ultrasonic bath for 0.5 hr, after which point we added 1 mL of HNO_3 (16 N) and placed the sample in an oven at 90°C overnight. The following day the sample was cooled and the lids removed and rinsed (twice) into vials with 25 mL of 6-N HCl. The solution was then evaporated close to dryness. Two additions of 0.5 mL of 6-N HCl were added with an evaporation step following each addition. Next, 0.5 mL of 16-N HNO_3 and 0.5 mL of 8-N HNO_3 were added with an evaporation step following each addition. Finally, 8 mL of 8-N HNO_3 was added; this final solution constitutes the working solution.

Prior to our sample analyses, the above technique was compared to an alkaline fusion technique and a microwave-enhanced acid dissolution technique (Table T1). This comparison was accomplished by analyzing standard reference materials in triplicate using each technique. Our results generally show agreement among the techniques and with the reported value (e.g., Potts et al., 1992), but there are notable exceptions. The Mg results for the U.S. Geological Survey (USGS) AGV-1 and MAG-1 reference materials using the microwave-assisted technique and the Ba results for the USGS W-2 standard for both the technique employed here and the microwave-assisted technique are low (also see Pozebon and Martins, 2002). Recognizing these individual exceptions, this comparison suggests that each technique resulted in complete sediment digestion and there was no obvious pattern of residual material for any of the techniques. In addition to these standard reference materials, we also digested the USGS standard SDO-1 and the National Institute of Standards and Technology standard reference material (SRM) 1645 along with the samples reported here. For the major elements, all analytes agree to within 15%.

T1. SRM for method calibration, p. 7.

In the case of the minor elements Mo and U, we also ran a number of samples for these analytes as well (Table T2). Agreement is typically within 16% or better with the exception of the SDO-1 value for Mo and the SRM 1645 for U. The precision of each analysis is generally superior to the agreement with the standard reference materials, indicating that each technique provides internally consistent results. One exception to this generalization is that the significantly different results for Mg and Ba referred to above (Table T1) also tend to have less precise results. This observation suggests that results that exhibit a high degree of sam-

T2. SRM for method calibration, p. 8.

ple-to-sample variability should be treated with caution until further work can validate the veracity of individual sample values.

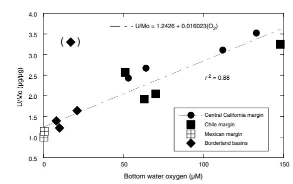
RESULTS

The results of metal analyses are presented in Table T3 along with the meters composite depth (mcd). Our primary target for this and future work is understanding the relationship between sedimentary signatures of ocean biogeochemistry and climate. Toward this end we compare the U/Mo ratio at the two study sites as an indicator of the relative change in bottom water oxygen from the last glacial to the present. Although this bottom water oxygen proxy (Fig. F1) is still under development, it exhibits significant promise (McManus et al., 2006). The data suggest relatively little change in bottom water oxygen at Site 1234 over the last ~20 k.y., but lower bottom water oxygen at ~24 k.y. before present (BP). Site 1233 exhibits considerably more variability over the last >21 k.y. with generally lower bottom water oxygen during the last glacial as compared to the more recent Holocene, but a distinct minimum between ~8 and 10 k.y. BP (Fig. F2).

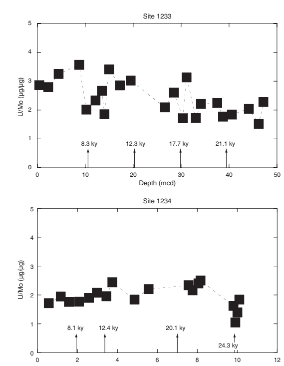
The relationships between climate change and intermediate water mass circulation are poorly defined. Yet because intermediate water masses interact with the euphotic zone and can outcrop in subpolar regions, they are significant both in terms of global nutrient transport and the global CO_2 balance. Our lack of understanding regarding this relationship stems in part from the limited availability of high-resolution sediment records and the complexity of existing continental margin records. Future work from Sites 1233 and 1234 will continue to build upon that data assembled here toward an improved understanding the climate–ocean interactive relationship.

