### Oxygen Isotope Ratio (δ18O)

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#### Overview of analysis

Oxygen isotopes,16O and 18O, are two common, naturally occurring oxygen isotopes. Through the meteoric water cycle of evaporation and precipitation, the lighter weight 16O is selected preferentially during evaporation, resulting in a larger fraction of 16O in meteoric water than in the source water (i.e. seawater). Sea-ice formation and melt on the other hand, only changes the source water’s 18O/16O ratio (noted as δ18O) slightly. River water is fed from meteoric sources and thus the δ18O is a valuable tool used in the Arctic Ocean to distinguish between fresh water from river (meteoric) sources and from sea-ice melt.

The 18O/16O ratio of natural waters is determined using the common CO2-H2O equilibration technique (Epstein, 1953; O'Neil et al., 1975) in which millimole quantities of CO2 are equilibrated with water samples under constant temperatures. Subsequently, the CO2 is cryogenically purified and analyzed by mass spectrometry for its 18O/16O ratio. Note that this technique measures the isotopic activity of 18O and not the actual 18O concentration. For dilute waters, differences between isotopic activity and concentration are negligible. For saline waters and brines, however, supplemental water chemistry data and longer equilibration times are needed to obtain true isotopic compositions (Horita, 1993; Sofer, 1972).

#### Sampling

Samples for δ18O were collected from all CTD/Rosette station (except 2 stations), from 0 to 122 m depth (see Table 2). Samples were drawn from the Niskin into 10 or 20 mL glass scintillation vials following three rinses of the vials with sample water. The vials were sealed with Polyseal caps and wrapped with Parafilm as a precaution to prevent evaporation and isotopic fractionation. Samples were returned to the Chesapeake Biological Laboratory of the University of Maryland Center for Environmental Science. A total of 176 unique samples were collected.

#### Analysis

Water samples were analyzed at the CBL-UMCES by equilibration with carbon dioxide using a Thermo Fisher Gas Bench II peripheral linked to a continuous flow Delta V Plus isotope ratio mass spectrometer. Results were expressed as δ18O, using the relation:

δ18O ; 18OV-SMOW = (Rsample-Rstandard / Rstandard) \*1000‰,

where R=18O/16O and V-SMOW = Vienna Standard Mean Ocean Water, as distributed by the International Atomic Energy Agency.

#### Precision

Analytical precision was better than ± 0.1‰ and was assessed by analysis of in-house water standards during sample analysis and calibration to international water isotope standards (V-SMOW, V-SLAP, GISP). Data corrections were made based upon analysis of the in-house standards relative to international standards, which were normalized as per recommendations of Paul et al. [2007].

#### References

Paul, D., G. Skrzypek, and I. Fórizs. 2007. Normalization of measured stable isotopic compositions to isotope reference scales–a review. Rapid Communications in Mass Spectrometry 21 (18): 3006-3014.