Oxygen isotope ratio, barium and salinity in waters around the North American coast from the Pacific to the Atlantic: Implications for freshwater sources to the Arctic throughflow

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ABSTRACT

In 2002, oxygen isotope ratios of water \((\text{H}_2\text{O}^{18}/\text{H}_2\text{O}^{16})\), dissolved barium, and salinity were measured in surface waters around northern North America to identify freshwater sources and to provide a large-scale background for interpretation of regional inputs and processes. Oxygen isotope ratios showed that precipitation, river runoff, and sea ice meltwater were all significant contributors to the freshwater carried by the coastal component of the Arctic throughflow. Precipitation and runoff contributed \(<40\%\) and \(>60\%\), respectively, to the freshwater found in surface waters along the Pacific coast. Sea ice meltwater contributed up to \(65\%\) to waters residing near the Mackenzie River and in the Canadian Arctic Archipelago. The salinity-barium relationship, after being corrected for dilution by sea ice meltwater, indicated that freshwater from the Mackenzie River flowed eastward into Amundsen Gulf. It did not, however, continue eastward through Dolphin Union Strait and Coronation Gulf in 2002. In the eastern part of the Canadian Arctic Archipelago, Baffin Bay and the Labrador Sea, barium concentrations in surface waters were low, the result of biological activity and/or local freshwater inputs with low barium concentrations.

1. Introduction

The clockwise flow of waters around northern North America, including passages through the Canadian Archipelago, connects North Pacific and North Atlantic waters and thus the global ocean circulation. Pacific water flows into the Arctic Ocean via the Bering Strait and flows from the Arctic Ocean into the North Atlantic through the Canadian Arctic Archipelago (CAA) and Fram Strait (Jones et al., 2003; Taylor et al., 2003; Steele et al., 2004; Falck et al., 2005). This throughflow transports nutrients (Jones et al., 2003; Taylor et al., 2003; Falck et al., 2005; Yamamoto-Kawai et al., 2006) and freshwater (e.g., Wijffels et al., 1992) from the Pacific to the Atlantic. The Arctic Ocean outflow delivers 9,200 km\(^3\) of freshwater to the North Atlantic each year as liquid water.

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97
and ice (Serreze et al., 2006). This transport corresponds to as much as 25% of the global continental discharge (37,288 km³ yr⁻¹) or 50% of the discharge into the Atlantic from surrounding continents (19,168 km³ yr⁻¹; Dai and Trenberth, 2002). The Arctic through-flow thus has a key role in balancing the global freshwater budget (Wijffels et al., 1992). Moreover, any change in freshwater export from the Arctic Ocean will alter the stratification (by changing salinity) of the North Atlantic and, in turn, affect the global thermohaline circulation (Aagaard and Carmack, 1989).

As shown in the map of surface salinity (S) (Fig. 1), relatively fresh water with S < 32.5 is found around the coast of northern North America. This pan-North American distribution of low S water is formed by local freshwater inputs, and constitutes a substantial component of freshwater transport by forming a contiguous band of baroclinic flow (Carmack et al., 2008). Such coastal domains can be rich in marine biota and provide food resources to humans. Changes in physical conditions linked to freshwater distributions will thus affect marine biota by altering nutrient availability, underwater light and other habitat conditions (Carmack and McLaughlin, 2001; Carmack and Macdonald, 2002). Therefore,
changes in freshwater inputs and distribution in the coastal areas will have both regional and global consequences.

In 2002, surface waters were collected around northern North America (Fig. 2) to investigate the composition of coastal waters during the expedition of the Sedna IV, a 50 m three-masted schooner that sailed from Montreal to Vancouver through the Arctic Ocean to film a documentary on Arctic natural history. Water samples were collected for salinity (S), dissolved barium (Ba) and oxygen isotope ratio ($\delta^{18}O$) analysis. Barium and $\delta^{18}O$ are freshwater tracers that have been used to identify freshwater sources in the Arctic Ocean (e.g., Macdonald et al., 1998; Guay et al., 2009). The concentration of Ba varies according

Figure 2. Map of stations of surface sampling during the Sedna IV expedition in 2002. Station numbers and dates of sampling are indicated for circled stations in map A. Locations of Amundsen Gulf (AG), Dolphin Union Strait (DU), Coronation Gulf (CG), Queen Maud Gulf (QMG), Bellot Strait (BS). Lancaster Sound (LS), Jones Sound (JS) and Smith Sound (SS) in the Canadian Arctic Archipelago are shown in map B.

