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#### Abstract

Paton, D.W., V. Knight and R.W. Macdonald, 1997, NOGAP B.6, Oxygen isotope data from water and ice cores from the Beaufort Sea, May 1992 Can. Data Rep. Hydrogr. Ocean Sci.: 149, 23 pp.

As part of the NOGAP B. 6 program (Beaufort Sea Oceanography), with objectives to determine hydrocarbon pathways and primary productivity of the waters overlying the Mackenzie Shelf, we conducted an ice-based spring sampling program (April 23-May 11, 1992, Institute of Ocean Sciences I.D. \#9207). Chemical and physical measurements for this mission have been previously reported [Pearson et al., 1994]. We report here the measurements made of oxygen isotope composition ( $\delta^{18} \mathrm{O}$ ) and salinity for ice-core and water samples collected in April- May, 1992 (Mission \#9207).


Key words: Arctic, $\delta^{18} \mathrm{O}$, coastal zone, ice.

## Résumé

Paton, D.W., V. Knight and R.W. Macdonald, 1997, NOGAP B.6, Oxygen isotope data from water and ice cores from the Beaufort Sea, May 1992 Can. Data Rep. Hydrogr. Ocean Sci.: 149, 23 pp.

Dans le cadre du programme NOGAP B. 6 (Océanographie de la mer de Beaufort), dont les objectifs sont de déterminer le cheminement des hydrocarbures et la productivité primaire dans les eaux du plateau Mackenzie, nous avons mené une campagne d'échantillonnage sur la glace au printemps 1992 (23 avril - 11 mai, Institute des Sciences de la Mer I.D. \#9207). Les mesures physiques et chimiques obtenues lors de chacune des ces campagnes ont été rapportées antérieurement [Pearson et al. 1994]. Dans le présent rapport, nous avons colligés les résultats de la composition isotopique de l'oxygène ( $\delta^{18} \mathrm{O}$ ) et de la salinité des échantillons d'eau et des carottes de glace prélevés en avril - mai 1992 (campagne \#9207).

Mots-clés: Arctique, $\delta^{18} \mathrm{O}$, glace, zone côtière.

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## 1 INTRODUCTION

The Northern Oil and Gas Action Program has as one of its sub- projects a major inter-disciplinary study of the oceanography of the Canadian Beaufort Sea (NOGAP B.6). The objectives of NOGAP B. 6 are to determine the transport and fate of materials (in particular, petroleum hydrocarbons) over the Beaufort Shelf, and the primary productivity of these coastal waters. Field work started in 1986 and the program was finally completed in March, 1994. Data reports in the NOGAP B. 6 series are listed on the inside of the back cover of this report. Here we provide a description of the sampling and analytical methods for oxygen isotope ( $\delta^{18} \mathrm{O}$ ) measurements made on water and ice cores collected during the 1992 NOGAP B. 6 mission. For other supporting data the reader is referred to Pearson et al., [1994] which includes CTD and bottle data for measurements of salinity, temperature, nutrients (silicate, phosphate and nitrate) and dissolved oxygen determinations. The application of similar ( $\delta^{18} \mathrm{O}$ ) measurements made on ice and water to understanding water-mass production and movement is available in Macdonald et al., [1995] and references contained therein.

### 1.1 April-May, 1992, Institute of Ocean Sciences mission \# 9207

Field work focused on the nearshore zone and the disposition of water from runoff or from the Beaufort Shelf in the Husky Lakes system in late winter. Previous studies ([Macdonald and Carmack, 1991; Macdonald et al., [1995]] led us to conclude that the Beaufort Sea nearshore regions are critical both to the biology and to physical processes that transport properties including contaminants. Wintertime is especially important as it sets the stage for spring breakup and the ensuing seasonal pulse of biological activity. Despite this importance, wintertime is a period of infrequent and sparse sampling due to the logistical difficulties. Accordingly, we collected CTD data and water samples for chemistry on transects through the Husky Lakes and Liverpool Bay area and then along the Tuktoyaktuk Peninsula coast in late winter. Additionally, we collected ice cores at many of the stations with the intention of developing seasonal records of surface water properties from them. These cores were sectioned and analyzed for salinity, $\delta^{18} \mathrm{O}$, and nutrients.

We operated the spring program out of Tuktoyaktuk, Polar Continental Shelf Project (PCSP), and used fixed-wing and rotary- wing support vehicles to carry out the sampling. Figure 1 shows the station locations.

