Chemical Results from the April 2002 NPEO Project

Water sampling procedure

The aircraft (Twin Otter) sampling approach that was successful in NPEO 2001 was undertaken at two stations in the Makarov Basin. A surface sample was also taken at the Borneo ice camp. For details regarding the sampling approach, please refer to the 2001 chemical data report. Kelly Falkner did not go into the field in 2002. Roger Anderson and Jamie Morison of APL-UW and the First Air team conducted seawater sampling on her behalf.

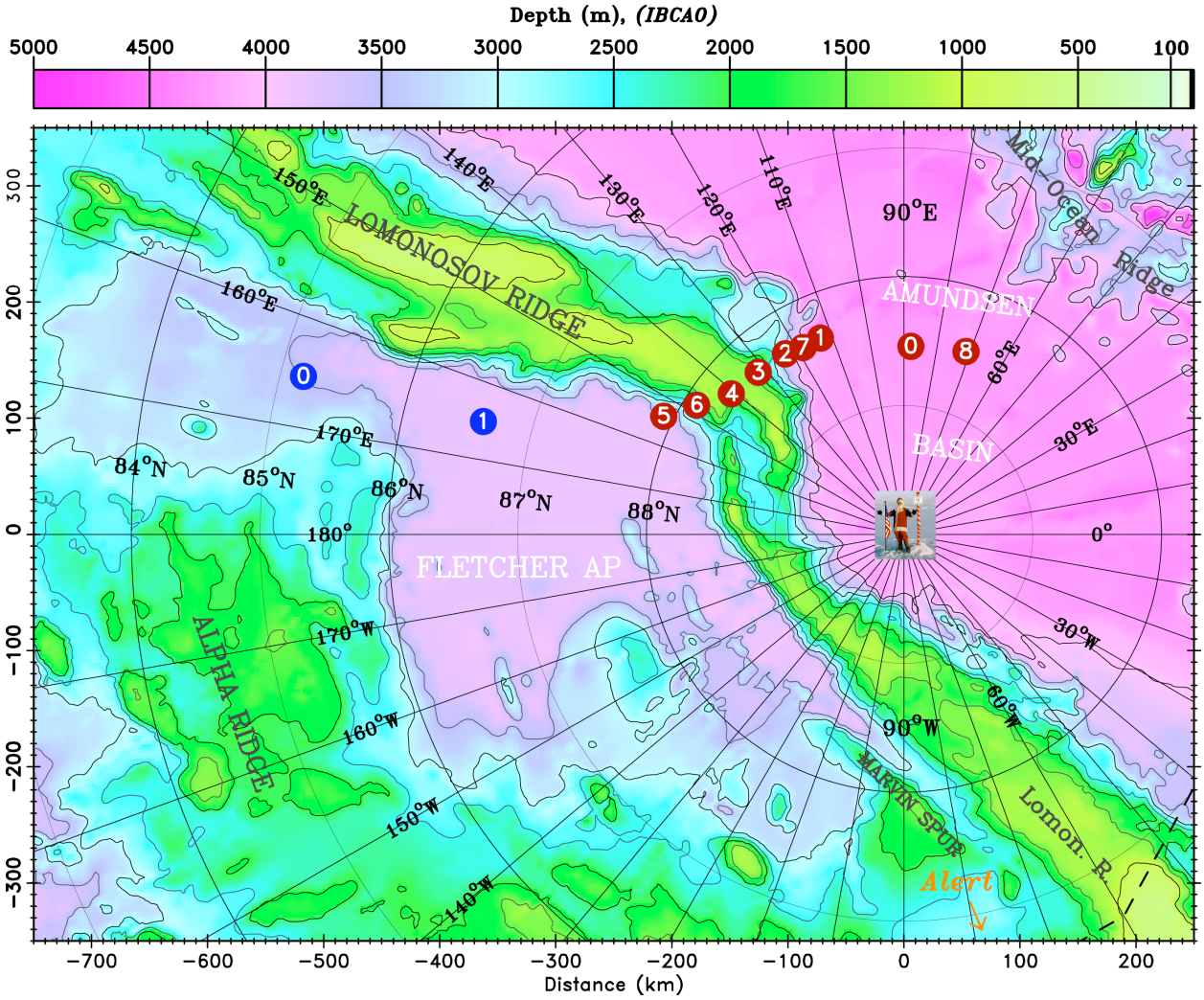

Fig. 1. Station locations: The blue dots are the hydrostations conducted from Twin Otter. The red dots are the CTD-stations conducted from helicopter and the surface water sample taken at Borneo is CTD-helo-cast 8. Bathymetry is from Jacobsson et al., 2000.