Yamamoto-Kawai et al.: Freshwater sources to the Arctic throughflow
to source, being higher in North American rivers and lower in Siberian rivers (Guay and Falkner, 1998) and low in precipitation. Sea ice meltwater has higher δ18O values than meteoric (river and precipitation) waters (Macdonald et al., 2002). Furthermore, meteoric water δ18O values decrease with increasing latitude, altitude and distance inland from the coast, ranging from −10‰ to −25‰ in northern North America (>50°N) (IAEA, 2001). Relationships of S and these two freshwater tracers (Ba and δ18O) are described along the Sedna IV track to infer freshwater contributions to the coastal component of Arctic throughflow in 2002. Note that our data do not resolve seasonal changes in flux of each freshwater source. For example, we observed the Gulf of Alaska during the peak discharge of rivers along the Pacific coast (Royer, 1982), whereas the Beaufort Sea was observed three months after the peak discharge from the Mackenzie River. Therefore, contributions of freshwater sources estimated here can be different in other seasons. The purpose of the present paper is, however, to provide a snap shot of hydrography around northern North America as a baseline in July–November 2002, for the future detection of temporal changes in freshwater sources to the Arctic throughflow.

2. Sampling and analysis

During the Sedna IV voyage, surface water was sampled at a depth of ~5 m by a 2.2-L clear acrylic Kemmerer sampler from Geneq Inc. at approximately 100 km intervals (Fig. 2). Water samples were transferred into either glass bottles (S and δ18O) or HCl-washed polyethylene vials (Ba) and stored at room temperature until shipment to the laboratory. Barium concentrations were determined by isotope dilution-inductively coupled plasma mass spectrometry (ID-ICPMS; as described in Taylor et al., 2003). Difference in duplicate analysis ranged from 10% at 15 nmol Ba L−1 to <3% at >100 nmol Ba L−1. Samples for δ18O were analyzed on a Finnegan Mat 251 stable isotope mass spectrometer after equilibration with CO2 with a precision of ±0.03‰. Accuracy is assured through the use of certified standards and a working standard that consists of a large volume Pacific seawater that was carefully led into ampoules by us. The oxygen isotope composition is referenced to Vienna-standard Mean Ocean Water (V-SMOW):

\[
\delta^{18}O = \frac{(H_2^{18}O/H_2^{16}O)_{\text{sample}}/(H_2^{18}O/H_2^{16}O)_{\text{VSMOW}} - 1)}{1000} \times 10^3 \text{[‰]}
\]

Values of S were determined using a Guildline Portasal 8410 calibrated with IAPSO standard seawater. Values are reported on the practical salinity scale with a precision of ±0.003.

3. Results and discussion

The distribution of surface S in October–November 2002 (Fig. 3) is similar to that of the climatology (Fig. 1): ~30 in the Pacific, Bering and Chukchi seas, low in the Beaufort Sea and CAA, and high in Baffin Bay and Labrador Sea (>30). The lowest and highest S were observed in the Beaufort Sea (S = 16.7) and Labrador Sea (S = 33.7), respectively. Based
on S and geographical distribution, stations are divided into three regions: Pacific-Bering-Chukchi, Beaufort-CAA, and Baffin-Labrador regions. Low values of $\delta^{18}O$ and high concentration of Ba are found in the Beaufort Sea-CAA region where S is low (Fig. 3). However, plots of S vs. tracers (Fig. 4) do not show simple linear relationships in any
region, indicating influence of multiple source waters (i.e. different combinations of tracer values) and/or processes that segregate $\delta^{18}O$ and Ba concentrations from S, e.g., injection of brine from sea ice, biological drawdown of Ba, or efflux of Ba from the sediment. In the Pacific-Bering-Chukchi and Beaufort-CAA regions, Pacific-origin seawater, river runoff, precipitation, and sea ice meltwater (and brine when sea ice forms) are expected to constitute the surface waters (Yamamoto-Kawai et al., 2008). Atlantic-origin water entering the Arctic Ocean through Fram Strait and the Barents Sea is not found in surface waters in these regions (Jones et al., 2003; McLaughlin et al., 2004; Yamamoto-Kawai et al., 2008). In the Baffin-Labrador region, however, Atlantic-origin water is also a component of surface water. Using a nitrate-phosphate relationship, Jones et al. (2003) found an influence of Atlantic-origin water in surface waters in the Baffin Bay and Labrador Sea, but not in the CAA. Therefore, mixing of both Pacific and Atlantic-origin waters with freshwaters (and brine) is expected in Baffin-Labrador region. In the following sections, the relationships between S and tracers in each region will be examined to investigate the composition of surface waters, starting from the Pacific side and moving toward the Atlantic side in accordance with the direction of the throughflow.

a. Pacific-Bering-Chukchi region

i. Regional background. A coastal flow system extends from British Columbia to the Chukchi Sea (Schumacher et al., 1982). In the eastern North Pacific, the Alaskan Coastal Current (ACC) carries low S water cyclonically around the Gulf of Alaska (GoA) in a narrow, high-speed jet, driven by winds and massive freshwater discharge from the land (Royer, 1982; Stabeno et al., 2004). A portion of the ACC enters the Bering Sea through Unimak Pass, a shallow (sill depth $\sim 70$ m) and narrow ($\sim 16$ km) pass that connects the North Pacific to the Bering Sea shelf (Stabeno et al., 2002). Here the ACC water mixes with relatively saline Bering Sea offshore water, precipitation and river runoff, and is also modified by sea ice formation and melt (Aagaard et al., 2006; Cooper et al., 1997). This mixture of waters, with various S values, flows northward, and enters the Chukchi Sea

