

## *Chemical Results from the April, 2000 NPEO Project*

### Water sampling procedure

Seawater samples were obtained during this aircraft supported mission by drilling 10-inch diameter holes in the ice and using an electric-powered portable winch to cast a single 1.5-L Niskin at a time. The custom constructed Niskin (General Oceanics model 1010 with 8" extension) was mounted on a small diameter Kevlar line 1 meter above the internally recording Seacat SBE19 CTD and lowered to target depth as indicated on the winch meter wheel. Upon retrieval, the Niskin was immediately transferred to a rack in the heated aircraft and samples were drawn. Salinity samples were collected into 125-ml amber glass bottles the caps of which were fitted with conical polyethylene inserts. Oxygen isotope samples were collected into similar containers of smaller volume (20-ml). Barium samples were collected into 20-ml polyethylene scintillation vials. Nutrient samples were collected into 60-ml polyethylene bottles and stored frozen until analysis.

In addition to the limitations of single bottle casts, two practical problems were encountered with this sampling approach. On several occasions, the messenger slipped between the plunger head and the Kevlar line and so failed to trip the bottle. Also, although the exposure to the subfreezing ( $\approx -30$  deg C) air temperatures was minimized, it appears that some of the Niskins experienced freezing of up to 5% of their contents. (Note: These problems were surmounted for the April 2001 effort by modifying the Niskins and sampling approach. The changes further permitted all 4 available Niskins to be hung per cast in 2001.)

### Analytical procedures

Bottle salinities were analyzed using a Guildline Autosol standardized with IAPSO standard seawater. Precision for these determinations was 0.002 practical salinity units. Analyses of the frozen phosphate, silicic acid, nitrate, nitrite and ammonia samples were performed ashore using a hybrid Alpkem RFA 300 and Technicon AA-II (AutoAnalyzer II) – based system and the JGOFS/WOCE suggested nutrient protocols (Gordon et al., 1994). The silicic acid, nitrate+nitrite and nitrite channels were RFA-based, the phosphate and ammonium channels, AA-II. The samples were thawed and immediately analyzed for all nutrients. After standing overnight in the dark, the samples were reanalyzed for silicic acid to avoid polymerization effects (Gordon et al., 1994). The short-term precision of the nutrient analyses is typically: Silicic acid, 0.2%; phosphate, 0.4%; nitrate 0.3%; nitrite, 0.02 $\mu$ M; and ammonium, 0.03 $\mu$ M. However, the inter-cruise reproducibility achieved during the WOCE Hydrographic Program, Pacific One-Time Survey was for silicic acid, phosphate and nitrate, respectively, ca. 1%, 2% and 1% (unpublished data, Ross et al., 2000). Barium was determined by isotope-dilution using an VG Thermo Excel inductively coupled quadrupole mass spectrometer as previously described with minor modifications (Falkner et al., 1994). Precision is estimated to be 3% for this suite of Ba measurements. Oxygen isotopes were analyzed by the CO<sub>2</sub> equilibration method on the COAS Finnegan Mat 251. Results are reported in  $\delta$  units relative to VSMOW and 1-sigma precision is estimated to be  $\pm 0.05$

### Results

The data are given in Table 1. The CTD data were assigned to the individual bottles by examining the continuous records in the vicinity closest to the successful bottle trip time. The interval over which the pressure record leveled (when the winch was stopped and the messenger

dropped through bottle closure) was averaged to obtain the best estimate and 1 standard deviation of CTD-based depth, temperature and salinity. Comparison of bottle and CTD salinities shows agreement well within analytical errors at the North Pole Base Camp site where the sampling site was sheltered. Deviations outside analytical error occurred at remote sites where conditions were somewhat less controlled. In all such cases, the bottle salinity exceeds the CTD salinity by  $\leq 5\%$ . The analytical data were corrected for this small factor under the assumption that dissolved constituents are excluded in the ice formation process. Oxygen isotope data were not corrected for this affect since the fractionation factor between sea ice and seawater is quite small.

