

Data report: $\delta^{18}\text{O}$ in pore fluids from NanTroSEIZE Expeditions 322 and 333¹

C. Destrigneville,² P. Agrinier,³ P. Henry,⁴ and M.E. Torres⁵

Chapter contents

Abstract	1
Introduction	1
Analytical methods	2
Results	2
Acknowledgments	3
References	3
Figures	4
Table	6

Abstract

We report on analyses of the oxygen isotopic composition of pore fluids in sediments from two sites drilled in the Shikoku Basin as part of the Nankai Trough Seismogenic Zone Experiment. Both Sites C0011 and C0012 were cored to sample the input section to the subduction zone offshore southern Japan during Integrated Ocean Drilling Program Expeditions 322 and 333. Pore fluid $\delta^{18}\text{O}$ analysis was performed using gas chromatography interfaced with isotope ratio mass spectrometry at the Institut de Physique du Globe de Paris. At both sites, pore fluids are depleted in ^{18}O relative to modern seawater: $\delta^{18}\text{O}$ decreases with depth to values of -4.66‰ (Site C0011) and -3.97‰ (Site C0012) at the bottom of lithologic Unit II and remains relatively constant at -4.5‰ in lithologic Units III and IV. In lithologic Unit V at Site C0011, $\delta^{18}\text{O}$ slightly decreases to a value of -5.30‰ at 858 meters below seafloor (mbsf), whereas at Site C0012, the $\delta^{18}\text{O}$ depth profile shows a reverse trend with $\delta^{18}\text{O}$ values increasing with depth from -4.5‰ to -3.15‰ at 529.2 mbsf.

Introduction

The Nankai Trough Seismogenic Zone Experiment (NanTroSEIZE) is a complex drilling project of the Integrated Ocean Drilling Program (IODP) focused on understanding the mechanics of seismogenics and rupture propagation along subduction plate boundary faults (Tobin and Kinoshita, 2006). Two sites were cored during IODP Expeditions 322 and 333 on the subducting Philippine Sea plate in order to characterize the sediment section and upper igneous basement prior to deformation at the subduction front (see the “[Expedition 322 summary](#)” chapter [Underwood et al., 2010]; Expedition 333 Scientists, 2012). IODP Sites C0011 and C0012 sampled the Shikoku Basin 100 km southeast of the Kii Peninsula at the summit and on the northwest flank of the Kashinosaki Knoll, a prominent basement high (Fig. F1). Coring reached 876 meters below seafloor (mbsf) at Site C0011 by using the hydraulic piston coring system (HPCS) from 21 to 184 mbsf and the extended shoe coring system (ESCS) from 207 to 360 mbsf during Expedition 333 and by using rotary core barrel (RCB) drilling from 340 to 876 mbsf during Expedition 322. Drilling at Site C0012 penetrated into the igneous basement to 630.5 mbsf, recovering the sediment/basalt interface intact at 537.8 and 525.7

¹Destrigneville, C., Agrinier, P., Henry, P., and Torres, M.E., 2016. Data report: $\delta^{18}\text{O}$ in pore fluids from NanTroSEIZE Expeditions 322 and 333. In Saito, S., Underwood, M.B., Kubo, Y., and the Expedition 322 Scientists, *Proceedings of the Integrated Ocean Drilling Program, 322*: Tokyo (Integrated Ocean Drilling Program Management International, Inc.).

doi:10.2204/iodp.proc.322.212.2016

²Université de Toulouse, UPS-OMP-GET, 14 Avenue Edouard Belin, 31400 Toulouse, France. christine.destrigneville@get.obs-mip.fr

³IPGP, Sorbonne Paris Cité, Université Paris Diderot, UMR 7154 CNRS, 1 Rue Jussieu, 75238 Paris Cedex 05, France.

⁴CEREGE, CNRS, Avenue Louis Philibert, BP80, 13545 Aix-en-Provence, France.