Objectives of mission \#9207 and the oceanographic data are described in [Pearson et al. 1994]. The logistic goals accomplished with respect to oxygen isotope sampling were as follows (data reported here are in bold font:

- Collect water column samples in late winter for temperature, nutrients, dissolved oxygen, salinity and $\delta^{18} \mathbf{O}$ determination on transects extending through the Husky lakes and Liverpool Bay system.
- Collect ice cores at most of the water sampling stations and measure these for $\delta^{18} \mathbf{O}$, salinity and nutrients.


### 1.1.1 Station Nomenclature for Mission \#9207

The stations have been given a two-part designation. The alphabetic before the hyphen refers generally to a coastal feature relevant to the location of the transect on the open shelf (described below) or an E designating Liverpool Bay and Husky Lakes and, after the hyphen, stations are generally numbered sequentially outward from the coast or from the head of the Husky Lakes system.


Figure 1: Station locations for April-May, 1992 (\# 9207)

CM C section off Tuktoyaktuk, Middle part
CD Cape Dalhousie
JJ Near shore stations where ice flooding occurs
E Husky Lakes - Liverpool Bay
MB Mason Bay
T Tuktoyaktuk Harbour

## 2 METHODS

### 2.1 Station Locations

All stations were navigated using the aircraft GPS, or for stations taken by snowmobile a Magellan hand-held GPS was used, again with C/A codes for positioning. During this field trip, the GPS "selective availability" was turned off and therefore positions are expected to have a reliability of about $\pm 50 \mathrm{~m}$. In the case of this field work, precision of the GPS was repeatedly demonstrated by our ability to navigate back to single, unmarked auger holes in the landfast ice zone.

### 2.2 Field Sampling

### 2.2.1 Ice-based operations

Detailed methods of sampling and analysis have been given previously in Paton et al., [1994] and we present here only a brief outline. The general plan was to sample along a pre- chosen transect along the axis of the Husky Lake system which would include stations in each major basin. Additional stations were occupied at a few points on the outer coast (Figure 1). Sampling equipment and personnel were flown from PCSP in Tuktoyaktuk to the selected site by fixed wing aircraft (Twin Otter) or helicopter (Bell 206L Long Ranger). The actual site for collecting water or ice cores was selected carefully from the air. We chose broad, flat regions of first-year ice that were well away from ridges or complex ice topography. Sampling equipment included a hand winch, 1.7 L Niskin sampling bottles as well as submersible pump systems for water and a Sipre ice corer for collecting the ice cores.

Water sampling The pumping system consisted of a 316 stainless steel magnetically coupled pump with Ryton gears coupled to a submersible well pump motor (Franklin Electric Co., 3450 RPM). Water was pumped through a 1.4 cm o.d. hose (Aeroquip 2807-8) constructed of smooth bore extruded Teflon TFE ( 1.0 cm i.d.) with a reinforcement and cover of one-braid, high tensile stainless steel wire. The pump delivered approximately $6 \mathrm{~L} / \mathrm{min}$, and the hose length (max depth) was 50 m .

On the ice, a 25 cm hole was first augered and, when required by weather, a tent was placed over the hole. Bottle sampling followed standard oceanographic procedures. One depth was sampled at a time and subsampling from the bottles followed the order dissolved oxygen, salinity, nutrients, and oxygen isotopes. Water samples for oxygen isotope determination were stored in 30 mL CPE bottles after 3 rinses from the sample water. Salinity samples were drawn into 200 mL salinity bottles after 3 rinses from Niskin bottles or the pumping system. The samples were then capped tightly and care was taken to avoid freezing during sampling or transport. When the pump was used, a dilute ethanol- water mixture was kept in the hose to prevent freezing during transport and
storage. Therefore, the hose was flushed at depth for 6 minutes before collecting the first sample at a station, and for 3 minutes at each specific depth after that. Samples were stored in an insulated box (with optional heating) to protect them from freezing and light; these were then shipped back to the Laboratory at Tuktoyaktuk on the same day (1-6 hours) when aircraft were used, and the next day when the snowmobile was used. Oceanographic thermometers were not used due to the difficulty of manipulating them through an ice hole, and the rough treatment they would receive in the field. Temperatures are generally available from CTD casts carried out at the same location.