Figure 4. Salinity vs. (a) $\delta^{18}O$ and (b) Ba.
through the Bering Strait (cf. Woodgate et al., 2005). In summer the warmest and freshest fraction of this water continues north-eastward along the Alaskan coast toward Pt. Barrow (cf. Weingartner, 2005) and is called Alaskan Coastal Water (e.g., Steele et al., 2004). Salinity of Alaskan Coastal Water is typically 31–32. The saltier fraction (32–33), referred to as Bering Sea Water, flows northward and enters the Arctic Ocean through canyons on the central and western Chukchi shelf (cf., Steele et al., 2004; Weingartner et al., 2005).

ii. $S$, $\delta^{18}O$ and $Ba$. In 2002, surface $S$ ranged from 27.7 to 32.5 around the perimeter of the GoA (stations 74–59) with low values ($S < 31.0$) observed in the inside passage near Juneau (stations 74–73) and near Cook Inlet (stations 65–68). The highest $S$ in the Pacific-Bering-Chukchi region was observed at station 58 in the Bering Sea, just north of the Unimak Pass ($S = 32.9$). Although $S$ in the Bering and Chukchi seas (stations 57–47; $S = 27.7–32.9$) is similar to $S$ observed in the GoA, waters in these regions have significantly different $S-\delta^{18}O$ relationships (Fig. 5a). Accordingly, we divide the Pacific-Bering-Chukchi region into two sub-regions: GoA (stations 74–59) and Bering-Chukchi seas (stations 58–47).

iii. GoA. Surface $S$ in ACC waters in the GoA (27.7–32.5) is lower than in offshore North Pacific waters (Fig. 1). Decreases in $S$ accompany decreases in $\delta^{18}O$ with a strong linear correlation ($r^2 = 0.97$) (Fig. 5a). Although the concentration of $Ba$ also has a linear relationship with $S$, the correlation is weaker ($r^2 = 0.68$) (Fig. 5b). The scatter in the $S-Ba$ diagram likely reflects patchy biological activity, the detrital flux of which is known to be associated with dissolved $Ba$ removal to the particulate phase (e.g., Dehairs et al., 1980; 1987; Bishop, 1988) and/or the large difference in $Ba$ values in freshwater sources (high in river water and low in precipitation). Nevertheless, the saline side of these regression lines
come close to $S$, $\delta^{18}O$ and Ba values found in offshore North Pacific waters (square in Fig. 5). The Y intercepts of $S-\delta^{18}O$ and S-Ba relationships imply that freshwater diluting seawater in the GoA has a mean $\delta^{18}O$ of $-15.5 \pm 1.5%$ (at 95% confidence interval) and a mean Ba concentration of 320 nM $\pm$ 100 nM. What is the source of this freshwater?

A substantial amount of freshwater is delivered to the GoA by both precipitation and discharge from rivers and streams (Royer 1982). The mean monthly precipitation is high (~200 mm) in coastal areas, with a maximum occurring in October (Royer, 1982; Spencer, 1993). About 23,000 m$^3$ s$^{-1}$ of freshwater, consisting of precipitation and glacial meltwater (Neal et al., 2010), is discharged from rivers and streams along the Pacific coast of Alaska (Royer, 1982). The average $\delta^{18}O$ value of rivers along the coast of the GoA (Stikine, Susitna, Copper, Talkeetna and Skagway rivers) is $-19.4%$, ranging from $-21.7%$ to $-17.7%$ with a seasonal variability of $\pm 1.0%$ (Coplen and Kendall, 2000). The source freshwater $\delta^{18}O$ value ($-15.5%$), as indicated by the S-$\delta^{18}O$ diagram, is significantly higher than $-19.4%$ and is due to local precipitation ($\delta^{18}O = -10%$; Hage et al., 1975) mixing into surface seawater. The reason why river water has a lower $\delta^{18}O$ values than coastal precipitation is that isotope fractionation during condensation leads air masses to lose more $^{18}O$ (to have lower $\delta^{18}O$ values) as they move inland to higher elevations (Dansgaard, 1964). The $\delta^{18}O$ value of minor rivers and local streams is thus expected to lie between $-10%$ of precipitation and $-19.4%$ of larger and longer rivers. The total freshwater in ACC surface waters are roughly estimated to be comprised of $>60%$ runoff (rivers + streams) and $<40%$ precipitation ($15.5 = <19.4 \times$ runoff fraction $+ 10 \times$ precipitation fraction).

