

Stable isotope composition of dissolved inorganic carbon and particulate organic carbon in sea ice from the Ross Sea, Antarctica

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[1] We examined controls on the carbon isotopic composition of sea ice brines and organic matter during cruises to the Ross Sea, Antarctica in November/December 1998 and November/December 2006. Brine samples were analyzed for salinity, nutrients, total dissolved inorganic carbon (ΣCO_2), and the $^{13}\text{C}/^{12}\text{C}$ ratio of ΣCO_2 ($\delta^{13}\text{C}_{\Sigma\text{CO}_2}$). Particulate organic matter from sea ice cores was analyzed for percent particulate organic carbon (POC), percent total particulate nitrogen (TPN), and stable carbon isotopic composition ($\delta^{13}\text{C}_{\text{POC}}$). ΣCO_2 in sea ice brines ranged from 1368 to 7149 $\mu\text{mol kg}^{-1}$, equivalent to 1483 to 2519 $\mu\text{mol kg}^{-1}$ when normalized to 34.5 psu salinity ($s\Sigma\text{CO}_2$), the average salinity of Ross Sea surface waters. Sea ice primary producers removed up to 34% of the available ΣCO_2 , an amount much higher than the maximum removal observed in sea ice free water. Carbonate precipitation and CO_2 degassing may reduce $s\Sigma\text{CO}_2$ by a similar amount (e.g., 30%) in the most hypersaline sea ice environments, although brine volumes are low in very cold ice that supports these brines. Brine $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ ranged from -2.6 to $+8.0\text{‰}$ while $\delta^{13}\text{C}_{\text{POC}}$ ranged from -30.5 to -9.2‰ . Isotopic enrichment of the ΣCO_2 pool via net community production accounts for some but not all carbon isotopic enrichment of sea ice POC. Comparisons of $s\Sigma\text{CO}_2$, $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$, and $\delta^{13}\text{C}_{\text{POC}}$ within sea ice suggest that ϵ_p (the net photosynthetic fractionation factor) for sea ice algae is $\sim 8\text{‰}$ smaller than the ϵ_p observed for phytoplankton in open water regions of the Ross Sea. These results have implications for modeling of carbon uptake and transformation in the ice-covered ocean and for reconstruction of past sea ice extent based on stable isotopic composition of organic matter in sediment cores.

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1. Introduction

[2] Sea ice influences the global carbon cycle by acting as a barrier to diffusive air-sea gas exchange and through biotic and abiotic transformations that occur within the ice. The sea ice microbial community is among the largest homogeneous sunlit ecosystems on Earth, encompassing nearly five percent of the planet's surface area at its maximum extent [Gloersen *et al.*, 1999; Lizotte, 2001; Zwally *et al.*, 2002]. While sea ice primary production accounts for just 1–2% of biogenic carbon produced in the Southern Ocean, 10–28% of primary

production within the seasonally ice-covered portions of the Southern Ocean takes place within sea ice microhabitats [Arrigo *et al.*, 1997, 1998; Arrigo and Thomas, 2004]. Sea ice algae are also an important food source for populations of krill and zooplankton during winter and may seed spring and summer phytoplankton blooms in surrounding open water ecosystems [Smith and Nelson, 1985, 1986; Priddle *et al.*, 1996; Arrigo, 2003]. In addition to their role in high-latitude marine ecosystems and biogeochemical cycles, ice algae may be more directly connected to regional climate through production of dimethyl sulfide (DMS) [Trevena *et al.*, 2003; Trevena and Jones, 2006]. In the atmosphere, DMS is oxidized to form sulfate aerosols that are potentially a major source of cloud condensation nuclei [Charlson *et al.*, 1987].

[3] Algae thrive in a variety of microhabitats associated with pack ice including meltwater ponds, gap waters, free-board layers, and the network of brine channels within the ice interior. The extraordinary variation of microenvironments

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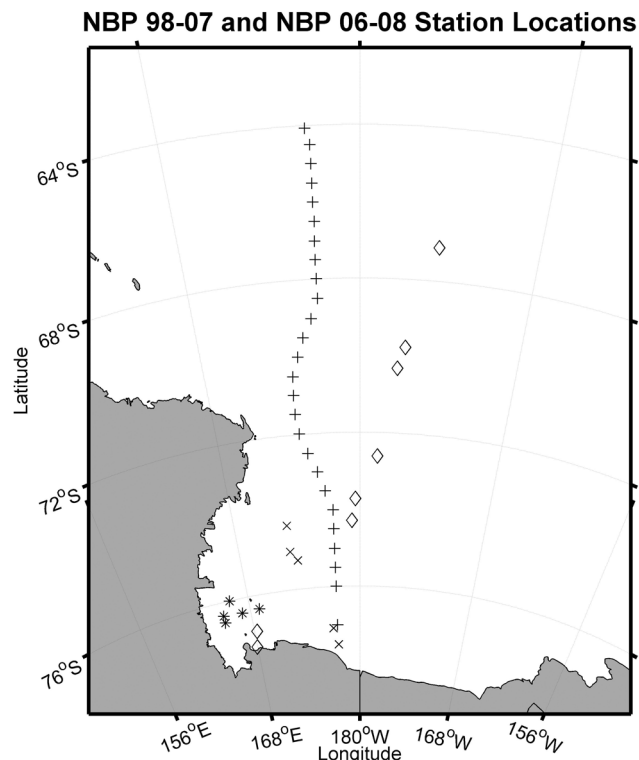


Figure 1. All station locations for NBP 98–07 and NBP 06–08. Pluses denote NBP 98–07 “early” stations. Asterisks denote NBP 98–07 “late” stations. Crosses denote NBP 98–07 stations not included in either subgroup. Diamonds denote all NBP 06–08 stations.

within and associated with sea ice makes quantification of chemical and biological processes challenging. Large-scale models of the Antarctic sea ice ecosystem suggest that while productivity rates peak during austral summer, spatially integrated primary production in Antarctic sea ice is greatest in spring with ~60% of annual sea ice primary production (30–70 Tg C) occurring in November and December [Arrigo *et al.*, 1997; Arrigo and Thomas, 2004].

[4] Abiotic processes occurring within sea ice may also play an important role in the cycling of carbon in the polar seas. Rysgaard *et al.* [2007] suggest that precipitation of CaCO_3 mineral phases within sea ice could result in the downward transport of 0.2–0.5 Pg C y^{-1} out of the surface ocean, a flux comparable to estimates of the net ocean-atmosphere CO_2 flux for the entire Southern Ocean south of 50°S [Takahashi *et al.*, 2002]. This abiotic carbon pump results from the high ΣCO_2 to alkalinity ratio (and subsequently high pCO_2) of brine expelled from sea ice during ice formation and subsequent brine drainage. When sea ice melts during spring, solid CaCO_3 phases within the ice dissolve into the surface ocean raising alkalinity and driving a CO_2 flux from atmosphere to ocean. Recent observations of ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) crystals in a range of sea ice types in the Weddell Sea including young nilas (thickness < 0.5 m) and multiyear floes (thickness > 2 m) suggest that precipitation of solid CaCO_3 phases may be widespread within Antarctic pack ice [Dieckmann *et al.*, 2008].

[5] Due in part to high $[\text{CO}_{2(\text{aq})}]$ associated with low-temperature seawater, bulk $\delta^{13}\text{C}_{\text{POC}}$ values in Southern Ocean surface waters are negative (–21 to –33‰) relative to POC from lower-latitude surface waters [Rau *et al.*, 1991a, 1991b; Dehairs *et al.*, 1997; Villinski *et al.*, 2000]. Significant enrichment in $\delta^{13}\text{C}_{\text{POC}}$ from the Southern Ocean has been documented in the water column and in habitats associated with sea ice [Rau *et al.*, 1991b; Fischer, 1991; Dunbar and Leventer, 1992; McMinn *et al.*, 1999; Kennedy *et al.*, 2002; Arrigo *et al.*, 2003]. Seasonal enrichment of more than 10‰ has been noted in suspended POC in the Ross Sea during summer [Dunbar and Leventer, 1992; Villinski *et al.*, 2000] as well as in seafloor sediments [Villinski *et al.*, 2008]. Factors that may be responsible for isotopic enrichment include high growth rates of primary producers during periods of high productivity, species-specific fractionation, increased heterotrophic recycling in the upper water column, and bloom-related drawdown of $[\text{CO}_{2(\text{aq})}]$ in stratified surface waters [Villinski *et al.*, 2000, 2008]. While similar mechanisms are likely responsible for isotopic variability in sea ice organic matter, these effects may be enhanced owing to the isolated nature of the brine channel environment.

[6] Lab experiments suggest that enrichment in $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ in sea ice brines could be associated with both biotic and abiotic effects [Gleitz *et al.*, 1996; Papadimitriou *et al.*, 2004]. Enrichment in $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ from sea ice environments has been documented from several different environments around Antarctica with most investigations of pack ice focused on the Weddell Sea [Gibson *et al.*, 1999; Thomas *et al.*, 2001; Kennedy *et al.*, 2002; Papadimitriou *et al.*, 2007]. Here we provide the first report of $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ variability in extracted sea ice brines from the Ross Sea. The purpose of our study is to provide an extensive new data set with which to investigate biogeochemical cycling within Antarctic pack ice during the austral spring. Several possible causes for isotopic enrichment of POC and ΣCO_2 are examined: (1) carbonate crystal growth and degassing; (2) photosynthetic drawdown of the ΣCO_2 pool via net community production; and (3) a decrease in the magnitude of ϵ_p for sea ice algae relative to phytoplankton in surrounding open water ecosystems.