Ice sampling Ice cores were collected using a hand-operated Sipre corer. The depth of snow was measured at several places in the vicinity of the site, snow was cleared from the site, and the corer was used to collect ice segments in lengths of about 70 cm . Discontinuities in the ice were noted during collection. The total length of core collected was carefully reconciled with the depth of the hole after each segment. This procedure was found to be particulary important for ice that had grown from brackish or fresh water and was, as a consequence, brittle and tended to fracture easily during the coring process. The ice cores were immediately cut with a saw into 10 cm sections. For the cutting, a half tube mounted in a frame was used to avoid contact of the core with the ice surface to avoid contamination of the sections with snow. Each cut section was placed immediately into a labelled plastic container which was sealed with a screw cap. Coring was continued until water was reached and at the end of this process, a sample of water from just beneath the ice was collected using a tube inserted through the cored hole. The containers were returned to the laboratory in Tuktoyaktuk where the contents were allowed to thaw at room temperature. The liquid was then homogenized and subsampled for salinity, $\delta^{18} \mathrm{O}$, and nutrient determinations.

### 2.3 Laboratory Methods

### 2.3.1 $\quad \delta^{18} \mathrm{O}$ determination

3.0 mL of sample water (seawater or melted ice) were pipetted into a $25 \times 150 \mathrm{~mm}$ culture tube. A micro stir bar was added to each sample tube and the tubes were secured by Vac-Torr fittings into a radially configured equilibration chamber with 16 sample positions [Whaite, 1982]. Each sample tube was stirred by four small electromagnets surrounding each test tube providing a switching magnetic field which powers the stirring process. A VWR Scientific refrigerated recirculator set at $16{ }^{\circ} \mathrm{C}$, provided a constant temperature of $20 \pm 0.5^{\circ} \mathrm{C}$ in the equilibration chamber. Software written in- house controlled the electronically activated solenoids which opened and closed valves as programmed for the equilibration process [cf. Paton et al. 1994]. A multi-tasking, MS-DOS computer controlled the sample equilibration, mass spectrometer inlet system valve control and data acquisition.

The mass spectrometer, built by Nuclide, has a 5 inch radius of curvature with a $45^{\circ}$ deflection. The normal operating conditions were: 4.5 A filament current, 0.2 mA trap current, 0.8 MA shield, 0 V repellor, 65 V electrometer accelerating potential and 4.1 kV ion accelerating potential. The instrument is a triple collector system equipped with evacuated electrometer heads (Nuclide EAH500 Faraday cup detectors). Under normal operating conditions there was about 4 cm of $\mathrm{CO}_{2}$ pressure on the high pressure side of the viscous leaks which resulted in a mass 44 ion beam intensity of $2.0 \times 10-8 \mathrm{~A}$. The introduction of gas samples into the mass spectrometer was accomplished with a dual gas inlet system with the ion beam intensities being balanced by manually adjusted bellows. We analyzed six of the standard water samples listed in Table 1, and one duplicate sample with each batch of 16 samples. Calibration curves were calculated for each day using the results of the six standard waters.

- The following steps were involved in this computer-controlled equilibration process.

1. All reservoir lines were opened, evacuated and tested for leaks to the atmosphere.
2. Transfer lines, reservoirs and sample tubes were evacuated and approximately 2.0 psi of $\mathrm{CO}_{2}$ was introduced into the sample test tubes.
3. Fifteen hours was allowed for equilibration with $\mathrm{CO}_{2}$, during which oxygen in the $\mathrm{CO}_{2}$ standard gas (Matheson Research grade) exchanges with the oxygen in water through the following equilibrium:

$$
\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{2} \mathrm{CO}_{3}
$$

4. After equilibration, the sample reservoirs were evacuated and transfer lines closed automatically.
5. The equilibrated $\mathrm{CO}_{2}$ head gas in each sample tube was allowed to expand into the reservoir and was then sealed and held awaiting the manual introduction of the gas sample to the mass spectrometer inlet system by the operator.
6. Each sample was passed through a Peltier cooler operating at about $-25^{\circ} \mathrm{C}$ during transfer to the inlet system. The Peltier cooler froze out and trapped any water vapour in the $\mathrm{CO}_{2}$ gas as it passed through the transfer line to the sample side of the mass spectrometer inlet system.
7. At the mass spectrometer, gas from the same $\mathrm{CO}_{2}$ tank used for the equilibration of the sample was used as the reference gas for the analysis. The pressure of the two gases was balanced using bellows in the sample inlet system.
8. The capillary valves were opened by computer control to allow alternating aliquots of sample and reference gas to enter the flight tube. Data acquisition parameters were user- selectable; here, we employed seven reference/sample gas cycles, each cycle comprising an average of seven ratio readings. The software allows the operator to modify the screening criterion so that statistically rejected (Chauvinet's criterion) outlying data points can be dropped from the data.