⁵College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, Corvallis OR 97331, USA.



mbsf during Expeditions 322 and 333, respectively (see the “[Expedition 322 summary](#)” chapter [Underwood et al., 2010]; Expedition 333 Scientists, 2012). At Site C0012, core samples were obtained from RCB drilling during Expedition 322.

Oxygen isotope geochemistry has been widely applied to the study of sedimentation and diagenetic processes in continental and oceanic environments because the isotopic fractionation depends on both the temperature and the chemical composition of the minerals undergoing diagenesis. Examples of applications of the $^{18}\text{O}/^{16}\text{O}$ ratio in pore fluids include ion filtration processes, alteration of volcanogenic tephra and oceanic crust, evidence of diagenetically evolved fluid fluxes, gas hydrate dynamics, opal transformations to cristobalite, and quartz and clay dehydration reactions (Coplen and Hanshaw, 1973; Lawrence et al., 1975; Kastner et al., 1993; Tomaru et al., 2006; Kashiwaya et al., 2013; Kim et al., 2013). Isotopic geothermometry laws based on experimental, empirical, and theoretical data are available in scientific literature for most carbonate, silicate, and oxide minerals (Friedman and O’Neil, 1977; Savin and Lee, 1988; Sheppard and Gilg, 1996). Thus, the $^{18}\text{O}/^{16}\text{O}$ ratio in pore fluids is a valuable tracer, which, in the context of a full gamut of geochemical tracers, provides information on the origin of the fluid and on the nature of water–rock interactions (Destrigneville et al., 1991; Wilkinson et al., 1992). Here, we focus on the oxygen isotopic signature of pore fluids sampled from the sediment column prior to subduction.

Analytical methods

The isotopic composition of oxygen was measured in pore fluid samples recovered from Sites C0011 and C0012 at the Institut de Physique du Globe de Paris (IPGP). A pore water aliquot (0.8 mL) sample was equilibrated with a He + CO₂ gas mixture at 25°C for 8 h, and the $^{18}\text{O}/^{16}\text{O}$ ratio on the CO₂ gas phase was measured with an isotope ratio mass spectrometer interfaced with gas chromatography (GC-IRMS; Analytical Precision 2003). The measurements were calibrated using a set of three house water standards calibrated versus standard mean ocean water (SMOW). $\delta^{18}\text{O}$ are reported against the SMOW standard scale. Measurements of $\delta^{18}\text{O}$ were determined with an analytical accuracy better than $\pm 0.1\text{‰}$.

Results

A total of 86 pore fluid samples were analyzed. Considering the poor core recovery due to RCB drilling during Expedition 322, hard claystones were selected for interstitial water (IW) samples, and careful cleaning prevented extensive drilling fluid contamination (see the “[Expedition 322 summary](#)” chapter [Underwood et al., 2010]). At Site C0011, pore fluid samples were affected by seawater contamination ranging from 2% to 14%. At Site C0012, IW shipboard analyses concluded contamination by seawater is minimal, considering the dissolved sulfate profile, which is consistent with the biogeochemical processes at this site (see the “[Expedition 322 summary](#)” chapter [Underwood et al., 2010]).

Consequently, no correction for seawater contamination was made on isotopic data for either Site C0011, which leads to underestimating the negative $\delta^{18}\text{O}$ signatures by an average value of 6‰, or Site C0012, where sulfate distribution precluded any correction for potential contamination.

The data are listed in Table T1. Figure F2 shows the downhole $\delta^{18}\text{O}$ depth profiles in the context of the corresponding lithology.