2. Methods

[7] The Research Vessel Ice Breaker (RVIB) *Nathaniel B. Palmer* (NBP) was used for two Ross Sea sampling programs. Samples were collected between 6 November and 6 December 1998 as part of the ROAVERRS (Research on Ocean-Atmosphere Variability and Ecosystem Response in the Ross Sea) program during cruise NBP 98–07, and between 9 November and 1 December 2006 as part of the CORSACS (Controls on Ross Sea Algal Community Structure) cruise NBP 06–08. During the first two weeks of NBP 98–07, sea ice was sampled on a N–S transect centered on 176°E, extending from the ice edge at ~64°S to the Ross Ice Shelf (~78°S) at roughly 0.5° increments (Figure 1). Along the southward transect, an average of 3 ice stations were completed every 24 h for a total of 27 stations from 6 to 14 November. Stations completed during this interval (i.e., stations 1–27) are hereafter referred to as “early” stations. A complete description of the physical setting, sea ice proper-

ties, and sampling methods during this segment of the cruise is given by *Arrigo et al.* [2003].

[8] During the last several weeks of NBP 98–07, ice stations were occupied less frequently and primarily located in the southwestern Ross Sea (Figure 1). These stations included fast ice and multiyear pack ice, in addition to much younger pack ice that formed during the spring. In order to investigate the evolution of brine environments during spring we focus on stations sampled from 4 to 6 December (i.e., stations 95–99), a subgroup representative of late spring/early summer conditions (Figure 1). Hereafter we refer to this subgroup as “late” stations. During NBP 06–08, a total of eight stations were sampled along a NE–SW transect from the outer pack near 67°S to $\sim 77^\circ\text{S}$ (Figure 1). Similar to the “early” stations of NBP 98–07, the ice sampled was exclusively first year pack ice. Ice thickness at most stations ranged from 0.6 m to just over 1 m except at the first (northernmost) station where cores were drilled near a pressure ridge where the sea ice was over 3 m thick.

[9] Multiple SIPRE cores were collected at each of 37 stations occupied during NBP 98–07 and 8 stations during NBP 06–08. Ice cores were drilled at least 30 m from the ship in both the middle of floes and along floe edges at level (unridged) sites. In the outer pack, where floes were smaller, four cores were typically drilled for POM analysis in a transect extending from the center to the floe edge. Separate SIPRE cores for the separation of brines were drilled adjacent to centrally positioned POM cores. Brine cores were cut into sections ~ 10 cm in length and POM cores cut into sections ~ 20 cm in length. Clean rubber gloves were worn while handling cores to avoid contamination. Segments for brine analysis were placed in individually labeled plastic containers and POM segments were placed in polyethylene bags. All sections were transferred to a cooler for transportation back to the ship, typically within 20 to 30 min. For the thickest floes (i.e., thickness > 1.6 m), we did not sample the entire core owing to logistical constraints; in these instances, we typically took samples from the top and bottom of the ice. In areas of thin ice (i.e., thickness < 20 cm), we sampled from a personnel basket suspended over the side using the ship’s crane. At these stations, an ice saw was used to cut segments directly from the ice. During NBP 98–07, a total of 161 cores were sampled for both brine and POM analysis. In all, 68 cores were collected for brine analysis and 93 cores were sampled for POM analysis. During NBP 06–08, 21 cores were sampled for brine and POM analysis.

[10] Brine cores were immediately transported to a cold room laboratory kept at -2°C and individual core sections were centrifuged in 1 L buckets at 1800 rpm for 5 min to separate liquid brines from ice; brine cores were typically processed within 1 h of collection. Centrifuged brine samples from vertically equivalent sections of different cores were typically combined in order to provide a volume large enough for the full suite of analyses. Brine samples were transferred to 10 ml vials; soon after, salinity, ΣCO_2 , and nutrients were determined from subsamples. Salinity of brines was measured using an Orion Instruments handheld conductivity-based salinometer calibrated before every set of samples using either Dickson ΣCO_2 standards or primary IAPSO seawater salinity standards. During NBP 98–07, ΣCO_2 was determined using a shipboard CO_2 stripping system coupled to a coulometric CO_2 titrator modeled after the LDEO design used

during the Southern Ocean JGOFS cruises [*Sweeney et al.*, 2000]. On the basis of analysis of several hundred replicate Dickson ΣCO_2 standards, our analytical precision is on the order of $\pm 1 \mu\text{mol kg}^{-1}$. During NBP 06–08, ΣCO_2 was determined using an automated shipboard CO_2 stripping system coupled to a LICOR infrared CO_2 analyzer after a design developed at the Monterey Bay Aquarium Research Institute (G. Friederich, personal communication, 2006). Samples are typically analyzed in triplicate using this system and we achieve an average analytical precision on the order of $\pm 1.2 \mu\text{mol kg}^{-1}$. For ΣCO_2 isotopic analysis on both cruises CO_2 gas was extracted at sea via acidification with phosphoric acid in a helium gas stream bubble stripper. The released CO_2 gas was collected by freezing with liquid nitrogen and sealed in glass ampoules for return to the Stanford University Stable Isotope Laboratory. The stable isotopic composition was determined using an automated Finnigan MAT 252 Stable Isotope Ratio Mass Spectrometer. Isotopic values are reported as the per mil (‰) difference between sample and standard using the convention $\delta^{13}\text{C} = [(\text{R}_{\text{sample}}/\text{R}_{\text{standard}}) - 1] \times 1000$ where R represents the $^{13}\text{C}/^{12}\text{C}$ ratio and the standard is PDB. On the basis of analysis of replicate stripped CO_2 samples, precision of the $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ values is $\pm 0.03\%$.

[11] A Technicon Autoanalyzer II system was used to determine concentrations of nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), phosphate (PO_4^{3-}), and silicic acid ($\text{Si}(\text{OH})_4$) according to JGOFS protocols as described in the work of *Knap et al.* [1996]. High-salinity samples suspected of having nutrient concentrations outside the optimal Autoanalyzer analytical range were diluted with artificial nutrient-free seawater prior to analysis. All samples were analyzed within 8 h of collection. Detection limits were $0.03 \mu\text{mol kg}^{-1}$ for NO_3^- , $0.005 \mu\text{mol kg}^{-1}$ for NO_2^- , $0.005 \mu\text{mol kg}^{-1}$ for NH_4^+ , $0.008 \mu\text{mol kg}^{-1}$ for PO_4^{3-} , and $0.1 \mu\text{mol kg}^{-1}$ for $\text{Si}(\text{OH})_4$. All nutrient and ΣCO_2 data were converted to units of $\mu\text{mol kg}^{-1}$ and normalized to 34.5 psu, roughly the average salinity of the Ross Sea, to remove the effects of dilution from melting sea ice or brine injection from ice formation [*Dunbar et al.*, 2003].

[12] The most commonly used method for collecting sea ice brine described by *Gleitz et al.* [1995] consists of drilling a hole in the ice, covering the hole with a lid, and allowing brine from surrounding ice to drain into the hole. Two drawbacks of this “sackhole” method are that brine from biologically active lower sections of the ice is typically not sampled and that vertical variability of biogeochemical parameters within the ice cannot be examined. In addition, at low temperatures and correspondingly low brine volume and ice porosity, up to 60 min of drainage time may be required to collect an adequate sample volume [*Gleitz et al.*, 1995] during which some equilibration with air is possible. The most notable drawback of the “centrifugation” method as employed here includes the possibility of melting, degassing, and/or mineral phase precipitation as a result of increased pressure during centrifugation. *Papadimitriou et al.* [2004] noted discrepancies in ΣCO_2 concentrations between “sackhole” and “centrifugation” samples collected during lab freezing experiments which the authors attributed to pressure effects during centrifugation; no discrepancies were apparent in $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ between the two sampling methods. While great care was taken during this study to keep brine samples close to in situ temperatures and to process samples in as little time as pos-

Table 1. Summary of All Sea Ice Segments Sampled During NBP 98–07 and NBP 06–08^a