Camp Borneo posed a number of challenging conditions for a field base. Carbon monoxide detectors indicated that the stoves' exhaust was problematic in the tents. Both the

quality and quantity of food and fuel were issues. You can learn more about Borneo on the NPEO web-site: http://psc.apl.washington.edu/northpole/2002.html. Despite the difficulties, Borneo did provide an convenient place from which to conduct sampling into the remote region of the Makarov Basin. A very complex set of fuel caching operations would have been necessary had the operation been staged out of Alert, for example.

Ice at both hydrostations was very broken up and rubbly. There were a lot of pressure ridges, blocks and hummocks making it difficult to find a relatively smooth place to land. The ice that served for hydrocast landings was about 2.5 m thick.

As in 2001, seawater samples were obtained using the generator-powered portable winch to cast 4 1.5-L Niskins at a time. The custom constructed Niskins (General Oceanics model 1010 with 8" extension and modified plunger) were mounted on a small diameter Kevlar line, with the deepest one mounted 1 meter above an internally recording Seabird SBE-19 Seacat CTD. This year, the CTD carried a new generation dissolved oxygen sensor (Seabird SBE43) for the first time. The CTD-O_2 package was set to acquired data at 2 scans/second and the package was lowered at about 60 m/min. Upon retrieval, each Niskin was transferred to a rack in the heated aircraft and samples were drawn immediately. Dissolved O_2 samples were drawn first into calibrated 125 ml flasks with ground glass stoppers. (K. Falkner trained Roger Anderson to draw O_2 samples into the flasks and to apply the Winkler "pickling technique" in the field. The usual pickling reagents ($MnCl_2$ and NaOH/NaI) were added to these samples immediately upon collection following standard procedures (Dickson, 1994). As is noted below these O_2 samples did not prove to be viable. Alternate means for deriving useful information from the O_2-sensor profiles is described below.) Salinity samples were collected into 125-ml 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.

Analytical procedures

Bottle salinities were analyzed using a Guildline Autosal 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 at OSU 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 plus 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, 0.02μM; and ammonium, 0.03μM. 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). The results of replicate sample analyses are reported as 1 standard deviation in data Table 1.

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_2 equilibration method on the COAS Finnegan Mat 251. Results are reported in del units relative to VSMOW and 1-sigma precision is estimated to be +/- 0.05. Again for both Ba and oxygen isotopes, results of replicate sample analyses are reported as 1 standard deviation in data Table 1.

After pickling the dissolved O_2 samples, Roger Anderson put distilled water in the space above the closed ground glass stopper joint of the titration flasks and sealed them with Parafilm. The five samples (including a replicate pair) were then hand carried them back to the U.S. and were titrated at OSU approximately 5 days after collection. (See the 2001 data report for a description of the experiement that showed that dissolved O_2 samples could be successfully stored in this way.) In the laboratory, dissolved oxygen was measured by whole-flask titrations and amperometric end-point detection using a PC-controlled titrator (Culberson and Huang, 1987). The actual apparatus was adapted to PC's following Knapp et al. (1989).

Results

Bottle chemical data are given in Table 1. The CTD depths were assigned to individual Niskin bottles by matching the bottle salinity to a linearly interpolated CTD salinity near the target depth value. Generally, salinities identical to the measured bottle values were observed in the CTD-casts near the target bottle depths. This lends confidence that the Niskins were tripped correctly and did not leak. Small offsets between true depth values as indicated by salinity and target depth values given by the meter wheel on the Kevlar line occurred as follows. Shallow samples all appeared to been derived from less than the target 5 m depth. This is probably not surprising given that property gradients are largest near the surface and the Niskin itself is approximately a meter in length. The deeper the Niskins were cast, the larger the discrepancy between actual and target depths as would be expected from a non-zero wire angle. Temperatures were linearly interpolated from the CTD casts to correspond to the measured bottle salinity. There appeared to be no problems with samples freezing in the Niskins.