T3. Elemental concentrations, Sites 1233 and 1234, p. 9.

F1. U/Mo ratio as a function of bottom water oxygen concentration, p. 5.



F2. U/Mo ratio as a function of depth, Sites 1233 and 1234, p. 6.



ACKNOWLEDGMENTS

This research used samples and/or data provided by the Ocean Drilling Program (ODP). ODP is sponsored by the U.S. National Science Foundation (NSF) and participating countries under management of Joint Oceanographic Institution (JOI), Inc. Reviewer comments from K.A. Kryc and A. Mix are appreciated. Financial support was also provided by JOI/U.S. Science Support Program (USSSP) for shore-based analyses. Andy Ross and Angela Bice assisted in the laboratory with analyses.

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Figure F1. The U/Mo ratio as a function of bottom water oxygen concentration (from McManus et al., 2006). Note that there are several sites from the Chile margin used for the data calibration. These sites were from the site survey cruise associated with ODP Leg 202. Data point in parentheses is not used for the statistical fit.

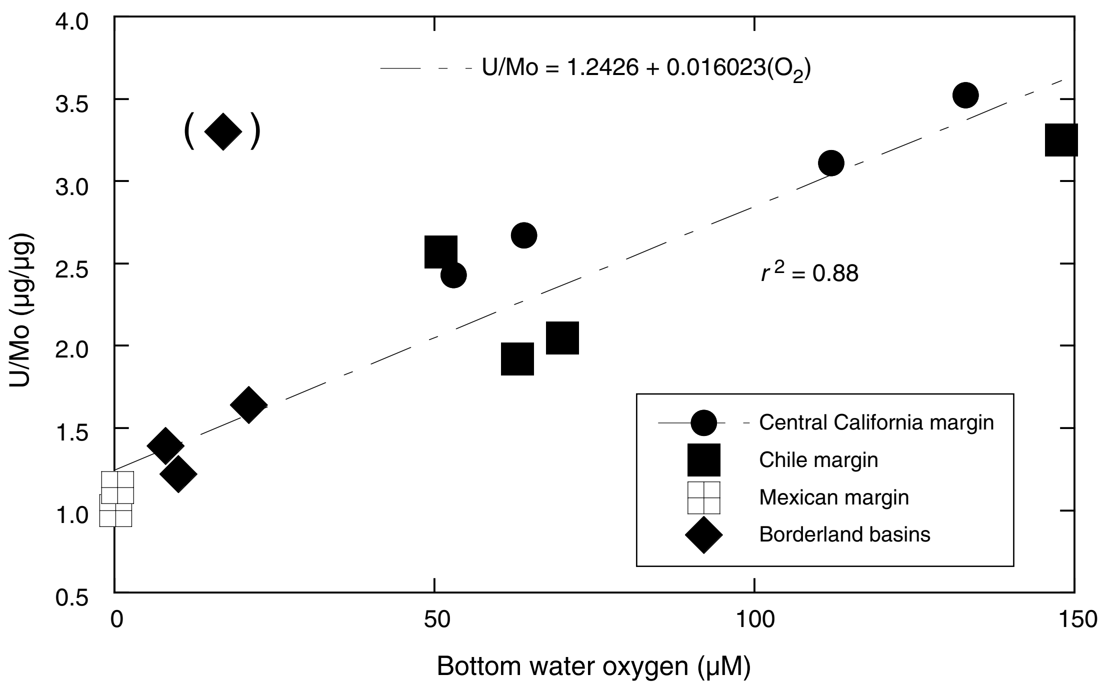

Figure F2. The U/Mo ratio as a function of depth for Sites 1233 and 1234. The age designations are taken from the age model of Lamy et al., (2004) for Site 1233 and A. Mix (pers. comm., 2006) for Site 1234.