The mean Ba concentration for the Copper, Stikine, Susitna, Talkeetna and Skagway rivers, observed between 1979 and 1996 (US Geological Survey, 2007), is ~200 nM. However, there are processes known to increase Ba concentration when river water meets seawater in the estuary, namely desorption of Ba from riverine particles in exchange for the more abundant cations of seawater (Guay and Falkner, 1998 and references therein), benthic efflux (Key et al., 1985; Colbert and McManus, 2005) or the influx of ground water (Moore, 1997). Therefore, the actual flux of Ba from a river to the ocean is different from observations in river water upstream of the estuary. For most river systems, such reactions are largely completed by $S \sim 5$–10 at the river mouth and therefore extrapolating the observed S-Ba relationship in seawater with $S > 10$ to $S = 0$ provides an estimate of the “effective” freshwater end-member Ba concentration (see, for example, Guay and Falkner, 1998), which is 320 nM for our observations in the GoA. However, the $\delta^{18}O$ data indicated that precipitation (Ba < 10 nM, Jickells et al., 1992) is $<40%$ of the freshwater source in the GoA. This requires the effective riverine Ba concentration to be 320–530 nM. The upper estimate is consistent with data from sediment laden rivers that drain high elevations at high latitudes (Guay and Falkner 1998).

iv. Bering and Chukchi seas. North of the Unimak Pass at the shelf break in the Bering Sea (300 m water depth, station 58), the surface $S$ increased to 32.9. This is higher than $S$ of the
ACC flowing through Unimak Pass (~31.7; station 59; Aagaard et al., 2006), and indicates mixtures with deeper water and/or offshore Bering Sea water (Aagaard et al., 2006) ($S \sim 33$ and $\delta^{18}O \sim -0.6\%e$; Cooper et al., 1999; Schmidt et al., 1999). On the Bering shelf, surface $S$ was lower ($S = 27.7 - 31.0$) than in inflowing ACC water or offshore Bering Sea water, due to mixing with new freshwater sources. North of the shallow Bering Strait (sill depth $\sim 50$ m), in the Chukchi Sea, $S$ was 29.3–31.9. Overall, except for one sample (a cross in Figs. 5a and 5b; $S = 27.7$; station 55), $S$ correlates well with $\delta^{18}O$ in the Bering-Chukchi seas;

$$\delta^{18}O = 0.639 \cdot S - 21.73 \quad (r^2 = 0.95).$$

The freshwater intercept of $-21.7 \pm 3.3\%e$ is lower than the $\delta^{18}O$ value of freshwater found in the GoA, local precipitation in the Bering-Chukchi area ($\sim -15\%e$; Hage et al., 1975) and sea ice meltwater ($\sim -2\%e$; Eicken et al., 2002), but close to the mean $\delta^{18}O$ value for the Yukon River water ($-20\%e$ with a seasonal variability of $\pm \sim 1.0\%e$; Coplen and Kendall, 2000; Cooper et al., 2005; 2008). The Yukon River, which discharges 6,700 m$^3$ s$^{-1}$ of freshwater (Milliman et al., 1995), is the largest source of meteoric water in the Bering Sea. The next largest rivers are the Kuskokwim and Anadyr (1,900 m$^3$ s$^{-1}$ each) and the total discharge onto the Bering shelf is $\sim 12,000$ m$^3$ s$^{-1}$ (Milliman et al., 1995). Although $\delta^{18}O$ data are not available for all rivers, the mean values in Kuskokwim and Nushagak rivers (river mouth locates at $\sim 60^\circ N$ and $\sim 59^\circ N$, respectively) are $-17\%e$ and $-15\%e$, respectively. This is consistent with the fact that $\delta^{18}O$ in meteoric water becomes progressively lower at higher latitudes. Therefore, the source freshwater $\delta^{18}O$ value of $-21.7 \pm 3.3\%e$ indicates that river runoff, from the Yukon River and similar high-latitude rivers flowing into the northern Bering Sea and Chukchi Sea, is the main source of freshwater diluting surface waters observed on the Bering and Chukchi shelves in October 2002.

Surface water at station 55 (Fig. 5a) suggests an influence of brine rejection during sea ice formation, possibly associated with formation of coastal polynya (Stringer et al., 1991), which results in a downward deviation in the $S$-$\delta^{18}O$ diagram ($S$ of seawater increases due to mixing with brine but $\delta^{18}O$ is virtually unchanged). Such deviations in low salinity waters in the $S$-$\delta^{18}O$ diagram were also observed near the mouth of Yukon River in 1990 (Cooper et al., 1997; Schmidt et al., 1999) and Mackenzie River in the Beaufort Sea in 1991 (Macdonald et al., 1995). The high Ba content (173 nM) at station 55 (Fig. 5b) also suggests brine-enriched waters were in contact with the sediment and subsequently mixed into the water column. The absence of an apparent influence of sea ice meltwater (Fig. 5a) differs from past observations in the same region that revealed both downward and upward deviations from the linear regression of $S$-$\delta^{18}O$ (Grebmeier et al., 1990; Cooper et al., 1997; Clement et al., 2004; Schmidt et al., 1999)(upward and downward deviations indicate mixing with sea ice meltwater ($\sim -2\%e$) and brine injection, respectively (Strain and Tan, 1993; Melling and Moore, 1995; Yamamoto et al., 2001; 2002)).

The intercept of $S$-Ba relationship ($r^2 = 0.86$) in the Bering and Chukchi seas is 420 ±
Table 1. Sources of fresh water (FW) diluting surface water and their contributions (%) to the total FW in each region.