	NBP 98–07			NBP 06–08	NBP 98–07			NBP 06–08	NBP 98–07			NBP 06–08	NBP 98–07			NBP 06–08
	All	Early	Late	(All)	All	Early	Late	(All)	All	Early	Late	(All)	All	Early	Late	(all)
	Salinity (psu)				$\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ (‰ relative to PDB)				ΣCO_2 ($\mu\text{mol kg}^{-1}$)				$s\Sigma\text{CO}_2$ ($\mu\text{mol kg}^{-1}$)			
Number	176	117	37	36	119	75	28	25	150	93	35	33	150	93	35	33
Minimum	27.4	27.4	29.0	31.5	−2.6	−1.3	−2.6	1.3	1368	2066	1368	1692	1483	1609	1483	1594
Maximum	100.8	84.6	49.8	79.0	8.0	6.0	8.0	4.2	7149	4458	3016	4217	2447	2326	2375	2519
Mean	44.8	46.8	35.3	46.5	2.0	1.9	2.4	2.5	2753	2979	1981	2779	2050	2103	1921	2021
$\pm 1 \sigma$	13.0	11.8	5.3	12.5	1.8	1.5	2.5	0.8	852	606	395	643	183	136	223	203
	Si(OH)_4 ($\mu\text{mol kg}^{-1}$)				$s\text{Si(OH)}_4$ ($\mu\text{mol kg}^{-1}$)				PO_4^{3-} ($\mu\text{mol kg}^{-1}$)				$s\text{PO}_4^{3-}$ ($\mu\text{mol kg}^{-1}$)			
Number	156	97	37	24	155	96	37	24	154	97	35	24	153	96	35	24
Minimum	0	17	0	15	0	17	0	13	0.2	0.2	0.6	0.3	0.1	0.1	0.6	0.1
Maximum	164	164	89	93	100	92	100	47	169.2	68.5	130.0	7.7	143.2	45.7	143.2	8.1
Mean	66	84	26	53	47	59	24	34	9.4	4.9	12.6	1.1	7.2	3.4	13.3	0.9
$\pm 1 \sigma$	41	35	24	25	24	17	21	11	23.7	9.5	23.8	1.5	17.2	6.4	26.3	1.6
	NO_3^- ($\mu\text{mol kg}^{-1}$)				$s\text{NO}_3^-$ ($\mu\text{mol kg}^{-1}$)				NO_2^- ($\mu\text{mol kg}^{-1}$)				$s\text{NO}_2^-$ ($\mu\text{mol kg}^{-1}$)			
Number	156	97	37	24	155	96	37	24	156	97	37	24	155	96	37	24
Minimum	0.0	0.2	0.0	3.3	0.0	0.1	0.0	1.5	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.2
Maximum	72.8	64.8	17.6	27.7	31.3	31.3	19.8	24.8	1.4	1.0	1.0	2.0	1.3	1.0	0.8	2.0
Mean	16.6	21.7	2.8	8.6	11.7	15.1	2.8	6.4	0.3	0.3	0.1	0.9	0.2	0.2	0.0	0.6
$\pm 1 \sigma$	16.2	15.6	4.9	5.8	9.7	8.9	4.9	5.2	0.3	0.3	0.2	0.4	0.2	0.2	0.2	0.4
	NH_4^+ ($\mu\text{mol kg}^{-1}$)				$s\text{NH}_4^+$ ($\mu\text{mol kg}^{-1}$)				$\text{TIN} (\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+)$ ($\mu\text{mol kg}^{-1}$)				$s\text{TIN}$ ($\mu\text{mol kg}^{-1}$)			
Number	156	97	37	24	155	96	37	24	156	97	37	24	155	96	37	24
Minimum	1.3	2.3	1.3	2.2	1.4	1.8	1.4	1.4	2.6	4.0	2.6	7.1	2.9	3.1	2.9	3.1
Maximum	1000.8	52.8	31.6	9.4	558.7	55.2	36.7	9.4	1011.4	81.2	44.6	38.1	564.6	85.4	51.9	34.1
Mean	25.3	10.0	8.5	5.4	16.5	7.7	8.4	4.0	42.2	32.0	11.4	14.9	28.4	23.0	11.2	11.0
$\pm 1 \sigma$	108.7	8.9	5.0	2.2	58.5	7.8	5.6	2.2	109.6	19.1	7.8	6.9	58.8	13.0	8.3	6.8
	$\delta^{13}\text{C}_{\text{POC}}$ (‰ relative to PDB)				Ice Segment POC ($\mu\text{g l}^{-1}$)				Ice Segment TPN ($\mu\text{g l}^{-1}$)				Depth-Integrated POC (mg m^{-2})			
Number	265	186	52	22	267	186	52	22	267	186	52	19	33	24	4	6
Minimum	−28.2	−27.9	−28.2	−30.5	169	169	385	185	23	23	42	13	36	63	930	229
Maximum	−9.2	−14.4	−9.2	−17.6	20744	6185	11650	2720	3530	763	1008	324	6692	2276	2256	304
Mean	−23.0	−23.4	−21.3	−24.4	1542	1123	1642	682	206	145	177	73	871	591	1646	259
$\pm 1 \sigma$	3.2	2.5	4.2	3.3	2591	1048	2285	609	414	139	202	83	1197	450	623	34

^a ΣCO_2 and nutrient data are from extracted brines. POC and TPN data are from bulk ice. All $\delta^{13}\text{C}$ data are in ‰ relative to PDB. Preceding “s” denotes normalization to 34.5 psu salinity. Depth-integrated POC represents the mean of all cores at each station.

sible, we acknowledge the possibility that centrifugation of sea ice segments may introduce some systematic error to the ΣCO_2 measurements presented here. Nevertheless we feel the centrifugation approach is preferable as we can directly sample the brines that are influenced by the active sea ice biological communities at the base of the pack ice.

[13] Sea ice core segments for POM analysis were taken aboard ship and stored in a thermally insulated cooler for no more than $\frac{1}{2}$ h before processing. In the ship’s cold room, ice segments were measured for length and placed into 2 L polyethylene bottles. To avoid cell lysing, a measured volume of filtered seawater was added to ensure that the solution salinity did not decrease below 28 psu [Arrigo *et al.*, 2003] as samples were allowed to melt in the dark. Between 200 to 1000 ml of diluted sample was filtered for POM through 25 mm Whatman GF/F glass-fiber filters washed with 0.1 N HCl; filters were frozen in liquid nitrogen and stored at -80°C prior to analysis. POC, TPN, and $\delta^{13}\text{C}_{\text{POC}}$ were determined using a Carlo Erba NA1500 elemental analyzer/Conflo II system coupled to a Finnigan DeltaPlus Stable Isotope Ratio Mass Spectrometer at the Stanford University Stable Isotope Laboratory. Precision for $\delta^{13}\text{C}_{\text{POC}}$ for this method, based on

replicate analyses of NIST and USGS standards, is 0.05‰. Reproducibility for $\delta^{13}\text{C}_{\text{POC}}$ of individual samples is on the order of 0.11‰. POC, TPN, $\delta^{13}\text{C}_{\text{POC}}$, pigment, and species composition data from “early” stations are reported and discussed in the work of Arrigo *et al.* [2003].

3. Results

3.1. Salinity

[14] Brine salinities of individual ice core segments from NBP 98–07 and NBP 06–08 ranged from 27 to 101 psu and from 32 to 79 psu, respectively (Table 1). The mean and standard deviation for NBP 98–07 (45 ± 13 psu) was nearly identical to that of NBP 06–08 (47 ± 12 psu). Brine salinities display an inverse relationship with ice temperature; salinities are typically greatest near the snow–ice interface and decrease with depth in the ice (data not shown). For comparison, Gleitz *et al.* [1995] reported brine salinities in the Weddell Sea ranging from 21 to 41 psu in January 1991 and 34 to 108 psu in April 1992. Papadimitriou *et al.* [2007] measured brine salinities in the Weddell Sea in December 2004 of 40 to 63 psu. Garrison *et al.* [2003] measured brine salinities in

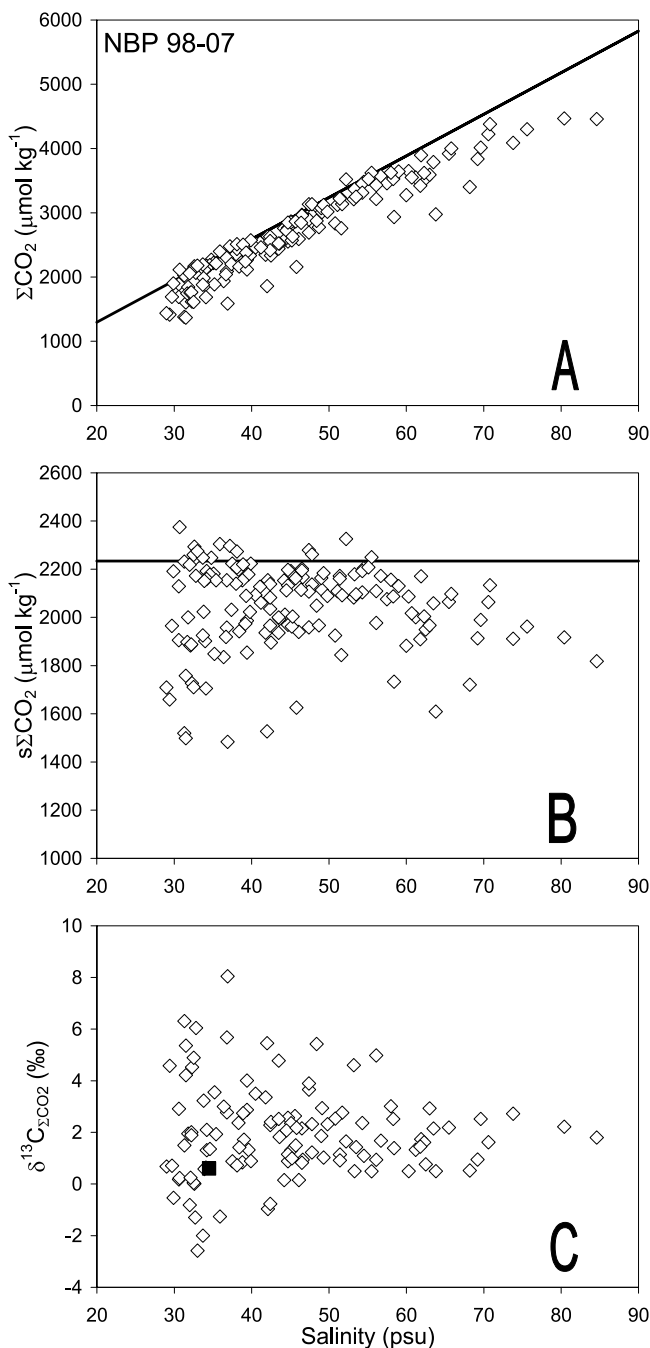


Figure 2. Brine salinity versus (a) ΣCO_2 in $\mu\text{mol kg}^{-1}$ (solid line represents expected values based on concentration effect during freezing); (b) $s\Sigma\text{CO}_2$ (i.e., ΣCO_2 in $\mu\text{mol kg}^{-1}$ normalized to 34.5 psu; solid line represents the preutilization value of $2234 \mu\text{mol kg}^{-1}$); and (c) $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ in ‰ relative to PDB (solid square represents preutilization (winter seawater) composition of 0.6‰ and $2234 \mu\text{mol kg}^{-1}$). All data are from cruise NBP 98–07.

the Ross Sea in May/June 1998 ranging from 35 to 157 psu with a mean of 109 psu.