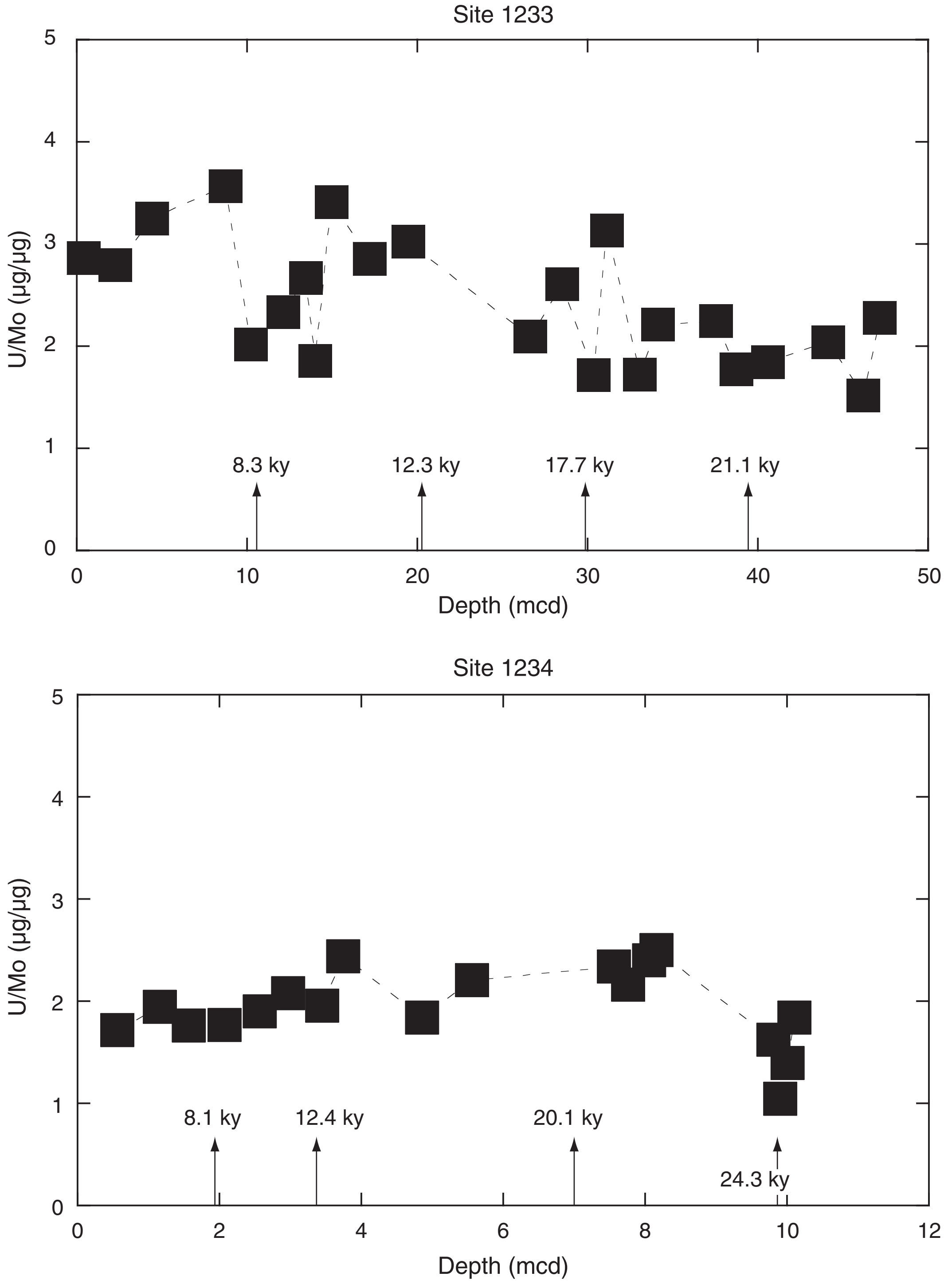

Table T1. Standard reference materials for method calibration.