Pore fluids in both sedimentary sequences are depleted in ^{18}O relative to modern seawater with values ranging from -0.70‰ to -5.66‰ . The lower values are obtained in the deeper sediments. At Site C0011, $\delta^{18}\text{O}$ values decrease with depth from -0.70‰ (Section 333-C0011D-3H-5; 44.80 mbsf) to -4.66‰ (Section 322-C0011B-16R-2; 478.21 mbsf) and then remain relatively constant with a mean value of $-4.7\text{‰} \pm 0.4\text{‰}$ until the deepest sample analyzed (-4.72‰) in Section 322-C0011B-59R-3 (867.50 mbsf) (Fig. F2). The change between the decreasing trend in $\delta^{18}\text{O}$ values and the constant trend occurs at the boundary between lithologic Unit II (volcanic turbidite facies) and lithologic Unit III (hemipelagic facies). Similarly, at Site C0012 $\delta^{18}\text{O}$ values decrease with depth from -1.58‰ (Section 322-C0012A-5R-2; 89.43 mbsf) to -3.97‰ (Section 322-C0012A-19R-2; 217.58 mbsf) and then remain relatively constant below the Unit II/III boundary with a mean value of $-4.5\text{‰} \pm 0.5\text{‰}$. In lithologic Unit V (volcaniclastic turbidite facies), in contrast to what was observed at Site C0011 the $\delta^{18}\text{O}$ depth profile at Site C0012 shows a reverse trend with $\delta^{18}\text{O}$ values increasing with depth from -4.70‰ (Section 322-C0012A-41R-3; 426.10 mbsf) to -3.15‰ (Sec-

tion 322-C0012A-52R-2; 529.20 mbsf). Such a reverse trend in concentration profiles of all major cations, chloride, and sulfate was observed in the Site C0012 pore fluids and has been attributed to ion diffusion from fluids in the permeable igneous basement (see the “[Expedition 322 summary](#)” chapter [Underwood et al., 2010]; Torres et al., 2015).

Acknowledgments

This research used samples provided by the Integrated Ocean Drilling Program (IODP). We gratefully acknowledge the efforts of the D/V *Chikyu* shipboard and drilling personnel and of the Expedition 322 and 333 science parties. We thank an anonymous reviewer for his constructive suggestions and M.B. Underwood for his constant support and sound advice. Funding was provided by the French INSU Program 3F (Fault-Fluid-Flux).

