# GSA Data Repository 2010007

# Post-glacial changes in El Niño and La Niña behavior

M.C. Makou, T.I. Eglinton, D.W. Oppo, and K.A. Hughen

### APPENDIX DR1: SAMPLING AND AGE SCALE

The uppermost 2 sections of the ODP Site 1228D core were sampled at 2 cm intervals. Dinosterol and cholesterol, among other productivity related compounds, exhibit high-amplitude parallel variability over the very short time period bounded by measured ages of 510 and 550 years before present (BP). For the remainder of the records, we assume that these short term changes are averaged over the longer time periods sampled.

The reported age scale (Table S1) represents a combination of radiocarbon results (NOSAMS) generated by the authors of this study and by Higginson and Altabet (2004). A constant reservoir age of 700 years was applied, based on mean <sup>14</sup>C differences between marine and terrestrial material recovered from southern Peruvian archaeological sites over the time periods of interest (Fontugne et al., 2004). The alkenone derived age at 122 cm is considered erroneous and is consistent with the presence of a <sup>14</sup>C-depleted contaminant. If this point is disregarded, both age scales are consistent with that of another shallow Peru Margin site (Rein et al., 2004). The 1228D age scale has been extended from the last dated sample at 260 cm down to the hiatus at about 274 cm, covering 15.9 to 12.8 ka. The age relationship between the youngest dates was likewise extended upwards by less than 20 years. Sediments near the top of the core were unconsolidated and likely disturbed during coring, and thus the alkenone <sup>14</sup>C age of 1.23 ka at 2 cm (there is not a comparable bulk date) was not included. This point would

constitute a significant reversal, and may also be subject to the potential errors ascribed to the alkenone age at 122 cm.

#### **APPENDIX DR2: ANALYTICAL METHODS**

All Peru Margin sediment samples were freeze dried and then extracted using a Dionex Accelerated Solvent Extraction system (9:1 dichloromethane:methanol) operating at a temperature and pressure of 100 °C and 1,000 psi, resulting in total lipid extracts (TLEs). Activated Cu was added to each concentrated TLE in order to remove elemental sulfur. For each sample, an aliquot of TLE was then transesterified at room temperature using equal volumes of Meth-Prep<sup>TM</sup> II (Alltech) and toluene, releasing ester-bound compounds and converting carboxylic acids to methyl esters. Subsequently, the samples were silylated using equal volumes of BSTFA + 1% TMCS (Pierce) and pyridine (60 °C for 20 min) in order to convert hydroxyl groups to trimethylsilyl ethers, rendering the compounds amenable to gas chromatography (GC). 1 µl was analyzed from each 150 µl sample, which consisted of equal parts pyridine, dichloromethane, and BSTFA. Hexatriacontane ( $C_{36}$  *n*-alkane) and cis-9-tricosene ( $C_{23:1}$  alkene) were added to all samples as internal standards to assess variability between individual runs. External standards consisting of *n*-alkanoic acids, *n*-alkanols, and *n*-alkanes were prepared in the same manner as the sediment samples and interspersed throughout the analyses, along with solvent blanks. Greater than half of the Peru Margin samples were analyzed in duplicate, and reported abundance values are averages, where applicable.

All analyses were conducted on a ThermoQuest TRACE GC with PTV injector and PAL autosampler, coupled to a Thermo Fisher Scientific Inc. Tempus TOF-MS. The PTV injector was run in solvent-split mode, a 0.4 ml/min constant He carrier gas flow was applied, and the GC

was equipped with a 10 m (0.10 mm i.d., 0.10 µm film thickness) Restek Rtx-1 column. The GC oven temperature program was as follows: 40 °C initial temperature, held for 3 minutes, then ramped at 75 °C/min to 120 °C, followed by a 37 °C/min increase to a final temperature of 320 °C, which was maintained for 4 minutes. The Tempus TOF-MS was operated at an acquisition rate of 20 spectra/second, and the Xcalibur software package (Thermo Fisher Scientific Inc.) was used to interpret chromatographic and spectral data, enabling molecular identification and quantitation (ICIS algorithm). Compound identification was achieved through comparison with the NIST/EPA/NIH Mass Spectral Library (Version 2.0 a) and quantitation was performed using extracted ion chromatograms that provided baseline resolution of analytes (Fig. S3). Concentrations of derivatized *n*-alkanoic acids and *n*-alkanols were determined by comparison with authentic external standards. Response factors for all other compounds were calculated by comparing their chromatographic peaks in the total ion chromatogram (TIC) of a representative sample (93 cm) with that of the  $C_{36}$  *n*-alkane internal standard, and were then adjusted for quantitation based on representative ions. Concentrations determined in this manner are not accurate due to co-elution between compounds in the TIC, and should thus be considered as estimates. However, the chosen response factors were applied uniformly throughout the records and thus do not impact interpretations based on patterns of abundance variability. Total carbon, total OC, and total nitrogen contents of each sediment sample were determined via elemental analyzer (Carlo Erba EA1108).

Analytical errors for the biomarker abundance records were determined as the pooled standard deviation of all replicate analyses (68 samples were analyzed in duplicate or triplicate), and ranged from  $\pm 1.7$  to  $1.8 \ \mu g/g$  dry weight sediment for the steroidal compounds presented in this study. Blank levels and carry-over between samples were negligible.