Standard	Sample ID*	Concentration (µg/g)											
		Ti	±	Ca	±	Mg	±	Fe	±	Mn	±	Ba	±
BCR-1	F7-A, B, C	13,147	166	54,401	1,300	21,972	287	96,952	1,595	1,475	12	654	15
	S7-A, B, C	13,770	125	50,585	4,247	21,546	99	96,832	1,333	1,467	8	618	14
	M7-A, B, C	13,538	91	48,225	980	21,694	513	96,669	734	1,468	9	640	8
	Literature	13,428		49,670		21,000		93,870		1,394		681	
	Meas./Lit.	1.00		1.03		1.04		1.03		1.05		0.94	
AGV-1	F5-A, B, C	5,881	116	36,844	508	9,356	162	45,839	622	716	15	1,176	10
	S5-A, B, C	6,227	67	32,816	152	8,810	122	47,222	741	703	18	1,204	18
	M5-A, B, C	6,395	322	34,644	204	*6,240*	384	48,566	2,013	776	20	1,248	66
	Literature	6,355		35,306		9,227		47,279		744		1,221	
	Meas./Lit.	0.97		0.98		0.88		1.00		0.98		0.99	
W-2	F6-A, B, C	6,356	46	84,119	1,678	40,097	656	77,886	1,077	1,343	24	144	5
	S6-A, B, C	6,525	45	77,027	329	40,928	131	78,133	1,273	1,333	4	*56*	9
	M6-A, B, C	6,537	254	77,854	3,050	40,210	1,152	78,396	2,154	1,341	29	*83*	14
	Literature	6,355		77,688		38,417		75,116		1,262		170	
	Meas./Lit.	1.02		1.03		1.05		1.04		1.06		0.55	
MAG-1	F4-A, B, C	3,952	28	10,684	32	18,296	53	47,066	756	727	12	456	4
	S4-A, B, C	4,085	56	7,699	55	18,113	149	47,604	420	701	2	401	10
	M4-A, B, C	4,167	56	7,562	285	*3,701*	1,197	47,953	990	736	20	411	48
	Literature	4,502		9,791		18,093		47,559		759		479	
	Meas./Lit.	0.90		0.88		0.74		1.00		0.95		0.88	
SDO-1	SDO-1-A, B, C	3,921	242	7,384	700	8,790	616	61,031	3,530	289	19	396	23
	Literature	4,200	185	7,500	336	9,300	229	65,324	1,469	325	39	397	38
	Meas./Lit.	0.93		0.98		0.95		0.93		0.89		1.00	
SRM 1645	NBS1645-A, B, C	564	44	28,692	755	6,954	173	98,421	1,157	704	12	344	4
	Literature					7,400	200	100,000	12,000	785	97		
	Meas./Lit.					0.94		0.87		0.90			

Notes: * = sample IDs for each reference material (BCR-1, AGV-1, W-2, and MAG-1) correspond to their digestion technique F (fusion), S (hotplate acid digestion), and M (microwave-assisted acid digestion). Designations A, B, and C are individual sample digestions that compose the average. SDO-1 and SRM 1645 samples were analyzed according to the hotplate acid digestion technique as described in **"Methods,"** p. 2. Literature = published value of SRM. Meas./Lit. = accuracy ratio. Italics = outliers.

Table T2. Standard reference materials for method calibration.