3.2. Total Dissolved Inorganic Carbon

[15] ΣCO_2 for all samples discussed here ranged from 1368 to $7149 \mu\text{mol kg}^{-1}$ and from 1483 to $2519 \mu\text{mol kg}^{-1}$ when

normalized to 34.5 psu salinity ($s\Sigma\text{CO}_2$) (Table 1). ΣCO_2 is highly correlated with brine salinity ($R^2 = 0.9$) owing to concentration effects during freezing/melting (Figures 2a and 3a). There is significantly greater $s\Sigma\text{CO}_2$ variability at low salinities (Figures 2b and 3b). ΣCO_2 is typically highest near the snow-ice interface and decreases with depth,

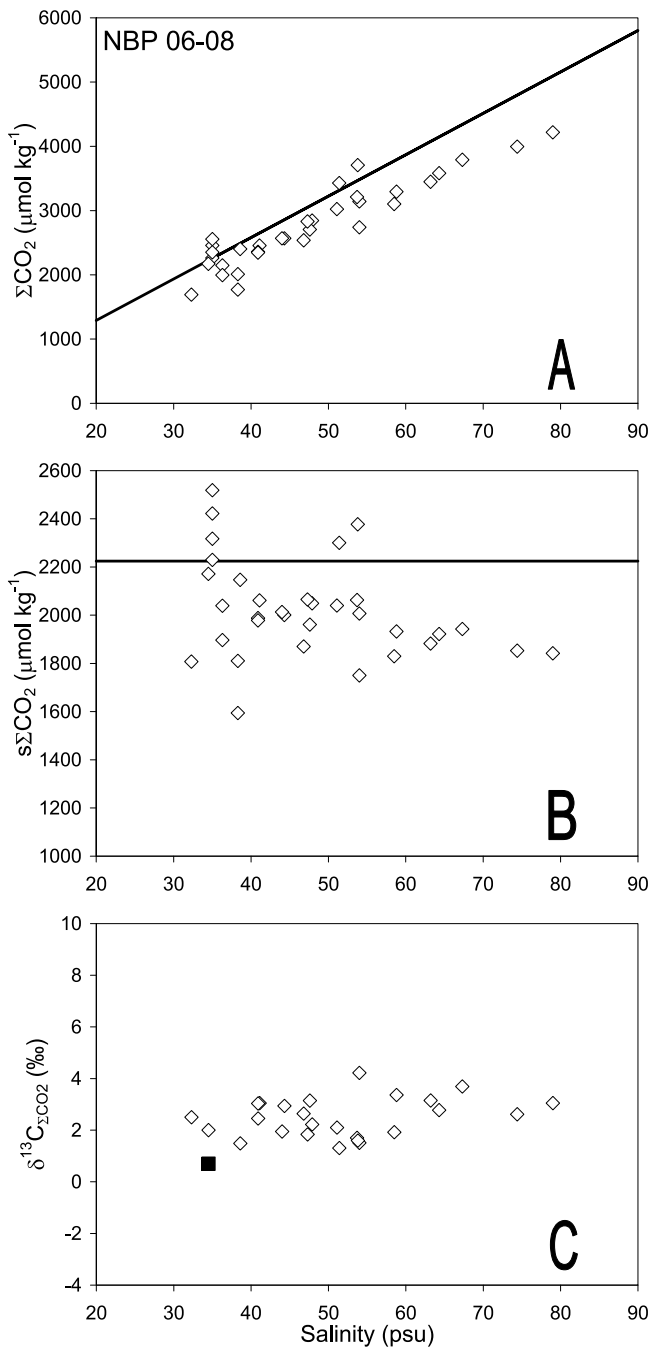


Figure 3. Brine salinity versus (a) ΣCO_2 in $\mu\text{mol kg}^{-1}$ (solid line represents expected values based on concentration effect during freezing); (b) $s\Sigma\text{CO}_2$ (i.e., ΣCO_2 in $\mu\text{mol kg}^{-1}$ normalized to 34.5 psu; solid line represents the preutilization value of $2225 \mu\text{mol kg}^{-1}$); and (c) $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ in ‰ relative to PDB (solid square represents pre-utilization (winter seawater) composition of 0.7‰ and $2225 \mu\text{mol kg}^{-1}$). All data are from cruise NBP 06–08.

similar to salinity (data not shown). For comparison, *Gleitz et al.* [1995] reported a ΣCO_2 range in the Weddell Sea of 839 to 2149 $\mu\text{mol kg}^{-1}$ in January 1991 and 1878 to 7261 $\mu\text{mol kg}^{-1}$ in April 1992; *Papadimitriou et al.* [2007] reported a range in the Weddell Sea in December 2004 of 2091 to 3551 $\mu\text{mol kg}^{-1}$; and *Garrison et al.* [2003] reported a range in the Ross Sea in May/June 1998 of 4176 to 8761 $\mu\text{mol kg}^{-1}$.

[16] Comparison of $s\Sigma\text{CO}_2$ to an estimated winter seawater or preutilization value allows estimation of the ΣCO_2 deficit associated with biotic and abiotic processes. Following the method of *Sweeney et al.* [2000], we estimate preutilization ΣCO_2 by averaging deep water (i.e., depth > 200 m) concentrations from all stations over the Ross Sea continental shelf. This approach relies on the fact that substantial overturn and homogenization of the shelf water column occurs during autumn through early spring each year. Winter seawater $s\Sigma\text{CO}_2$ estimated by this method for NBP 98–07 was 2234 $\mu\text{mol kg}^{-1}$, within 1 $\mu\text{mol kg}^{-1}$ of the early spring value estimated by *Sweeney et al.* [2000] for 1997. Winter seawater $s\Sigma\text{CO}_2$ for NBP 06–08 was 2225 $\mu\text{mol kg}^{-1}$. By differencing with preutilization values, the lowest $s\Sigma\text{CO}_2$ value we observed in 1998 corresponds to a deficit of 751 $\mu\text{mol kg}^{-1}$ or 34% of the preutilization ΣCO_2 pool. The greatest $s\Sigma\text{CO}_2$ deficits for individual ice core segments correspond to interior sections (i.e., >20 cm from both the snow-ice interface and the ice-water interface) from “late” stations; significant depletion was also observed near the ice-water interface at several stations from both the “early” and “late” periods (Figure 4). Studies in the Weddell Sea indicate similar deficits; *Gleitz et al.* [1995] reported ΣCO_2 drawdown in first year sea ice in January 1991 of up to 1200 $\mu\text{mol kg}^{-1}$ and *Papadimitriou et al.* [2007] reported deficits in December 2004 of 700 $\mu\text{mol kg}^{-1}$. During NBP 98–07, large deficits were also noted in extremely cold hypersaline brine environments near the snow/ice interface from the central pack (Figure 4).

[17] $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ of brine from individual core sections ranged from -2.6 to $+8.0\text{‰}$ for all samples (Table 1). This range is significantly greater than the range in $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ reported for surface waters in the Ross Sea ($+0.47$ to $+3.58\text{‰}$) (R. B. Dunbar, unpublished data, 2009; P. D. Quay, unpublished data, 2009; *Villinski et al.* [2000]). We observed a large range in $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ in low-salinity brines during NBP 98–07 (Figure 2c) and the greatest variability at “late” stations (Table 1). Variability in $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ was significantly smaller during NBP 06–08 compared to NBP 98–07 (Figures 2c and 3c). Enriched values are generally associated with indicators of active algal growth (i.e., high chlorophyll *a*, NO_3^- depletion) (Figures 4 and 5; see also Figure 9). *Kennedy et al.* [2002] measured a lesser degree of enrichment in gap waters and surface ponds ($+0.15$ to $+2.98\text{‰}$) in Weddell Sea pack ice in January/February 1997, environments that are typically less isolated than interior brines. *Papadimitriou et al.* [2007] reported a similar range compared to our study for brine collected from the Weddell Sea in December 2004 ($+2.9$ to $+6.4\text{‰}$).

3.3. Nutrients

[18] Nutrient data from the “early” stations of NBP 98–07 are reported by *Arrigo et al.* [2003]. Ranges and means for NO_3^- , NO_2^- , NH_4^+ , $\text{Si}(\text{OH})_4$, and PO_4^{3-} for both cruises

including “late” stations from NBP 98–07 are summarized in Table 1; vertical profiles of $s\text{NO}_3^-$ and $s\text{PO}_4^{3-}$ are displayed in Figure 4. NO_3^- was greatest in the upper ice for “early” stations and generally decreased with depth in the ice; extreme $s\text{NO}_3^-$ depletion coincides with significant $s\Sigma\text{CO}_2$ depletion at “late” stations (Figure 4). NH_4^+ and PO_4^{3-} ranged widely with concentrations for many samples greater than expected from the concentrating effects of freezing. During NBP 98–07, NH_4^+ and PO_4^{3-} were most elevated at “late” stations and at “early” stations in the central pack around 72°S (Figure 4). $s\text{Si}(\text{OH})_4$ followed similar spatial and depth patterns compared to $s\text{NO}_3^-$ except that depletion was less frequent (data not shown). Among “late” stations complete $s\text{Si}(\text{OH})_4$ depletion occurred in only two highly productive interior sections; however, levels approached complete depletion in a significant number of other “late” samples.

3.4. Particulate Organic Matter

[19] POC for all individual ice segments collected during NBP 98–07 and NBP 06–08 ranged from 169 to 20744 $\mu\text{g l}^{-1}$ (14 to 1729 $\mu\text{mol l}^{-1}$) and from 185 to 2720 $\mu\text{g l}^{-1}$ (15 to 227 $\mu\text{mol l}^{-1}$), respectively. Sea ice POC showed distinct latitudinal trends for the “early” NBP 98–07 transect with high levels near the northern edge of the pack, a smaller local maximum near 72°S , and steadily decreasing values to the south, approaching the Ross Sea polynya [*Arrigo et al.*, 2003]. The highest POC observed in this study was from “late” pack ice in the southwestern Ross Sea sampled during NBP 98–07. Very low POC was observed in young thin ice near the polynya. High POC was generally observed at the bottom of the ice with very high POC observed in bottom segments from “late” stations (Figure 5). The range in POC was less than observed by *Kennedy et al.* [2002] who reported POC greater than 6000 $\mu\text{mol l}^{-1}$ in Weddell Sea pack ice in January/February 1997.