# **REFERENCES CITED**

- Fontugne, M., Carré, M., Bentaleb, I., Julien, M., and Lavallée, D., 2004, Radiocarbon reservoir age variations in the south Peruvian upwelling during the Holocene: Radiocarbon, v. 46, p. 531–537.
- Higginson, M.J., and Altabet, M.A., 2004, Initial test of the silicic acid leakage hypothesis using sedimentary biomarkers: Geophysical Research Letters, v. 31, p. L18303, doi: 10.1029/2004GL020511.
- Reynolds, R.W., Rayner, N.A., Smith, T.M., Stokes, D.C., and Wang, W., 2002, An improved in situ and satellite SST analysis for climate: Journal of Climate, v. 15, p. 1609–1625, doi: 10.1175/1520-0442(2002)015<1609:AIISAS>2.0.CO;2.



Figure DR1. Eastern tropical Pacific average SST anomalies during El Niño (top panel, December 1997) and La Niña (bottom panel, December 1999) events (NOAA NCEP; Reynolds et al., 2002). The coring location on the Peru Margin (ODP Site 1228D) and direction of the Peru Countercurrent (white arrows), which impinges on the continental shelf, are indicated.



Figure DR2. 1228D age scale, comprised of bulk OC (filled black circles) and alkenone (open diamonds) <sup>14</sup>C ages. Radiocarbon data from Higginson and Altabet (2004) are included.



Figure DR3. TIC and extracted ion chromatograms for cholesterol  $(m/z \ 129+329+368)$  and dinosterol  $(m/z \ 271+359)$  from the 89 cm sample.

Bulk Organic Carbon Dates					
Depth (cm)	<u><sup>14</sup>C Age</u>	<u>Age Error (± yr)</u>	Calendar Age (yr BP)		
32	1,180	40	510		
*56	1,230	35	550		
79	2,030	35	1,280		
122	2,240	30	1,490		
165	2,660	40	1,990		
194	4,200	45	3,870		
206	8,040	40	8,220		
229	9,790	70	10,350		
254	10,750	65	11,530		
*260	11,550	60	12,850		
Alkenone Dates					
Depth (cm)	<u><sup>14</sup>C Age</u>	<u>Age Error (± yr)</u>	Calendar Age (yr BP)		
*2	1,990	140	1,230		
32	1,190	95	510		
*58	1,710	40	950		
*80	2,320	190	1,590		
*122	3,890	250	3,500		
165	2,910	110	2,290		
194	4,220	130	3,910		
*206	8,110	210	8,260		
254	10,500	160	11,170		

Table DR1. 1228D  $^{14}\mathrm{C}$  measurements and age scale data

\*Results from Higginson and Altabet (2004).

1228D Analytical Results				
<u>Age (ka BP)</u>	Cholesterol (µg/g OC)	Dinosterol (µg/g OC)		
0.494	245.2	272.9		
0.499	207.2	233.5		
0.501	211.5	230.2		
0.504	399.3	449.7		
0.507	179.1	204.7		
0.512	392.0	445.4		
0.514	393.1	485.8		
0.517	351.0	439.0		
0.520	382.2	423.1		
0.526	247.8	247.3		
0.529	386.1	448.2		
0.532	397.8	507.6		
0.537	379.6	453.3		
0.540	318.2	387.4		
0.543	374.3	466.4		
0.610	452.8	650.8		
0.673	381.5	525.8		
0.737	368.3	449.7		
0.832	412.8	408.9		
0.896	373.0	370.6		
0.960	295.5	236.9		
1.023	339.0	314.2		
1.119	322.1	348.8		
1.183	289.5	359.3		
1.246	332.9	371.0		
1.283	308.2	326.0		
1.302	286.1	310.4		
1.312	334.8	406.1		
1.327	319.9	342.6		
1.336	324.1	334.2		
1.346	363.5	369.6		
1.365	348.9	316.8		
1.375	311.1	314.3		
1.385	287.7	270.1		
1.404	323.0	313.8		
1.414	306.0	251.7		
1.424	272.6	265.1		
1.443	220.1	176.8		
1.453	279.9	208.5		
1.463	286.0	191.5		
1.522	241.3	196.3		
1.545	292.0	261.6		
1.592	333.9	336.6		
1.616	348.3	323.3		
1.662	298.4	252.6		
1.686	288.1	254.4		
1.709	283.8	284.3		

1.756	302.3	284.8
1.779	336.8	519.4
1.803	307.8	247.6
1.849	286.8	328.3
1.873	338.2	336.2
1.908	298.5	403.4
1.931	292.3	424.7
1.954	292.0	567.4
1.990	341.6	500.1
2.119	196.1	210.7
2.249	231.0	231.4
2.443	180.8	138.6
2.702	210.1	168.2
3.026	310.7	251.0
3.155	167.4	131.7
3.479	201.7	119.8
3.738	203.9	123.7
3.868	228.8	139.1
8.494	201.1	127.9
8.681	254.8	113.6
9.051	231.5	117.1
9.236	234.8	126.5
9.608	260.1	116.8
9.793	261.8	137.5
9.979	225.8	100.0
10.350	218.3	111.4
10.444	241.2	142.7
10.538	270.4	172.5
10.680	197.9	102.7
10.774	241.5	179.0
10.868	225.9	177.2
11.009	181.6	117.4
11.104	228.2	148.1
11.198	213.3	124.5
11.292	150.0	/1.1
11.433	154.7	81.3
11.528	234.2	136.4
12.188	406.6	186.2
12.628	401.6	188.1
13.508	346.1	127.9
13.948	297.7	107.6
14.388	362.3	134.4
15.048	290.4	115.8
15.488	269.4	110.9
15.928	241.3	102.0