Results are reported relative to Vienna Standard Mean Ocean Water (V-SMOW) as $\delta^{18} \mathrm{O}$ where:

$$
\delta^{18} \mathrm{O}=\left[\frac{\left({ }^{18} \mathrm{O} /{ }^{16} \mathrm{O}\right)_{\text {sample }}}{\left({ }^{18} \mathrm{O} /{ }^{16} \mathrm{O}\right)_{V-S M O W}}-1\right] \times 1000
$$

We used V-SMOW standard plus in-house standard water samples intercalibrated through the University of Washington (Table 1)

The equilibration chamber consisted of evenly-distributed air circulation ports with a forced air heat exchanger controlled through a constant-temperature recirculating bath. This system maintains the equilibrator at a constant temperature of $\pm 0.5 \mathrm{C}^{\circ}$.

Treatment of Error, Control Charts The V-SMOW $\delta^{18} \mathrm{O}$ values were determined through the use of a linear regression model for mixtures of in-house standards [Macdonald and O'Brien, 1985] which have been intercalibrated against V-SMOW by the University of Washington - Quaternary Research Centre. This error model is more robust in that it allows one to trace a measurement to two or more references simultaneously.

The 9207 water column dataset was run from January 1996 to May 1996. The accuracy of the calibration curve over the calibration range is given in Table 2 and the control chart in Figure 2.

Table 1: Composition of Reference and Control Water Samples

| Water | $\delta^{18} \mathrm{O}$ | Precision |
| :--- | ---: | ---: |
| V-SMOW | 0.00 |  |
| Institute of Ocean Sciences | -9.74 | 0.06 |
| Tuktoyaktuk Snow | -27.17 | 0.07 |
| University of British Columbia-LTW | -16.62 | 0.03 |
| University of Washington (Antarctic) | -33.46 |  |



Figure 2: Control chart for January, 1996 to May, 1996

Table 2: Summary of calibration data for the period January 1996 to May 1996

| Y value | $\mathrm{X}_{\text {calc }}$ | 95\% C.I. | Replicates |
| ---: | ---: | ---: | ---: |
| (V-SMOW) |  | $(\mathrm{k})$ | n |
| -26.45 | -20 | 0.371 | 1 |
|  |  | 0.264 | 2 |
|  |  | 0.216 | 3 |
| -10.53 | -5 | 0.369 | 1 |
|  |  | 0.262 | 2 |
|  |  | 0.214 | 3 |
| +0.1 | +5 | 0.370 | 1 |
|  |  | 0.263 | 2 |
|  |  | 0.216 | 3 |

Table 3: Error Summary for Salinity Determinations

| Mission \# | Precision | $\nu$ | Reference Water |
| :--- | ---: | ---: | ---: |
| 9207 | 0.002 | 5 | IAPSO K $_{15}=0.99986$ |

The pooled standard deviation for same day duplicate analysis of samples was $0.12(\mathrm{n}=39)$. To estimate the long-term stability of the calibration curve, the daily standards were combined and outlying data points were rejected by applying Chauvenet's criterion. This demonstrated that the isothermal, forced-air equilibrator maintained a reproducible equilibration environment over the period of analysis.

### 2.3.2 Salinity determination

The salinities were analyzed at the DFO laboratory in Tuktoyaktuk or at IOS on a Guildline Autosal (Model 8400A) instrument as described previously [Macdonald et al., 1991, 1992]; data are reported in practical salinity units (psu) [see Lewis and Perkin; 1978]. Instrumental precision determined from repeated analyses on the same sample was about $\pm 0.003$. During analyses the instrument was standardized against Standard Sea Water obtained from the Standard Seawater Service, Institute of Oceanography, Wormley, Godalming, Surrey, England. Pooled variance, $\mathrm{s}_{p}$, is calculated as:

$$
s_{p}=\sqrt{\frac{\nu_{1} s_{1}^{2}+\cdots+\nu_{i} s_{i}^{2}}{\nu_{1}+\cdots+\nu_{i}}}
$$

where $\nu_{i}=n_{i}-1$ degrees of freedom, and the $n_{i}$ and $s_{i}$ refer to the number of replicates and their standard deviation for the individual components used in the pooled standard deviation calculation. Table 3 shows the estimated error (from Pearson et al. [1994]) for the salinity determinations.

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4 APPENDIX A, DATA TABLES






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Station:
Cruise:
Date:
Time Arrive (Z-6):
Time Depart (Z-6):
Latitude:
Longitude:

Hole Depth (cm):
Core Depth (cm):
Freeboard (cm):
Snow Depth (cm):
core interval
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