<table>
<thead>
<tr>
<th>Region</th>
<th>FW source 1</th>
<th>%</th>
<th>$\delta^{18}O$ [%]</th>
<th>Ba [nM]</th>
<th>FW source 2</th>
<th>%</th>
<th>$\delta^{18}O$ [%]</th>
<th>Ba [nM]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GoA</td>
<td>runoff</td>
<td>&gt;60</td>
<td>$-1.0 \sim -1.94$</td>
<td>&lt;530</td>
<td>precipitation</td>
<td>&lt;40</td>
<td>$-1.0$</td>
<td>0</td>
</tr>
<tr>
<td>Bering Sea-Chukchi</td>
<td>runoff (Yukon + o)</td>
<td>~100</td>
<td>-21.7</td>
<td>425</td>
<td>sea ice meltwater</td>
<td>21-65</td>
<td>-2</td>
<td>5</td>
</tr>
<tr>
<td>Sea-Amundsen Gulf</td>
<td>Mackenzie runoff</td>
<td>35-79</td>
<td>-20</td>
<td>530</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAA east of 115W</td>
<td>Meteoric water</td>
<td>34-100</td>
<td>-20</td>
<td>&gt;0</td>
<td></td>
<td>0-66</td>
<td>-2</td>
<td>5</td>
</tr>
<tr>
<td>Baffin Bay-Labrador Sea</td>
<td>Meteoric water</td>
<td>?</td>
<td>$-1.0 \sim -20$</td>
<td>?</td>
<td></td>
<td>?</td>
<td>-2</td>
<td>5</td>
</tr>
</tbody>
</table>

$\delta^{18}O$ and Ba values for each source are also shown. Numbers in italic are from the literature (see text). br and bd indicates influence of brine and biological drawdown of Ba, respectively.

110 nM except station 55 (Fig. 5b), higher than in the GoA (320 nM ± 110 nM). It is also somewhat higher than Ba concentration of the Yukon River water (370 nM, Cooper et al., 2008). As mentioned in the Section 3a, the “effective” Ba can be significantly different from the measurement in the fresh (S ~ 0) riverine water because the latter does not account for Ba from desorption or benthic efflux in the estuary (Guay and Falkner, 1998). If data from station 55 are included, the apparent effective Ba concentration increases to 690 nM, but the correlation decreases ($r^2 = 0.78$). The correlation between S and Ba is higher in the Bering-Chukchi seas than the GoA ($r^2 = 0.68$) and indicating there is less influence of nonconservative behavior of Ba and/or a dominant influence of a single, not multiple, freshwater source. In contrast, Falkner et al. (1994) have shown both drawdown and enrichment of Ba in the same region in September/October 1992. They reported Ba concentrations of ~70 nM in Bering Strait, noting the presence of both depleted (~50 nM) and enriched (~120 nM) waters in western surface water (S ~ 29) and in eastern bottom water (S ~ 32), respectively. They attributed drawdown to biologically related removal and enrichment to regeneration at depth or in the sediments. They reported surface water Ba concentrations decreased northward across the Chukchi Sea, reaching <20 nM near Pt. Barrow (S ~ 30) where the ice edge was located and attributed this depletion to removal of Ba in association with enhanced biological activity and particulate fluxes along the ice-edge. Our surface water data showed similar Ba values in Bering Strait (~70 nM) but did not show any obvious biological drawdown of Ba farther north. In fact, the ice edge was located farther offshore in 2002 and this is consistent with the absence of sea ice meltwater influence in the S-$\delta^{18}O$ diagram (Fig. 5a).

In summary, in October 2002 the freshwater source to the ACC in the GoA was precipitation (<40%) and runoff (>60%) with the effective riverine Ba of 320–530 nM (Table 1). In contrast, runoff from the Yukon and other high-latitude rivers was the main source of freshwater in the Bering-Chukchi region without any obvious contribution of sea ice meltwater or biologically related drawdown on Ba but with some modification by
mixing with brine-enriched water (Table 1). The effective Ba of runoff in the Bering and Chukchi seas was 420 ± 110 nM.

b. Beaufort-CAA region

i. Regional background. Rounding Pt. Barrow, some fraction of Alaskan Coastal Water spills off into Canada Basin interior, and the rest flows eastward along the continental slope (Steele et al., 2004 and references therein). En route to the east, Alaskan Coastal Water mixes with the ambient Canada Basin surface water, which consists of Pacific-origin water (both Alaskan Coastal Water and saltier Bering Sea Water), meteoric water and sea ice meltwater/brine. This mixture eventually flows out of the Arctic Ocean through the CAA or Fram Strait.

The Mackenzie River is a large source of meteoric water in this region, and is the fourth largest river in the Arctic with a mean annual discharge of 10,500 m³ s⁻¹ (Carmack et al., 2000). Previous studies show that sea ice meltwater is also the major source of freshwater to the surface Beaufort Sea in summer (see Macdonald et al., 2000 regarding seasonal cycles). Relatively large rivers draining into the CAA, consisting of numerous passages and straits between the Arctic islands and mainland of Canada (Fig. 2B), are the Coppermine River (~350 m³ s⁻¹) into Coronation Gulf, and Back River (~500 m³ s⁻¹) into Queen Maud Gulf. Inputs from small rivers, as well as precipitation and sea ice meltwater in the CAA, are poorly quantified in the literature.