Table 1: North Pole Environmental Observatory hydrostation data

CTD cast	Stn ID	latitude	longitude	time (UTC)	date	target depth m	bottle sal pss	CTD-depth m	Temp degC
10	Hydro-0	85˚10.7'N	165˚16.4'E	14:33	4/27/02	5	31.855	2.6	-1.746
10	Hydro-0	85˚10.7'N	165˚16.4'E	14:33	4/27/02	100	34.101	97.5	-1.556
10	Hydro-0	85˚10.7'N	165˚16.4'E	14:33	4/27/02	110	34.183	106.6	-1.430
10	Hydro-0	85˚10.7'N	165˚16.4'E	14:33	4/27/02	260	34.855	249.5	1.120
11	Hydro-1	86˚37.1'N	164˚59.5'E	18:50	4/27/02	5	30.850	3.0	-1.695
11	Hydro-1	86˚37.1'N	164˚59.5'E	18:50	4/27/02	60	33.365	60.4	-1.713
11	Hydro-1	86˚37.1'N	164˚59.5'E	18:50	4/27/02	110	34.220	109.6	-1.220
11	Hydro-1	86˚37.1'N	164˚59.5'E	18:50	4/27/02	260	34.861	251.5	1.064
9	Helo-8 Borneo	88˚30.1'N	71˚14.1'E	10:41	4/28/02	5	33.549	2.2	-1.849

Stn ID	CTD cast	target depth m	bot O2 ml/l*	botO2 stdev*	PO4 µM	PO4 stdev	NO3+NO2 µM	N+N stdev	NO2 µM	NO2 stdev
Hydro-0	10	5			0.350	0.001	2.21	0.03	0.023	0.004
Hydro-0	10	100			0.671	0.001	8.30	0.01	0.018	0.006
Hydro-0	10	110	6.84		0.675	0.005	8.59	0.06	0.014	0.003
Hydro-0	10	260	7.54		0.851	0.001	12.58	0.03	0.011	0.001
Hydro-1	11	5			0.453	0.001	2.38	0.03	0.013	0.002
Hydro-1	11	60			0.666	0.001	6.76	0.03	0.018	0.001
Hydro-1	11	110			0.692	0.002	8.99	0.00	0.020	0.000
Hydro-1	11	260	6.00	0.16	0.854		12.63		0.016	
Helo-8 Borneo	9	5	8.14		0.371	0.000	3.26	0.00	0.023	0.000

Stn ID	CTD cast	target depth m	Si µM	Si stdev	Ba nM	Ba stdev	δ18O SMOW	δ18O stdev
Hydro-0	10	5	4.51		53.3		-2.90	0.04
Hydro-0	10	100	5.42	0.01	45.2	1.7	-0.52	
Hydro-0	10	110	5.14	0.01	43.2		-0.36	
Hydro-0	10	260	6.31		43		0.19	
Hydro-1	11	5	6.57		62		-4.18	
Hydro-1	11	60	7.43	0.06	47.5		-1.48	0.01
Hydro-1	11	110	5.34	0.01	42.6		-0.34	
Hydro-1	11	260	6.25		41.3		0.24	
Helo-8 Borneo	9	5	3.06	0.01	46.1	1.6	-1.60	0.01

*The bottle O_2 results appear to be subject to large errors and therefore were judged to be unreliable.

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References

Culbertson, C.H. and S. Huang, Automated amperometric oxygen titration, Deep-Sea Res., 34: 875-880, 1987.

Dickson, A.G., *Determination of dissolved oxygen in sea water by Winkler titration*, WOCE Hydrographic Program, Woods Hole, MA, pp. 11. 1994.

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.

Jakobsson, M.N.Z., N.Z. Cherkis, J. Woodward, R. Macnab, and C. B., New grid of Arctic bathymetry aids scientists and mapmakers, *EOS, Transactions, American Geophysical Union*, *81* (9), 2000

Knapp, GP, MC Stalcup and RJ Stanley, Dissolved oxygen measurements in sea water at the Woods Hole Oceanographic Institution, Technical Report, WHOI-89-23, Woods Hole Oceanographic Institution, Woods Hole, MA 02543. 13 pp., 1989.