Table 1 (panel A)

Date	Station	target depth m	db of ctd	stdev db	sal ctd psu	stdev sal ctd psu	bot sal psu	ctd temp degC	stdev degC
22-Apr-00	1	5	12.52	0.02	32.097	0.004	32.134	-1.752	0.003
22-Apr-00	1	125	136.0	0.2	34.255	0.002	34.256	-1.398	0.004
21-Apr-00	1	deep ( $\approx 350$ )	378.1	0.7	34.886	0.001	34.356	1.375	0.001
24-Apr-00	2	5	5.23	0.01	NA	NA	33.756	-1.793	0.008
24-Apr-00	2	125	137.8	0.1	34.191	0.005	36.026	-1.280	0.010
23-Apr-00	3	5	11	2	33.020	0.002	33.891	-1.811	0.002
22-Apr-00	4	5	12.8	0.3	31.46	0.001	32.278	-1.749	0.001
22-Apr-00	5	5	5.89	0.04	30.31	0.29	30.366	-1.661	0.006
22-Apr-00	5	125	160.5	0.1	34.329	0.002	34.370	-0.651	0.002
25-Apr-00	6	5	4.97	0.07	NA	NA	31.092	-1.660	0.010
25-Apr-00	6	125	132.3	0.9	33.706	0.003	34.341	-1.530	0.020
28-Apr-00	7	5	5.61	0.02	NA	NA	31.658	-1.718	0.003
28-Apr-00	7	125	135	3	34.01	0.02	34.496	-1.480	0.030

Table 1 (panel B)

Station	target depth m	Ba nM	P $\mu$ M	NO3 $\mu$ M	Si $\mu$ M	NO2 $\mu$ M	NH3 $\mu$ M	del180	del180 stdev	% Pacific
1	5	60.2	0.51	2.93	6.55	0.01	0.04	-3.37	0.03	28
1	125	44.1	0.61	7.51	3.56	0.00	0.02	-0.36	0.04	1
1	deep ( $\approx 350$ )	45.9	0.71	9.24	4.75	0.00	0.02	-0.12	0.02	0
2	5	58.3	0.49	3.37	5.65	0.01	0.04	-2.97	0.07	20
2	125	43.9	0.64	7.40	5.48	0.00	0.03	-0.90	0.07	6
3	5	52.4	0.46	3.61	4.79	0.01	0.03	-2.33	0.05	13
4	5	56.3	0.65	2.03	5.43	0.01	0.02	NA	NA	57
5	5	71.3	0.76	0.54	2.99	0.01	0.03	-2.88	0.04	85
5	125	51.1	1.04	12.54	14.66	0.01	0.03	-0.14	0.05	19
6	5	67.3	0.77	0.46	2.82	0.01	0.03	-2.93	0.06	86
6	125	53.5	1.10	10.66	18.64	0.00	0.01	-1.01	0.15	42
7	5	62.3	0.71	1.42	5.76	0.01	0.07	-3.19	0.05	71
7	125	NA	0.87	9.98	11.03	0.00	0.05	-0.56	0.04	18

## References

Falkner, K.K., R.W. MacDonald, E.C. Carmack, and T. Weingartner, The potential of barium as a tracer of Arctic water masses, in *The Polar Oceans and Their Role in Shaping the Global Environment: The Nansen Centennial Volume*, AGU Geophys. Monograph Series, edited by O.M. Johannessen, R.D. Muench, and J.E. Overland, pp. 63-76, AGU Books, Washington DC, 1994.

Gordon, L.I., J.J.C. Jr., A.A. Ross, and J.M. Krest, A suggested protocol for continuous flow automated analysis of seawater nutrients (phosphate, nitrate, nitrite and silicic acid) in the WOCE Hydrographic Program and the Joint Global Ocean Fluxes Study. WOCE Operations Manual, Vol. 3: The Observational Programme, Section 3.1: WOCE Hydrographic Programme, Part 3.1.3: WHP Operations and Methods., pp. 52 loose-leaf pp., Woods Hole, Mass., 1994.

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