The Sedna IV cruise track extended from Amundsen Gulf via Coronation Gulf, Queen Maud Gulf and Bellot Strait to Lancaster Sound. Due to the shallow sills between Amundsen Gulf and Coronation Gulf (30 m) and north of Queen Maud Gulf (40 m), waters in Coronation Gulf and Queen Maud Gulf are relatively isolated from the saltier water of the Arctic Ocean. In the CAA, tidal mixing and complex flow structures due to geography alter the vertical and horizontal distribution of freshwater (cf. Melling, 2000; McLaughlin et al., 2005).

ii. δ¹⁸O and Ba. In September 2002, surface S in the Beaufort-CAA region ranged from 16.7 to 30.7. Surface S was relatively high (S > 26) east of Bellot Strait (95°W). West of Bellot Strait, S was less than 26 and very low S values were observed in the Beaufort Sea near the mouth of Mackenzie River at stations 42 (S = 16.7) and 40 (S = 16.8). At these two stations, δ¹⁸O was also very low (−7.3 and −8.6‰) and Ba was very high (174, 221 nM), indicating an influence of river water. However, correlations between S and tracers (Fig. 6) are weaker than those in the Pacific-Bering-Chukchi region (Fig. 5).

In the Beaufort Sea, δ¹⁸O has been used to distinguish meteoric water from sea ice meltwater/brine (Bédard et al., 1981; Macdonald et al., 1989; 1995; 1999; 2002; Melling and Moore, 1995), because Arctic meteoric water has a low δ¹⁸O value of ~ −20‰ (Macdonald et al., 1989; Cooper et al., 2005) compared to δ¹⁸O of sea ice meltwater of ~ −2‰ (Melling and Moore, 1995; Eicken et al., 2002). Here we estimate contributions of meteoric water and sea ice meltwater to surface waters in this region, and combine
results from $\delta^{18}$O with Ba observations to investigate distribution of Mackenzie River water in September 2002.

First, using mass balance equations for S and $\delta^{18}$O, the fraction of each end-member (saline end-member, meteoric water ($f_{MW}$) and sea ice meltwater ($f_{SIM}$)) is calculated for each sample. For the saline end-member, we selected water found in the northern Chukchi Sea ($S = 31.5$) with a corresponding $\delta^{18}$O value of $-1.6\%$ (see Fig. 5a). In previous studies, the Polar Mixed Layer with $S = 32.2$ and $\delta^{18}$O = $-2.5\%$ (Macdonald et al., 1995), or Pacific Water with $S = 32.5$ and $\delta^{18}$O = $-0.8\%$ (Yamamoto-Kawai et al., 2008; 2009) were used as the saline endmember. When we use these end-members, the estimated fractions of freshwater sources will range by up to 0.08. Relative spatial distribution, however, does not change due to selection of end-member values. For sea ice meltwater and meteoric water, $S = 4$ and $\delta^{18}$O = $-2\%$ and $S = 0$ and $\delta^{18}$O = $-20\%$ are assigned, respectively (Yamamoto-Kawai et al., 2008; 2009 and references therein). Although $\delta^{18}$O of $-20\%$ for meteoric water is based on observations in the larger Arctic rivers such as Ob’, Yenisey, Lena and Mackenzie, we also observed $\delta^{18}$O of some smaller rivers flowing into the CAA in late August-September 1999 (McLaughlin et al., 2009) and confirmed that the $\delta^{18}$O values of these small rivers are not different from those of the large rivers ($-19\%$ for Coppermine River, $-17\%$ for Deas Thompson Point River, $-20\%$ for Croker River, and $-20\%$ for Hood River). Furthermore, $\delta^{18}$O of sea ice meltwater varies with the $\delta^{18}$O of surface seawater from which sea ice has grown. Results will vary 0.03 or less when the $\delta^{18}$O value of sea ice meltwater varies from $-4$ to $0\%$.

Results from 2002 show that meteoric water was the major source of freshwater ($f_{MW} > f_{SIM}$) at stations 42–30, between the mouth of Mackenzie River and Queen Maud Gulf (Fig. 7). At these stations, meteoric water constituted 53–80% of the total freshwater. Relatively high fractions of sea ice meltwater (0.10–0.20) were found at stations 46–40, 31 and 29–28. In the CAA east of Bellot Strait (stations 21–27), both meteoric water and
sea ice meltwater fractions were smaller and S was higher than the west. This is consistent with the fact that river input and shallow sill depths characterize the western part of the CAA, whereas tidal mixing and exchange with deeper water characterize the eastern part (McLaughlin et al., 2005).