Standard	Concentration (µg/g) Mo	±	*N*	Literature	Meas./ Lit.	Concentration (µg/g) U	±	*N*	Literature	Meas./ Lit.
BCR-1	1.64	0.06	13 (5)	1.54	1.06	2.0		1	1.8	1.16
MAG-1	1.14	0.08	11 (5)	1.17	0.97	2.5	0.2	3 (3)	2.7	0.93
AGV-1	2.4	0.1	7 (3)	2.1	1.14					
W-2	0.47	0.03	7 (3)	0.44	1.07					
SDO-1	192	12	3 (3)	134	1.43	56	5	3 (3)	49	1.14
SRM 1645	11.3	0.5	3 (3)			0.3	0	3 (3)	1.1	0.27

Notes: Standards are as described for Table T1, p. 7. *N* = the number of individual sample analyses that comprise each value, where the number in parentheses is the number of individually weighed and digested samples. When the two numbers differ it means that an individual sample was rerun on a different day and that number was also used to compute the average value. When the two numbers are the same it means that each individually digested sample was only run on one occasion. Meas./Lit. = the measured value divided by the reported or literature value. For Mo, a more up-to-date review is given in Wieser and DeLaeter (2000).

Table T3. Elemental concentrations, Sites 1233 and 1234.

Hole, core, section, interval (cm)	Depth (mcd)	Trace elements (ppm)											
		K	Ca	Mg	Mn	Cu	Fe	Ti	Ba	U	Cd	Mo	V
1233C-1H-1, 40–42	0.40	11,397	45,959	16,458	606	49.7	46,270	4,844	450	3.4	0.20	1.2	193
1233C-1H-2, 76–78	2.27	11,790	50,321	16,120	629	46.8	46,518	4,915	492	3.6	0.20	1.3	195
1233C-1H-3, 142–144	4.44	11,764	71,780	16,720	629	45.6	50,132	4,928	527	3.6	0.23	1.1	191
1233C-2H-2, 76–78	8.73	12,879	78,147	17,944	662	46.3	52,552	5,092	528	3.7	0.23	1.0	207
1233C-2H-3, 76–78	10.24	12,104	63,892	16,032	598	44.0	49,824	5,012	463	3.1	0.20	1.6	206
1233C-2H-4, 112–114	12.15	11,784	79,605	22,369	776	42.8	54,782	5,050	474	2.4	0.19	1.0	199
1233D-3H-2, 40–42	13.47	11,184	59,178	16,423	684	40.7	48,862	5,266	383	2.6	0.18	1.0	202
1233C-2H-5, 148–150	14.01	11,325	61,295	16,462	738	40.9	53,122	5,633	400	3.1	0.24	1.7	228
1233D-3H-3, 40–42	14.98	11,096	66,866	16,322	715	40.9	50,222	5,110	383	3.3	0.25	1.0	209
1233D-3H-4, 112–114	17.20	10,796	61,596	16,128	692	39.7	49,012	5,133	348	3.1	0.18	1.1	209
1233D-3H-6, 40–42	19.48	11,756	49,376	17,958	735	41.1	49,376	5,290	359	3.6	0.22	1.2	219
1233D-4H-3, 4–6	26.65	12,315	48,915	18,674	794	46.0	48,628	5,122	337	2.8	0.21	1.3	213
1233D-4H-4, 40–42	28.50	12,828	51,188	21,006	855	46.8	50,251	4,900	334	3.8	0.18	1.5	211
1233D-4H-5, 76–78	30.36	11,692	58,766	21,906	865	49.2	49,228	4,800	332	2.8	0.18	1.6	201
1233B-3H-2, 148–150	31.13	11,823	52,930	17,921	745	48.9	46,026	4,804	319	3.3	0.18	1.0	215
1233B-3H-4, 40–42	33.06	11,940	54,875	20,323	805	55.2	47,429	4,715	342	2.4	0.17	1.4	198