[20] $\delta^{13}\text{C}_{\text{POC}}$ values ranged from -30.5 to -9.2‰ for all sea ice samples from both cruises ($n = 287$, Table 1). The range in water column $\delta^{13}\text{C}_{\text{POC}}$ for the upper 150 m during NBP 98–07 was notably smaller (-22.1 to -31.0‰ , $n = 452$) than for samples from sea ice. Mean sea ice $\delta^{13}\text{C}_{\text{POC}}$ during NBP 98–07 (-23.0‰) was enriched by 5‰ relative to mean water column $\delta^{13}\text{C}_{\text{POC}}$ (-28.1‰) (Figure 6). Mean sea ice $\delta^{13}\text{C}_{\text{POC}}$ during NBP 06–08 was slightly more depleted (-24.4‰) than during NBP 98–07. Enriched $\delta^{13}\text{C}_{\text{POC}}$ generally coincided with high POC both spatially and with depth in the ice (Figures 5 and 7). $\delta^{13}\text{C}_{\text{POC}}$, like POC, was typically highest near the ice-water interface (Figure 5). However, enriched $\delta^{13}\text{C}_{\text{POC}}$ was also observed in interior sections from “late” stations during NBP 98–07 (Figure 5). The observed sea ice range is similar to that observed by *Kennedy et al.* [2002] in Weddell Sea pack ice in January/February 1997 (-27.3 to -10.0‰).

4. Discussion

4.1. Influence of Abiotic Processes on ΣCO_2 and $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$

[21] Recent studies based on field observations from the Weddell Sea [*Papadimitriou et al.*, 2007; *Dieckmann et al.*, 2008] and freezing experiments [*Papadimitriou et al.*, 2004] indicate that CaCO_3 precipitation and CO_2 degassing may have a significant impact on both ΣCO_2 and $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ in

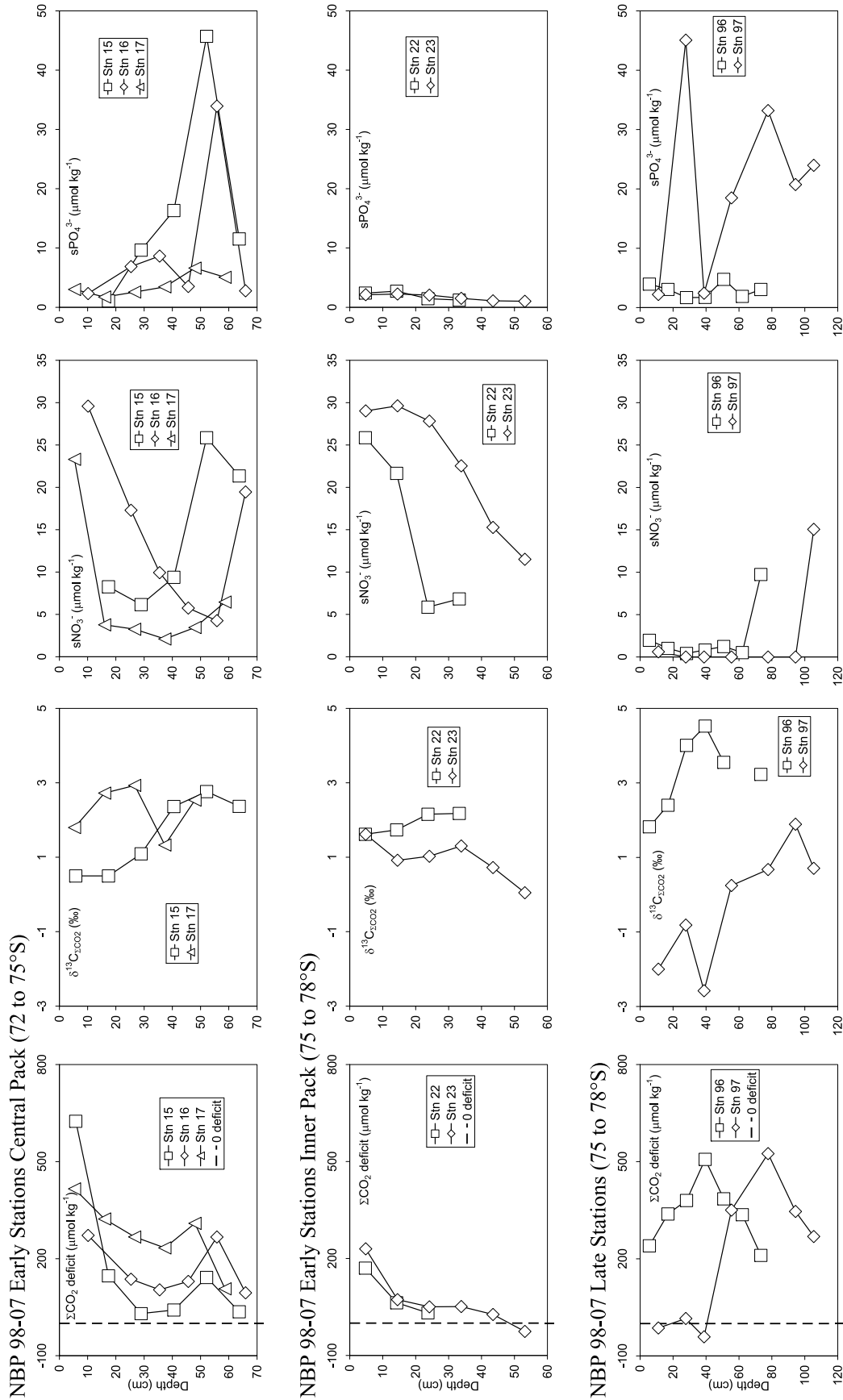
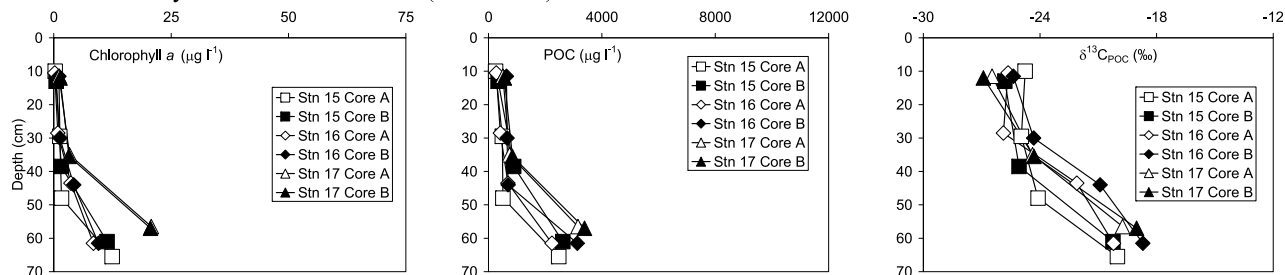
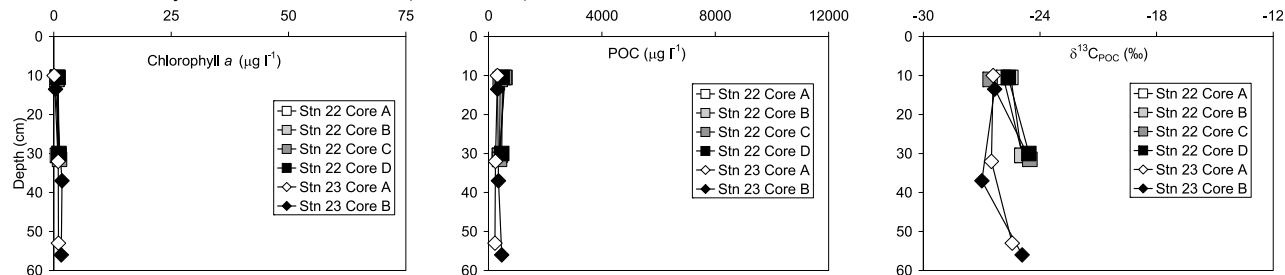


Figure 4. Vertical profiles of sea ice brine chemical composition for selected stations from NBP 98–07 for different regions of the Ross Sea in centimeters below the ice surface. From left to right: ΣCO_2 deficit (i.e., $s\Sigma\text{CO}_2$ preutilization value of 2234 $\mu\text{mol kg}^{-1}$ minus observed $s\Sigma\text{CO}_2$), where the dashed line represents zero deficit; $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ in ‰ relative to PDB; $s\text{NO}_3^-$ in $\mu\text{mol kg}^{-1}$; and $s\text{PO}_4^{3-}$ in $\mu\text{mol kg}^{-1}$.

NBP 98-07 Early Stations Central Pack (72 to 75°S)



NBP 98-07 Early Stations Inner Pack (75 to 78°S)



NBP 98-07 Late Stations (75 to 78°S)

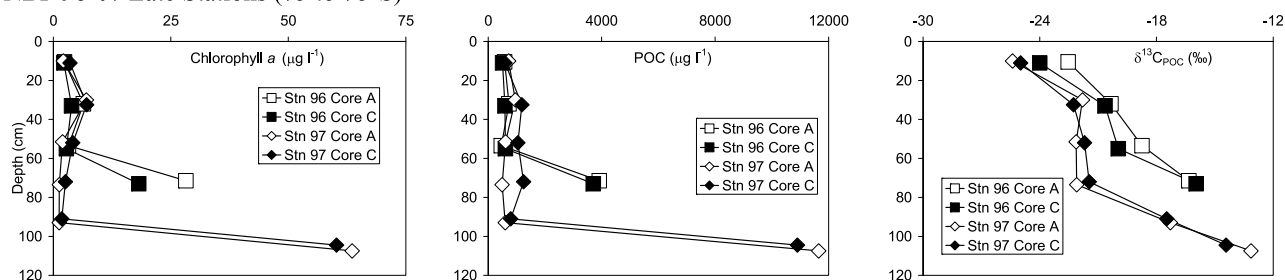


Figure 5. Vertical profiles of sea ice particulate organic composition for selected stations from NBP 98–07 in centimeters below the ice surface. From left to right: chlorophyll *a* in $\mu\text{g l}^{-1}$; POC in $\mu\text{g l}^{-1}$; and $\delta^{13}\text{C}_{\text{POC}}$ in ‰ relative to PDB.