References

- Coplen, T.B., and Hanshaw, B.B., 1973. Ultrafiltration by a compacted clay membrane. I. Oxygen and hydrogen isotopic fractionation. *Geochimica et Cosmochimica Acta*, 37(10):2295–2310. [http://dx.doi.org/10.1016/0016-7037\(73\)90105-1](http://dx.doi.org/10.1016/0016-7037(73)90105-1)
- Destrigneville, C., Schott, J., Caristan, Y., and Agrinier, C., 1991. Evidence of an early alteration process driven by magmatic fluid in Mururoa volcano. *Earth and Planetary Science Letters*, 104(2–4):119–139. [http://dx.doi.org/10.1016/0012-821x\(91\)90199-r](http://dx.doi.org/10.1016/0012-821x(91)90199-r)
- Expedition 333 Scientists, 2012. Expedition 333 summary. In Henry, P., Kanamatsu, T., Moe, K., and the Expedition 333 Scientists, *Proceedings of the Integrated Ocean Drilling Program*, 333: Tokyo (Integrated Ocean Drilling Program Management International, Inc.). <http://dx.doi.org/10.2204/iodp.proc.333.101.2012>
- Friedman, I., and O’Neil, J.R., 1977. Compilation of stable isotope fractionation factors of geochemical interest. In Fleischer, M. (Ed.), *Data of Geochemistry* (6th edition). U.S. Geological Survey Professional Paper, 440-KK:1–12.
- Kashiwaya, K., Hasegawa, T., and Nakata, K., 2013. Effect of silica phase transformations on hydrogen and oxygen isotope ratios of coexisting water. *Procedia Earth and Planetary Science*, 7:401–404. <http://dx.doi.org/10.1016/j.proeps.2013.03.174>
- Kastner, M., Elderfield, H., Jenkins, W.J., Gieskes, J.M., and Gamo, T., 1993. Geochemical and isotopic evidence for fluid flow in the western Nankai subduction zone, Japan. In Hill, I.A., Taira, A., Firth, J.V., et al., *Proceedings of the Ocean Drilling Program, Scientific Results*, 131: College Station, TX (Ocean Drilling Program), 397–413. <http://dx.doi.org/10.2973/odp.proc.sr.131.143.1993>
- Kim, J.-H., Torres, M.E., Hong, W.-L., Choi, J., Riedel, M., Bahk, J.-J., and Kim, S.-H., 2013. Pore fluid chemistry from the second gas hydrate drilling expedition in the Ulleung Basin (UBGH2): source, mechanisms and consequences of fluid freshening in the central part of the Ulleung Basin, East Sea. *Marine and Petroleum Geology*, 47:99–112. <http://dx.doi.org/10.1016/j.marpetgeo.2012.12.011>
- Lawrence, J.R., Gieskes, J.M., and Broecker, W.S., 1975. Oxygen isotope and cation composition of DSDP pore waters and the alteration of Layer II basalts. *Earth and Planetary Science Letters*, 27(1):1–10. [http://dx.doi.org/10.1016/0012-821X\(75\)90154-5](http://dx.doi.org/10.1016/0012-821X(75)90154-5)
- Savin, S.M., and Lee, M., 1988. Isotopic studies of phyllosilicates. In Bailey, S.W. (Ed.), *Hydrous Phyllosilicates (Exclusive of Micas)*. Reviews in Mineralogy and Geochemistry, 19:189–223.
- Sheppard, S.M.F. and Gilg, H.A., 1996. Stable isotope geochemistry of clay minerals, *Clay Minerals*, 31(1):1–24. <http://dx.doi.org/10.1180/claymin.1996.031.1.01>
- Tobin, H.J., and Kinoshita, M., 2006. NanTroSEIZE: the IODP Nankai Trough Seismogenic Zone Experiment. *Scientific Drilling*, 2:23–27. <http://dx.doi.org/10.2204/iodp.sd.2.06.2006>
- Tomaru, H., Torres, M.E., Matsumoto, R., and Borowski, W.S., 2006. Effect of massive gas hydrate formation on the water isotopic fractionation of the gas hydrate system at Hydrate Ridge, Cascadia margin, offshore Oregon. *Geochemistry, Geophysics, Geosystems*, 7(10). <http://dx.doi.org/10.1029/2005GC001207>
- Torres, M.E., Cox, T., Hong, W.-L., McManus, J., Sample, J.C., Destrigneville, C., Gan, H.M., Gan, H.Y., and Moreau, J.W., 2015. Crustal fluid and ash alteration impacts on the biosphere of Shikoku Basin sediments, Nankai Trough, Japan. *Geobiology*, 13(6):562–580. <http://dx.doi.org/10.1111/gbi.12146>
- Underwood, M.B., Saito, S., Kubo, Y., and the Expedition 322 Scientists, 2010. Expedition 322 summary. In Saito, S., Underwood, M.B., Kubo, Y., and the Expedition 322 Scientists, *Proceedings of the Integrated Ocean Drilling Program*, 322: Tokyo (Integrated Ocean Drilling Program Management International, Inc.). <http://dx.doi.org/10.2204/iodp.proc.322.101.2010>
- Wilkinson, M., Crowley, S.F., and Marshall, J.D., 1992. Model for the evolution of oxygen isotope ratios in the pore fluids of mudrocks during burial. *Marine and Petroleum Geology*, 9(1):98–105. [http://dx.doi.org/10.1016/0264-8172\(92\)90007-2](http://dx.doi.org/10.1016/0264-8172(92)90007-2)

Initial receipt: 11 May 2016

Acceptance: 15 August 2016

Publication: 7 October 2016

MS 322-212

Figure F1. Bathymetric map showing locations of Sites C0011 and C0012 on the NanTroSEIZE transect, southeast of Kii Peninsula (Japan) (see the “[Expedition 322 summary](#)” chapter [Underwood et al., 2010]).