1233B-3H-4, 148–150	34.14	12,107	40,117	12,799	659	50.1	46,564	5,182	298	2.8	0.18	1.3	223
1233C-5H-1, 148–150	37.54	12,974	45,218	18,855	807	56.2	46,991	4,936	352	2.8	0.18	1.3	196
1233C-5H-2, 112–114	38.73	12,395	47,164	20,735	831	46.0	51,190	5,004	342	3.3	0.19	1.9	202
1233C-5H-4, 148–150	40.60	12,477	47,823	25,076	941	49.0	50,889	4,874	334	3.4	0.20	1.8	212
1233D-6H-2, 148–150	44.13	11,639	44,068	27,215	1,002	50.5	53,151	5,046	336	2.9	0.17	1.4	228
1233D-6H-4, 54–56	46.19	12,013	42,366	19,706	825	55.7	49,056	4,683	332	3.1	0.22	2.0	211
1233D-6H-5, 4–6	47.17	12,901	46,937	18,213	860	53.4	47,499	4,834	354	3.2	0.19	1.4	197
1234A-1H-1, 6–8	0.06	12,492	22,413	9,645	415	47.0	40,626	4,367	343	4.3	0.36	2.7	159
1234A-1H-1, 26–28	0.26	13,083	28,433	13,973	522	37.3	43,610	4,332	399	4.6	0.42	2.7	146
1234A-1H-1, 56–58	0.56	13,471	35,484	18,038	608	39.4	44,355	4,370	434	4.4	0.40	2.5	151
1234A-1H-1, 116–118	1.16	13,695	31,150	13,829	534	34.9	41,891	4,404	403	4.9	0.55	2.5	158
1234A-1H-2, 6–8	1.57	13,936	33,802	13,576	524	52.6	43,222	4,488	393	4.7	0.47	2.7	155
1234A-1H-2, 56–58	2.07	13,632	36,404	14,030	569	31.9	43,048	4,570	367	4.4	0.38	2.5	162
1234A-1H-2, 106–108	2.57	13,652	37,284	14,311	614	34.4	43,593	4,703	379	4.1	0.40	2.1	166
1234A-1H-2, 146–148	2.97	14,066	43,473	18,109	720	36.0	45,965	4,624	413	3.6	0.35	1.7	159
1234B-1H-3, 58.8–60	3.45	13,861	39,512	14,626	612	82.8	43,973	4,557	376	3.7	0.27	1.9	178
1234B-1H-5, 88.8–90	3.75	14,616	37,893	16,112	675	41.4	43,943	4,554	379	3.7	0.28	1.5	184
1234B-1H-4, 48.8–50	4.86	14,171	33,621	16,310	622	33.3	41,678	4,418	350	3.4	0.20	1.9	176
1234B-1H-4, 118.8–200	5.56	12,669	12,138	6,570	392	35.4	35,943	4,567	209	3.9	0.21	1.8	163
1234B-1H-5, 18.8–20	6.07												
1234A-2H-2, 88.8–90	7.56	15,789	41,338	20,411	775	40.2	45,357	4,651	399	4.2	0.33	1.8	173
1234A-2H-2, 108.8–110	7.76	14,675	38,255	15,709	640	40.8	44,839	4,672	361	4.6	0.29	2.1	179
1234A-2H-2, 138.8–140	8.06	14,313	33,804	13,796	603	36.5	41,113	4,599	335	3.9	0.32	1.6	180
1234A-2H-2, 148.8–150	8.16	14,783	37,504	15,502	656	37.5	43,130	4,532	363	4.4	0.27	1.8	175
1234A-2H-4, 8.75–10	9.81	14,630	34,591	15,594	638	36.9	41,963	4,451	366	4.3	0.44	2.6	164
1234A-2H-4, 18.75–20	9.91									4.0	0.27	3.9	174
1234A-2H-4, 28.75–30	10.01	15,203	35,292	16,771	697	39.2	44,341	4,555	383	3.8	0.23	2.7	171
1234A-2H-4, 38.75–40	10.11	14,775	34,388	17,048	702	40.8	43,713	4,459	364	4.2	0.23	2.3	174

Notes: Missing data are from two samples lost prior to analyses; these samples will be rerun and presented as part of future efforts. Depth is from Mix, Tiedemann, Blum, et al. (2003).