sea ice brines. *Papadimitriou et al.* [2007] noted dramatic reductions in alkalinity in combination with ΣCO_2 deficits in second year ice in the Weddell Sea suggesting carbonate precipitation. *Dieckmann et al.* [2008] observed the metastable hydrated CaCO_3 phase ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) in sea ice environments in the Weddell Sea ranging from young to multiyear pack ice. Additionally, *Papadimitriou et al.* [2004] measured $s\Sigma\text{CO}_2$ depletions of up to $376 \mu\text{mol kg}^{-1}$ in brine samples during an 18 day freezing experiment where biological effects on ΣCO_2 and $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ were assumed to be minimal; on the basis of isotopic constraints, the authors suggest that both CaCO_3 precipitation and CO_2 degassing may occur in sea ice. On the basis of equilibrium thermodynamic considerations, both anhydrous and hydrated forms of CaCO_3 may precipitate at brine temperatures lower than -1.9°C , assuming conservative behavior of ΣCO_2 [*Anderson and Jones, 1985; Marion, 2001*]. PO_4^{3-} is a known inhibitor of precipitation of anhydrous CaCO_3 minerals [*Bischoff et al., 1993*] and high PO_4^{3-} levels have been linked to ikaite precipitation in Antarctic sediments [*Whitcar and Suess, 1998*] and other high-latitude environments. Elevated PO_4^{3-} was observed in many brines sampled in this study, likely resulting from both concentration during freezing and regeneration

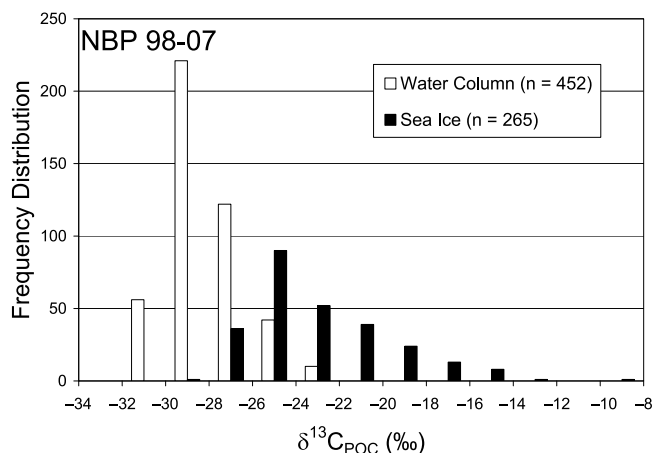


Figure 6. Histogram of all individual sea ice and water column $\delta^{13}\text{C}_{\text{POC}}$ samples from NBP 98–07; all isotopic values are in ‰ relative to PDB.

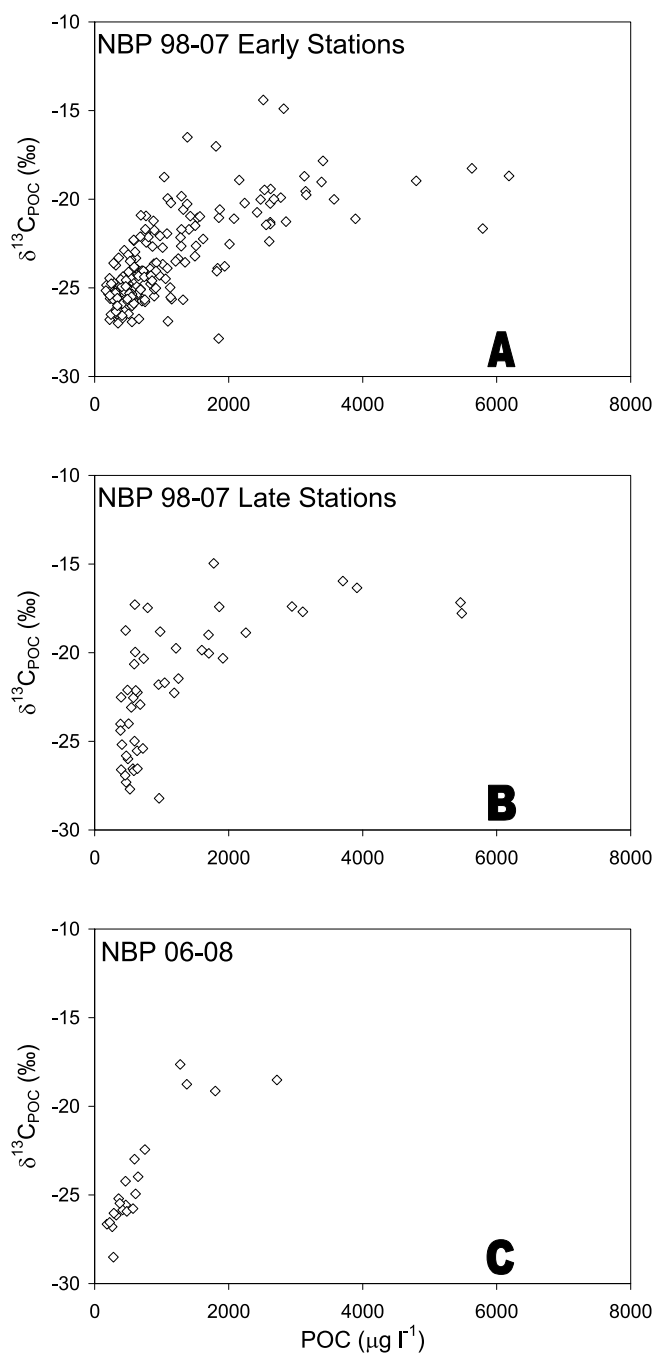


Figure 7. Relationship between POC and $\delta^{13}\text{C}_{\text{POC}}$ of ice segments from (a) NBP 98–07 “early” stations, (b) NBP 98–07 “late” stations, and (c) all NBP 06–08 stations; all isotopic values are in ‰ relative to PDB.

of POM within brine channels (Table 1 and Figure 4), so we expect that conditions favorable to ikaite precipitation were achieved. Degassing of CO_2 occurs owing to the concentrating effects of brine formation and as a result of CaCO_3 precipitation. Nucleation of gas bubbles within brine pockets is facilitated by the presence of nucleation sites (e.g., authigenic particles); resultant gas bubbles are trapped within the ice matrix but may eventually escape to the atmosphere or the underlying water column [Killawee et al., 1998; Papadimitriou

et al., 2004]. Degassing may be more pronounced in sea ice than in freshwater ice due to the porous nature of the sea ice matrix and, to a lesser degree, the decreasing solubility of CO_2 with increasing salinity.

[22] We observed large $s\Sigma\text{CO}_2$ deficits in upper sections of the ice at low-productivity stations (Figure 4). Deficits near the top of the ice were particularly large (up to $625 \mu\text{mol kg}^{-1}$) in the central pack during NBP 98–07 (72 to 75°S). Previous field investigations suggest that significant biological activity under these conditions is unlikely. Arrigo and Sullivan [1992] found greatly reduced photosynthetic rates in fast ice algal communities at salinities above 50 psu and total photosynthetic shutdown above 100 psu salinity. Brine salinities among “early” stations of NBP 98–07 were routinely greater than 50 psu, especially in upper sections of the ice where ice temperatures were consistently below -7°C [Arrigo et al., 2003]. Considering that brines had likely been colder and therefore even more saline in the months prior to our investigation, it is unlikely that conditions in upper sections of the central pack would have allowed for significant photosynthesis. Support for this interpretation is provided by nutrient distributions and observations of POC and chlorophyll *a*. $s\Sigma\text{CO}_2$ deficits in upper ice layers were not accompanied by significant drawdown of NO_3^- or other nutrients (Figure 4). Low concentrations of chlorophyll *a* and POC in surface layers of the central pack (Figure 5) suggest that little photosynthesis had occurred in situ following ice formation during the previous autumn. Biological data from an investigation of microbial communities in the Ross Sea during autumn 1998 support this assumption [Garrison et al., 2003, 2005]. Depleted $\delta^{13}\text{C}_{\text{POC}}$ in upper sections of the central pack suggest that the bulk of existing POC may have been entrained during ice formation.

[23] The effect of abiotic processes on $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ of sea ice brines is complicated by the opposing isotopic fractionation effects associated with CaCO_3 precipitation and CO_2 degassing and by the degree of exchange with the atmosphere and seawater below. If we assume the brine is completely isolated and biological effects are negligible, we can consider only the temperature-dependent equilibrium fractionation between evolved $\text{CO}_2(\text{g})$ and HCO_3^- ($\epsilon_{\text{CO}_2(\text{g})-\text{HCO}_3^-}$) and between $\text{CaCO}_3(\text{s})$ and HCO_3^- ($\epsilon_{\text{CaCO}_3(\text{s})-\text{HCO}_3^-}$). At 0°C , $\epsilon_{\text{CO}_2(\text{g})-\text{HCO}_3^-}$ is -10.8‰ [Zhang et al., 1995]. Precipitation of ikaite has a much smaller fractionation effect in the opposite direction. Whiticar and Suess [1998] estimated a fractionation during the precipitation of ikaite ($\epsilon_{\text{CaCO}_3 \cdot 6\text{H}_2\text{O}(\text{s})-\text{HCO}_3^-}$) of between 1 and 2‰ at -1.4°C which is nearly identical to the observed fractionation during the precipitation of calcite at 0°C ($\epsilon_{\text{CaCO}_3(\text{s})-\text{HCO}_3^-} = +1.2\text{‰}$) [Romanek et al., 1992; Papadimitriou et al., 2004]. Degassing of ^{12}C -enriched CO_2 enriches the remaining ΣCO_2 pool in ^{13}C whereas precipitation of ^{13}C -enriched CaCO_3 phases depletes the ΣCO_2 pool; therefore, the overall isotopic effect depends on the fractional contribution of each process to overall ΣCO_2 reduction [Papadimitriou et al., 2004]. If the system is open to significant exchange with the atmosphere, Rayleigh dynamics no longer hold and kinetic fractionation effects associated with gas exchange must also be considered [Stiller et al., 1985; Papadimitriou et al., 2004].