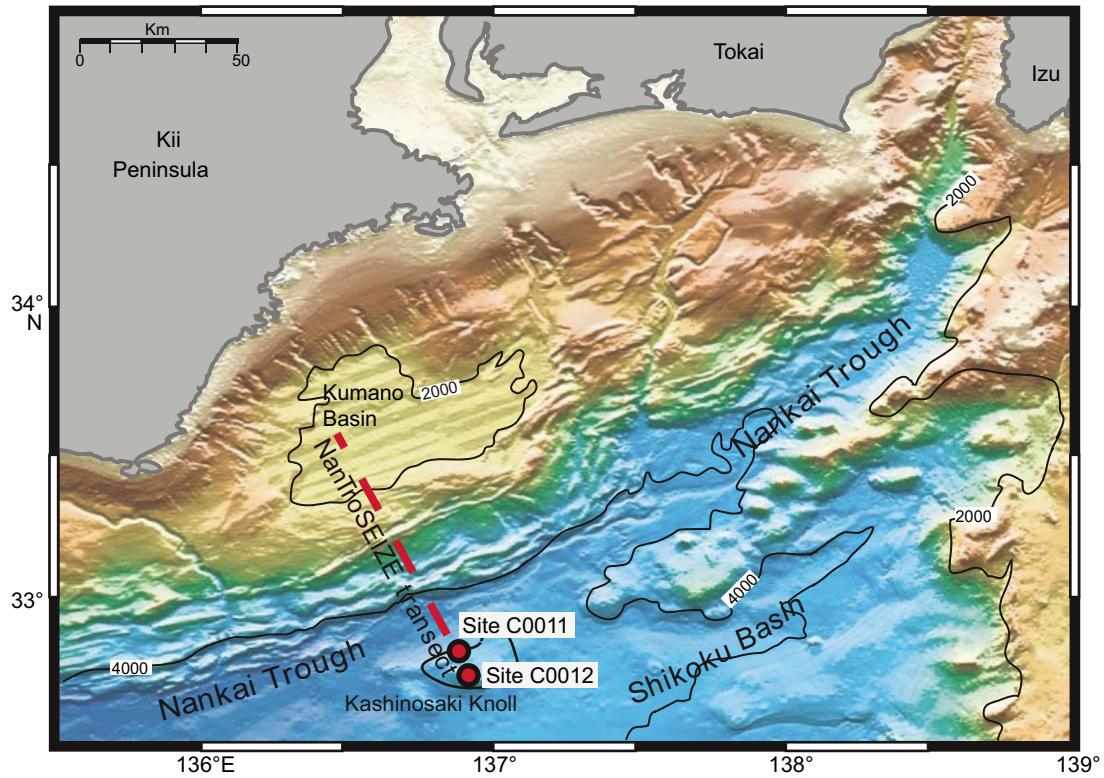


Figure F2. Downhole profiles of $\delta^{18}\text{O}$ in pore fluids from Sites C0011 and C0012 in the context of the sediment lithology. Stratigraphic columns are from Expedition 333 Scientists, 2012. $\delta^{18}\text{O}$ is reported against standard mean ocean water. Light blue line = $\delta^{18}\text{O}$ of seawater.