Now, Ba is used to distinguish the sources of meteoric water within this region. The effective Ba of the Mackenzie River is 520 nM (Guay and Falkner, 1998), whereas the flow weighted mean Ba content in the river is 370 nM (Cooper et al., 2008). This discrepancy is due to the nonconservative behavior of Ba in the estuary (Guay and Falkner, 1998). Effective Ba of the Mackenzie River is much higher than the effective Ba of Siberian rivers (~100 nM) or precipitation (0 nM). Although effective Ba values have not been assigned for smaller rivers entering the Beaufort-CAA region, they are expected to be lower than that of the Mackenzie River based on a small survey in August–September 1999 (McLaughlin et al., 2009) (Ba in river water was lower than 370 nM of the Mackenzie River; 95 nM and 224 nM for Croker River and Deas Thompson Point River flowing into Amundsen Gulf, respectively; 85 nM and 31 nM for Coppermine River and Hood River entering the Coronation Gulf, respectively).

The apparent effective Ba of freshwater in this region was 306 nM (Fig. 6b). The δ18O data showed meteoric water and sea ice meltwater were the sources of freshwater. Similar to the effect of precipitation in the Pacific region, sea ice meltwater dilutes S and Ba concentrations in seawater and the dilution varies between areas (Fig. 7). In order to estimate the effective Ba concentration of meteoric water, the influence of dilution by sea
Equation 1: $S_0 = (S - S_{SIM}f_{SIM})/(1 - f_{SIM})$

Equation 2: $Ba_0 = (Ba - Ba_{SIM}f_{SIM})/(1 - f_{SIM})$,

and $f_{SIM}$ is the fraction of sea ice meltwater calculated from $\delta^{18}O$ and S. Calculated $S_0$ and $Ba_0$ represent S and Ba concentrations in water that has no sea ice meltwater contribution and thus the relationship between $S_0$ and $Ba_0$ indicates a mixing between the saline-end member and meteoric water. The S and Ba of sea ice meltwater ($S_{SIM}$ and $Ba_{SIM}$) are set to be 4 and 5, respectively (Macdonald et al., 2002; Guay and Falkner, 1997). After the data have been corrected for sea ice meltwater effect, waters in the Beaufort Sea and the Amundsen Gulf (at stations 46–36) show a strong linear relationship between $S_0$ and $Ba_0$, with $Ba_0$ increasing as $S_0$ decreases ($r^2 = 0.98$) (Fig. 8). The highly linear relationship of the $S_0$-$Ba_0$ also suggests a single meteoric water source rather than multiple sources. The Y-intercept shows that the effective Ba concentration in meteoric water at these stations is 530 ± 50 nM. This indicates the Mackenzie River is the source of meteoric water in the Beaufort Sea and Amundsen Gulf. It is interesting to note that the effective Ba of the Mackenzie River of 520 nM obtained by Guay and Falkner (1998) was from observations in the estuary in April under the ice before break-up and in August, and our observations in late September gave a similar value, despite a large seasonal variability in Ba upstream of the estuary (Cooper et al., 2008).

The spreading of Mackenzie River water depends on winds and ice conditions and, in 2002, the Mackenzie River water was found in Amundsen Gulf. However, the obvious
influence of the Mackenzie water was not evident in Ba concentrations east of Dolphin Union Strait (115°W) (Fig. 8). At stations 35–21, from Coronation Gulf to the Lancaster Sound, the correlation between $S_0$ and $Ba_0$ was weak ($r^2 = 0.19$) and $Ba_0$ slightly decreased as $S_0$ decreased (Fig. 8). Low Ba intercept of the $S_0$-$Ba_0$ relationship in this region ($-8$ uM) is due to input of local runoff with low Ba, precipitation, and biologically related drawdown of Ba. Without further additional information on biological activity and effective Ba of small rivers, the source of meteoric water in this region cannot be definitively identified. In summary, the major source of freshwater in Beaufort-CAA region in 2002 was meteoric water: in particular Mackenzie River water at stations 46–36 in the Beaufort Sea and the Amundsen Gulf; and local freshwater inputs and/or biologically related effects dominated CAA east of Dolphin Union Strait (Fig. 7).

c. Baffin-Labrador region
i. Regional background. Water from the Arctic Ocean enters Baffin Bay not only through Lancaster Sound but also through Jones and Smith sounds (see Fig. 2 for locations). Baffin Bay also receives Arctic and North Atlantic waters from the south via eastern Davis Strait and the West Greenland Current (extending from the East Greenland Current), as well as glacial melt water from Greenland. All of these waters converge in northern Baffin Bay and flow southward along the western side of Davis Strait (Tang et al., 2004). Water from the Arctic Ocean can be detected as far south as the Grand Banks and Gulf of Maine from both nutrients (Jones et al., 2003) and $\delta^{18}$O (Khatiwala et al., 1999). A large influence of sea ice melt water has been observed in Baffin Bay (Tan and Strain, 1980) and the eastern Labrador Sea north of Hudson Strait, whereas river runoff is the main freshwater source south of Hudson Strait (Tan and Strain, 1996). Contributions from net precipitation are less significant (Ikeda, 1987).