[24] We can use the empirically determined fractionation factors described above to calculate the fractional contri-

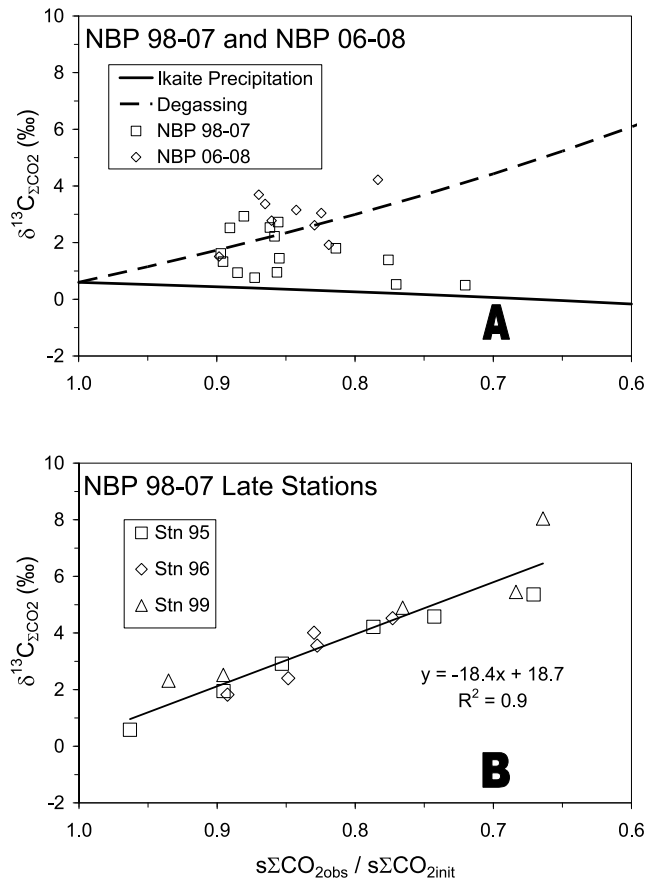


Figure 8. (a) Estimation of the fractionation factor (ε_i) due to abiotic processes based on $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ and $s\Sigma\text{CO}_2$ from extracted sea ice brines. Experimentally determined fractionation effects for abiotic processes are used to calculate theoretical isotopic composition of the remaining brine assuming Rayleigh behavior: $R_t/R_o = f^{(\alpha-1)}$, where R_o is the ratio of ^{13}C to ^{12}C of the initial ΣCO_2 pool divided by the ratio of ^{13}C to ^{12}C of the PDB standard, and R_t is the analogous ratio for the remaining $s\Sigma\text{CO}_2$ pool at time t ; f is the fraction of the $s\Sigma\text{CO}_2$ pool remaining, and α is the fractionation factor. Here ε for each process equals $(\alpha - 1) \times 1000$. Theoretical lines are calculated assuming an initial $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ of 0.6‰ and an initial $s\Sigma\text{CO}_2$ of $2234 \mu\text{mol kg}^{-1}$. Here $\varepsilon_{\text{CaCO}_3 \cdot 6\text{H}_2\text{O} - \text{HCO}_3^-} = +1.5\text{‰}$ for ikaite precipitation; $\varepsilon_{\text{CO}_2(\text{g}) - \text{HCO}_3^-} = -10.8\text{‰}$ for degassing based solely on equilibrium fractionation. Only data from samples with $s\Sigma\text{CO}_2$ deficits greater than $200 \mu\text{mol kg}^{-1}$ and brine salinities greater than 50 psu are shown. (b) Relationship between $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ and $s\Sigma\text{CO}_2$ from extracted sea ice brines from selected NBP 98–07 “late” stations.

contributions of CaCO_3 precipitation and degassing to inorganic carbon loss using the Rayleigh-type distillation equation of Barkan *et al.* [2001] after Papadimitriou *et al.* [2004]:

$$\delta^{13}\text{C}_{\Sigma\text{CO}_{2,t}} = \delta^{13}\text{C}_{\Sigma\text{CO}_{2,i}} + (f_{\text{degas}} \cdot \varepsilon_{\text{degas}} + f_{\text{precip}} \cdot \varepsilon_{\text{precip}}) \cdot \ln(s\Sigma\text{CO}_{2,t}/s\Sigma\text{CO}_{2,i}), \quad (1)$$

where $\delta^{13}\text{C}_{\Sigma\text{CO}_{2,t}}$ is the observed isotopic composition at time t , $\delta^{13}\text{C}_{\Sigma\text{CO}_{2,i}}$ is the initial isotopic composition estimated

from assumed winter seawater conditions, $s\Sigma\text{CO}_{2,t}$ is the observed salinity-normalized concentration at time t , $s\Sigma\text{CO}_{2,i}$ is the initial salinity-normalized concentration estimated from assumed winter seawater conditions, f_{degas} is the fractional contribution of inorganic carbon loss due to degassing, and f_{precip} is the loss due to carbonate precipitation. Using an $\varepsilon_{\text{degas}}$ of -10.8‰ for degassing and an $\varepsilon_{\text{precip}}$ of $+1.5\text{‰}$ for $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ precipitation, f_{precip} estimates ranged from 0 to 0.9 for all individual NBP 98–07 brine samples with a $s\Sigma\text{CO}_2$ drawdown greater than $200 \mu\text{mol kg}^{-1}$ and a brine salinity above 50 psu ($n = 15$); f_{precip} for the sample with the greatest drawdown ($625 \mu\text{mol kg}^{-1}$) was 0.9. f_{precip} for all NBP 06–08 brine samples satisfying the same criteria ranged from 0 to 0.4 ($n = 9$) with most samples indicating that degassing was solely responsible for $s\Sigma\text{CO}_2$ deficits. Uncertainty increases to infinity for segments with deficits less than $200 \mu\text{mol kg}^{-1}$. Given the complex and variable history of brine channel environments and the small number of segments that meet the above criteria for this calculation, our estimates should be viewed with caution. As mentioned above, we assume that segments with deficits greater than $200 \mu\text{mol kg}^{-1}$ are closed to the atmosphere and surrounding seawater and thus can be accurately described by Rayleigh-type equations. We also assume that photosynthesis is negligible at brine salinities above 50 psu and that salinities prior to sampling had been continuously too high (and in situ temperatures too low) for significant photosynthesis. Figure 8a shows the theoretical Rayleigh curves for degassing and precipitation of ikaite including all samples that meet the above criteria for both cruises. Rearranging equation (1) and making the same assumptions as above, we can estimate an effective fractionation factor for all abiotic processes in sea ice brines:

$$\varepsilon_i = (\delta^{13}\text{C}_{\Sigma\text{CO}_{2,t}} - \delta^{13}\text{C}_{\Sigma\text{CO}_{2,i}}) / [\ln(s\Sigma\text{CO}_{2,t}/s\Sigma\text{CO}_{2,i})], \quad (2)$$

where ε_i is the effective fractionation factor due to all abiotic processes; all other terms are the same as described for equation (1). We estimate an ε_i of $-7 \pm 6\text{‰}$ for NBP 98–07 and $-13 \pm 5\text{‰}$ for NBP 06–08.

[25] If degassing accounted for a significant fraction of the reduction of ΣCO_2 in cold upper ice, we would expect to find isotopic enrichment in upper ice relative to lower sections among “early” stations of NBP 98–07 in the cold interior pack ice and from similar stations during NBP 06–08. Indeed, $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ ranged from $+0.5$ to $+3.5\text{‰}$ in topmost sections at all such stations suggesting the possibility of isotopic enrichment due to degassing. Nevertheless, this range is nearly identical to the range in $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ in Ross Sea surface waters so it seems unlikely that degassing is a dominant control on $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ and hence isotopic enrichments in sea ice POC. However, isotopic enrichment may be partially offset or “masked” by remineralization of low $\delta^{13}\text{C}$ POC entrained during ice formation. On the basis of this limited quantitative approach, we suggest that precipitation of solid CaCO_3 phases such as ikaite and CO_2 degassing may both contribute to ΣCO_2 loss from Ross Sea sea ice brine, but we cannot conclusively state which is more important, what if any mineral phases are precipitating in the pack ice, and what conditions may favor one process over the other. A more quantitative analysis including measurement of alkalinity,

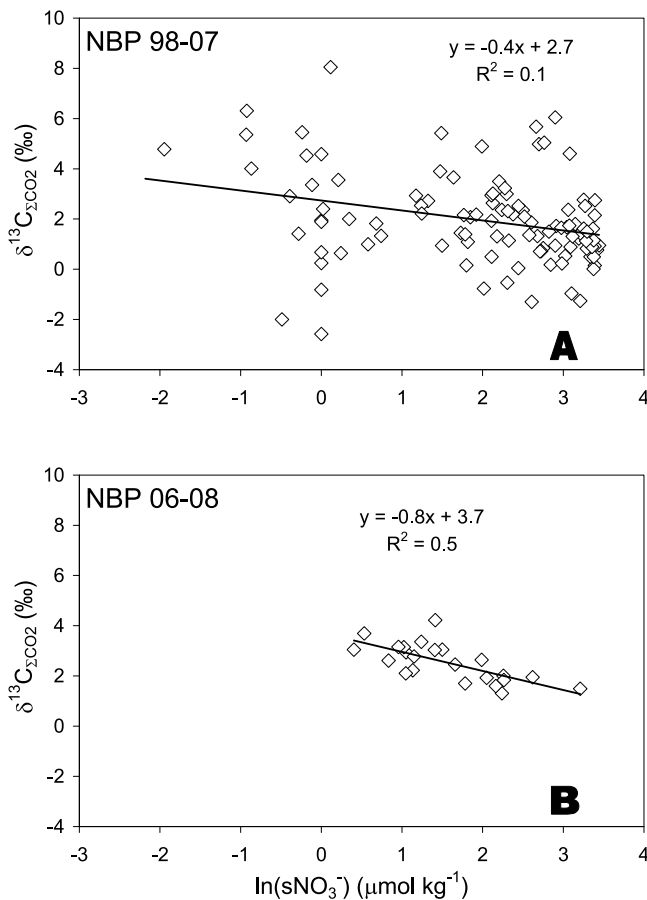


Figure 9. Relationship between $\ln(\text{sNO}_3^-)$ in $\mu\text{mol kg}^{-1}$ and $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ for (a) NBP 98–07 and (b) NBP 06–08; all isotopic values are in ‰ relative to PDB.