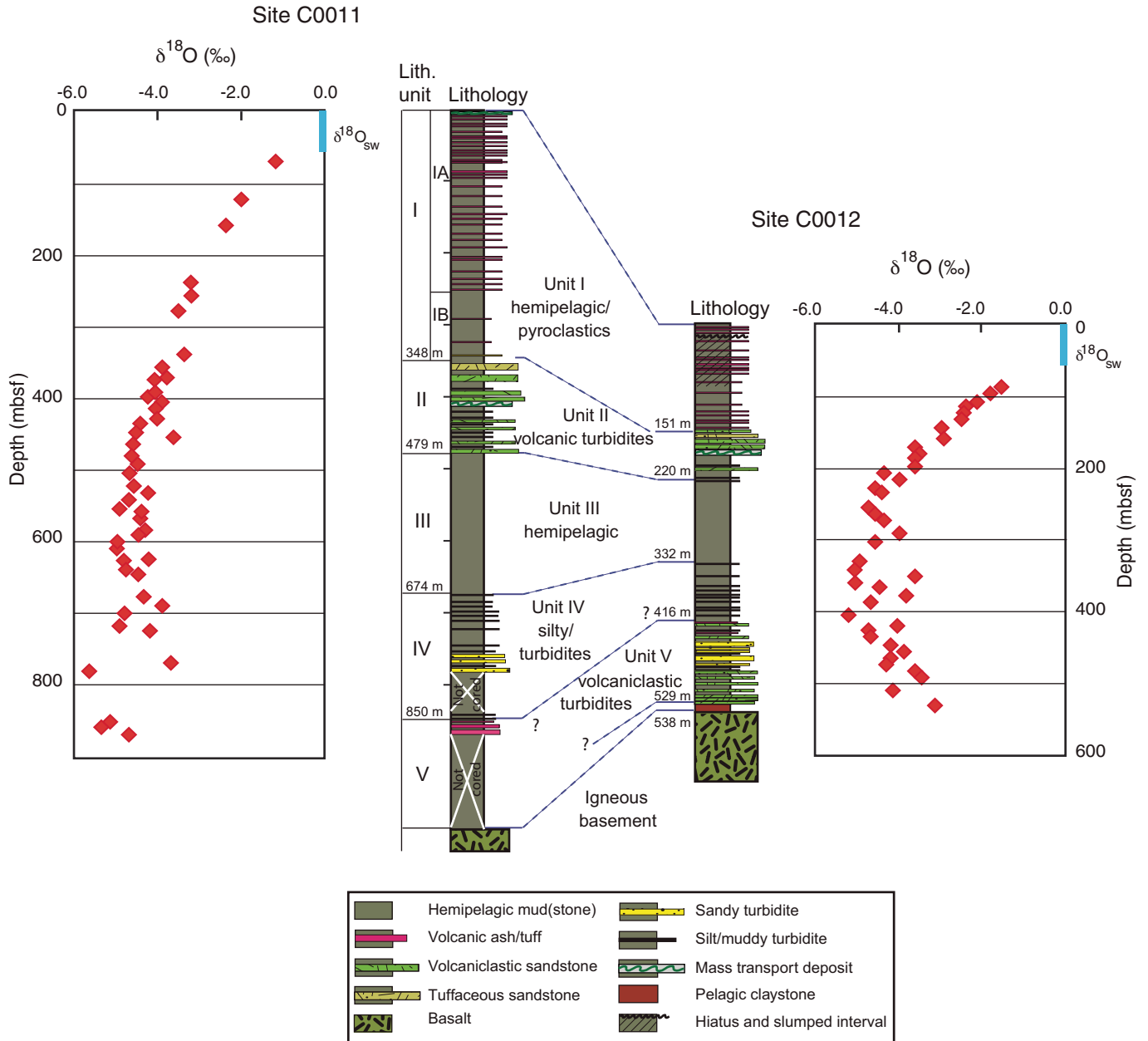


Table T1. $\delta^{18}\text{O}$ of pore fluids, Expeditions 322 and 333.