ii. $S$, $\delta^{18}$O and Ba. In 2002, the surface $S$ varied from 27.8 to 33.7 in the Baffin-Labrador region. The lowest $S$ was observed at station 1, near the mouth of the St. Lawrence River. The highest values of $S$ and $\delta^{18}$O (Fig. 3) along the entire cruise track were observed at station 5 in the Labrador Sea. Samples from stations 5 and 10 with $S > 33.5$ and $\delta^{18}$O $>-0.6‰$ clearly show mixing with Atlantic-origin water (black circle in Fig. 9). When we take values observed in Lancaster Sound (station 21; $S = 30.7$ and $\delta^{18}$O $=-2.2‰$; black cross in Fig. 9) as representative of Arctic Ocean throughflow water and draw a line connecting this point and Atlantic-origin water ($S = 34.7$, $\delta^{18}$O $=0.0‰$), most of the data from the Baffin-Labrador region lie to the left of this line, consistent with contributions from sea ice meltwater (Tan and Strain, 1980). However, the composition of surface water cannot be quantified without information about waters flowing through passages other than Lancaster Sound, as well as additional tracers such as nutrients, to fully distinguish the influences of Atlantic and Pacific-origin waters. The freshest sample, from station 1 just north of the Strait of Belle Isle, will also be influenced by St. Lawrence River water which
has a higher $\delta^{18}O$ of $\sim -10$‰ than Arctic meteoric water ($\sim -20$‰) (Khatiwala et al., 1999).

The Ba concentration of high S waters at stations 5 and 10 was about 45 nM, close to the value observed in the northwestern Atlantic ($\sim 50$ nM), upstream of the West Greenland Current (Taylor et al., 2003). However, S and Ba do not show a significant correlation ($r^2 = 0.0$) in the Baffin-Labrador region (Fig. 9b), most likely because this region is the confluence of pathways. At stations 17 and 18 in the southern part of Baffin Bay, Ba content as low as 15 nM with relatively high S of $\sim 32$ indicate an influence of biologically related drawdown.

4. Summary and conclusion

During the Sedna IV expedition in July–November 2002, S, $\delta^{18}O$ and Ba in surface waters surrounding northern North America were analysed to investigate the nature of freshwater composition of the coastal component of the Arctic throughflow. Surface S ranged between 27.7 and 32.9 from the Pacific to Pt. Barrow, decreased in Beaufort Sea to as low as 16.7, and then increased to higher than 30 in the Baffin Bay and the Labrador Sea. In the GoA, the contribution of precipitation to total freshwater was calculated to be $<40\%$ from S-$\delta^{18}O$ relationship, and the contribution of runoff was $>60\%$. Although extrapolation of the S-Ba relationship indicated the apparent Ba concentration of the freshwater end-member to be 320 nM, when dilution by precipitation was considered, the effective Ba concentration of runoff is estimated to be $<530$ nM. In the Bering-Chukchi region, the S-$\delta^{18}O$ relationship indicated that the Yukon River and other high-latitude rivers were the main source of freshwater. The influence of sea ice meltwater and large biological drawdown of Ba in the Chukchi Sea, observed in previous studies, were not observed in 2002. In the Beaufort-CAA region, meteoric water was the major source of freshwater at
most of stations in August–September 2002. After correcting for the effect of sea ice meltwater using $\delta^{18}O$, the S-Ba correlation in Beaufort Sea and Amundsen Gulf showed a good linear relationship, and regression line indicated 530 nM for Ba at $S = 0$, consistent with the effective Ba value assigned for Mackenzie River water (Guy and Falkner, 1998). However, in the region east of Dolphin Union Strait (115°W), the influence of Mackenzie River water was not evident, likely due to dominant inputs of other local freshwater sources with low Ba and/or to biological drawdown of Ba. The very low Ba concentrations observed at some stations in the CAA and Baffin-Labrador regions also suggest an influence of biological drawdown of Ba.

There are some difficulties in the application of Ba as a quantitative freshwater tracer in coastal waters, due to its non-conservative behaviour in the estuary and as a consequence of biological activity. Barium can be a useful tracer of river water, however, when the effective riverine Ba is known and biological effects are negligible, as shown for Beaufort-CAA region. Our analysis also demonstrated that a combination of S, $\delta^{18}O$ and Ba enables the effective riverine Ba value to be estimated in the presence of sea ice meltwater or precipitation.

Freshwater sources in the Arctic throughflow vary from region to region along the Pan-North American pathway. Precipitation, river runoff, and sea ice meltwater are all large contributors to the freshwater carried by the Arctic throughflow and their integration determines the S of the throughflow. All of these freshwater sources will be altered by climate change. Increases in precipitation, river discharge, melting of sea ice and a decrease in sea ice formation have already been observed (e.g., Peterson et al., 2002, Yamamoto-Kawai et al., 2009) and are predicted to continue into the future (e.g., Holland et al., 2006). Our results present the composition of the coastal component of Arctic throughflow as a baseline in 2002, and continuing tracer observations will enable the detection of on-going changes in these freshwater sources.

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