Core, section	Depth (mbsf)	$\delta^{18}\text{O}$ (‰)	\pm (‰)	Core, section	Depth (mbsf)	$\delta^{18}\text{O}$ (‰)	\pm (‰)
333-C0011D-				58R-3	858.34	-5.30	0.03
3H-5	44.804	-0.70	0.10	59R-3	867.50	-4.72	0.06
6H-4	68.80	-1.23	0.07	322-C0012A-			
13H-5	121.72	-2.00	0.10	5R-2	89.43	-1.58	0.09
17H-6	154.83	-2.42	0.09	6R-3	100.35	-1.80	0.07
31X-4	238.14	-3.26	0.03	7R-5	107.66	-2.16	0.07
34X-4	254.44	-3.20	0.10	8R-5	116.62	-2.40	0.06
37X-4	279.35	-3.51	0.12	9R-4	124.03	-2.47	0.07
44X-4	337.21	-3.41	0.07	10R-3	132.17	-2.51	0.13
48X-3	356.49	-3.90	0.10	11R-4	144.03	-2.99	0.06
322-C0011B-				13R-2	159.64	-2.93	0.17
4R-3	366.94	-3.81	0.13	14R-2	169.69	-3.61	0.10
5R-2	375.36	-4.07	0.03	15R-3	180.09	-3.52	0.08
6R-5	388.43	-4.05	0.05	16R-3	189.03	-3.58	0.07
7R-3	395.13	-4.26	0.03	17R-3	198.82	-3.62	0.12
8R-2	404.27	-3.95	0.06	18R-2	207.90	-4.38	0.07
9R-2	413.63	-4.06	0.07	19R-2	217.58	-3.97	0.05
10R-3	424.74	-4.04	0.09	20R-3	227.50	-4.57	0.09
11R-4	434.64	-4.44	0.10	21R-2	234.70	-4.39	0.14
12R-6	446.96	-4.57	0.10	23R-3	256.10	-4.70	0.11
13R-3	453.32	-3.66	0.12	24R-2	263.93	-4.59	0.18
14R-4	463.15	-4.57	0.08	25R-2	273.92	-4.33	0.07
16R-2	478.21	-4.66	0.13	27R-2	292.04	-3.98	0.02
19R-3	492.65	-4.59	0.05	28R-2	302.16	-4.54	0.11
21R-2	501.65	-4.69	0.06	31R-3	330.59	-4.94	0.07
23R-2	521.15	-4.60	0.07	32R-2	340.13	-5.06	0.12
24R-1	529.90	-4.26	0.09	33R-2	349.21	-3.63	0.09
25R-2	539.86	-4.72	0.04	34R-3	359.54	-5.05	0.09
26R-2	550.22	-4.92	0.20	35R-2	366.81	-4.43	0.12
27R-2	559.36	-4.38	0.11	36R-2	376.20	-3.81	0.22
28R-2	569.46	-4.42	0.09	37R-2	386.30	-4.68	0.09
30R-2	581.78	-4.32	0.08	39R-3	404.50	-5.17	0.04
31R-5	587.86	-4.46	0.14	40R-4	417.40	-4.01	0.07
32R-5	601.39	-5.00	0.09	41R-3	426.10	-4.70	0.08
33R-2	605.94	-5.03	0.16	42R-2	433.90	-4.69	0.11
35R-4	628.15	-4.84	0.06	43R-4	446.00	-4.20	0.11
36R-2	634.67	-4.74	0.05	44R-2	453.30	-3.88	0.11
37R-2	644.71	-4.50	0.06	45R-3	462.80	-4.17	0.06
40R-3	674.82	-4.34	0.13	46R-2	471.03	-4.30	0.14
43R-3	685.87	-3.92	0.10	47R-2	480.52	-3.59	0.08
45R-3	700.28	-4.83	0.08	48R-1	490.00	-3.46	0.16
47R-2	712.61	-4.91	0.11	50R-2	509.00	-4.12	0.07
48R-3	722.54	-4.21	0.14	52R-2	529.20	-3.15	0.13
53R-2	767.73	-3.71	0.09	$\delta^{18}\text{O}$ is reported against standard mean ocean water.			
55R-2	779.50	-5.66	0.14				
57R-4	850.44	-5.17	0.11				