chemistry and amount of authigenic mineral phases, and dissolved gas ratios during the coldest winter months may provide more conclusive evidence of the influence of abiotic processes on the sea ice carbonate system. Such investigations might be justified given the potential impact of degassing/ CaCO_3 precipitation on regional carbon budgets. A simple calculation suggests that a ten percent loss of ΣCO_2 from the top meter (the approximate thickness of first year pack ice) of seawater degassed over a season from five percent of the Earth surface (the approximate global coverage of seasonal pack ice) yields an annual ocean-atmosphere CO_2 flux of 0.07 Pg C y^{-1} assuming the degassed CO_2 escapes through the ice to the atmosphere. For comparison, the net ocean-atmosphere CO_2 flux for the entire Southern Ocean south of 50°S has been estimated at $-0.47 \text{ Pg C y}^{-1}$ [Takahashi et al., 2002]. This estimate of degassed CO_2 flux from sea ice is purely speculative, but the observation of $\text{s}\Sigma\text{CO}_2$ deficits from sea ice demonstrates the potential importance of degassing and CaCO_3 precipitation within sea ice on regional carbon cycling in the ice-covered seas. While abiotic processes are assumed to be the dominant cause of $\text{s}\Sigma\text{CO}_2$ deficits in cold upper ice, most brine samples were from environments with salinities less than 50 psu suggesting that most environments with large $\text{s}\Sigma\text{CO}_2$ deficits have a mainly biological origin (Figures 2b and 3b).

4.2. Influence of Sea Ice Biology on ΣCO_2 and $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$

[26] We invoke photosynthetic drawdown of ΣCO_2 to explain enrichment of both $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ and $\delta^{13}\text{C}_{\text{POC}}$ in sea ice. The strong correlation between $\text{s}\Sigma\text{CO}_2$ deficits and $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ at “late” stations during NBP 98–07 (Figures 4 and 8b) coincident with other indicators of biological activity (i.e., elevated chlorophyll *a* and POC concentrations shown in Figure 5) suggests that biological uptake was a dominant control on $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ variability at productive stations and that uptake occurred at a rapid rate relative to replenishment from surrounding seawater. Further evidence of biological drawdown of $\text{s}\Sigma\text{CO}_2$ is provided by the relationship between $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ and brine sNO_3^- (Figure 9) where nutrient depletion was coincident with isotopic enrichment. The relationship between $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ in sea ice is not always straightforward. While many stations show significant $\delta^{13}\text{C}_{\text{POC}}$ enrichment, a large number of measurements fell toward the depleted end of the range ($< -25\text{‰}$) suggesting that a significant fraction of POM in the ice at less productive stations was entrained from surface seawater during ice formation and thus its isotopic composition does not entirely reflect in situ primary production. In addition, the low $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ end-member for sea ice brines is $\sim 3.0\text{‰}$ lower than values observed in the water column suggesting significant remineralization of ^{13}C -depleted POC can occur within isolated brine environments. Furthermore, it seems possible that the semisolid gelatinous nature of POM within the sea ice matrix may contribute to longer residence times for POC compared to brine ΣCO_2 which drains continuously through channels as air and sea ice temperatures increase. These factors may explain why ΣCO_2 depletion accounts for less than a third of observed POC at most stations (data not shown). Despite these complications, there is a strong positive correlation between POC concentration and $\delta^{13}\text{C}_{\text{POC}}$ for all stations from NBP 98–07 and NBP 06–08 (Figure 7). The overall range in $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ from sea ice brines (-2.6 to $+8.0\text{‰}$) compared to the range in surface seawater $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ ($+0.5$ to $+3.5\text{‰}$) suggests that biological drawdown of ΣCO_2 can account for up to a 7.5‰ enrichment in sea ice POC relative to water column POC in the most isolated/productive environments.

[27] The degree of isotopic fractionation by marine phytoplankton during photosynthetic carbon fixation (ε_p) is defined as the difference between $\delta^{13}\text{C}_{\text{CO}_{2(\text{aq})}}$ and $\delta^{13}\text{C}_{\text{POC}}$. A number of factors are known to influence ε_p including $[\text{CO}_{2(\text{aq})}]$, growth rate, species specific fractionation effects, and direct HCO_3^- uptake [Laws et al., 1995; Popp et al., 1999; Tortell et al., 1997, 2008; Cassar et al., 2004]. Estimation of ε_p for sea ice algae is complicated by the dynamic nature of sea ice microenvironments described above. Abiotic isotopic effects, brine drainage and seawater recharge, and remineralization of entrained POC and POC produced in situ can potentially offset or inflate enrichment of $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$. Previous studies also indicate that heterotrophic products are enriched in ^{13}C relative to algae, another potential complication in the interpretation of isotopic measurements from sea ice POC [Fischer et al., 1988].

[28] We estimate variability of ε_p within sea ice by comparing $\delta^{13}\text{C}_{\text{CO}_{2(\text{aq})}}$ and $\delta^{13}\text{C}_{\text{POC}}$ from highly productive “late” stations (stations 95–99) sampled during NBP 98–07.

$\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ can be calculated from measured $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ and temperature (T_k in Kelvin) using the equation $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})} = \delta^{13}\text{C}_{\Sigma\text{CO}_2} * 23.644 - 9701.5/T_k$ from *Burkhardt et al.* [1999] and the equation $\varepsilon_p = (\delta^{13}\text{C}_{\text{CO}_2(\text{aq})} - \delta^{13}\text{C}_{\text{POC}})/(1 + 0.001 * \delta^{13}\text{C}_{\text{POC}})$ after *Rau et al.* [2001] and *Kennedy et al.* [2002]. For the biologically active “late” stations of NBP 98–07, we calculate an ε_p of $\sim 11 \pm 2\%$ ($n = 14$) with a range from 5 to 14‰. This value is $\sim 8\%$ smaller in magnitude than the apparent ε_p for phytoplankton in open waters of the Ross Sea (R. B. Dunbar, unpublished data, 2009). *Kennedy et al.* [2002] observed a similar range in ε_p from 5 to 20‰ in sea ice environments from the Weddell Sea and no apparent correlation between ε_p and $[\text{CO}_2(\text{aq})]$. The sea ice algae ε_p estimated in this study is also similar to the ε_p estimated during upwelling conditions in Monterey Bay [*Rau et al.*, 2001] and off the coast of Peru [*Pancost et al.*, 1997]. *Rau et al.* [2001] observed that ε_p was relatively insensitive to $[\text{CO}_2(\text{aq})]$, growth rate, and cell size and suggested that active uptake of HCO_3^- could account for a lower ε_p than predicted by a purely diffusive CO_2 transport model; the lower ε_p results from the 9 to 11‰ offset between $\delta^{13}\text{C}_{\text{HCO}_3^-}$ and $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ due to the temperature-dependent fractionation presented above. If we assume that sea ice algae predominantly fix carbon derived from HCO_3^- at highly productive “late” stations instead of $\text{CO}_2(\text{aq})$ and that fractionation during transport and acquisition of HCO_3^- is negligible, we calculate an $\varepsilon_{\text{pHCO}_3^-}$ of $23 \pm 2\%$ ($n = 14$), closer to the $\varepsilon_{\text{pCO}_2(\text{aq})}$ observed in open water regions of the Ross Sea.

[29] Our estimation of ε_p assumes that abiotic fractionation effects at “late” NBP 98–07 stations were negligible, a reasonable inference given that temperature, brine salinity, and ΣCO_2 were close to seawater, and that enrichment coincided with evidence of in situ biological production (i.e., nutrient depletion, huge stocks of POC and chlorophyll *a*). We also note that the sensitivity of ε_p to $[\text{CO}_2(\text{aq})]$, growth rates, and cell size was not quantified in this study. Size fractionation studies from open water regions of the Southern Ocean have found significant (up to 8‰) enrichment in large organic particulates (derived mainly from diatoms) relative to fine particulates [*Trull and Armand*, 2001]. Given that the sea ice community was almost exclusively composed of diatoms as reported in the work of *Arrigo et al.* [2003], species composition and/or the cell surface/volume ratio could also contribute to a reduced sea ice algae ε_p .

5. Conclusions

[30] Stable carbon isotopic signatures in sea ice ΣCO_2 and POC reflect a dynamic combination of biotic and abiotic processes that grow increasingly complex as sea ice ages. ^{13}C -enrichment observed in both POC and ΣCO_2 suggests that microenvironments within the sea ice ecosystem remain isolated well into spring when rates of primary production remain high relative to rates of nutrient replenishment. Our results suggest high rates of primary production within brine environments close to the ice-water interface and also within interior communities of thick persistent pack ice as demonstrated by large accumulations of POC and dramatic reductions in $s\Sigma\text{CO}_2$. We find evidence for the influence of degassing and/or carbonate precipitation on the CO_2 system within some brine environments, particularly within cold hypersaline brines. At such sites, deficits in $s\Sigma\text{CO}_2$ of up to

625 $\mu\text{mol kg}^{-1}$ accompanied by variability in $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ and a lack of nutrient drawdown suggest that significant CaCO_3 precipitation and/or CO_2 degassing can occur in the upper ice during the austral winter. At sites exhibiting significant primary productivity, based on the relationships between $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$, $\delta^{13}\text{C}_{\text{POC}}$, and $s\Sigma\text{CO}_2$, we conclude that photosynthetic drawdown is the dominant control on isotopic enrichment of POC in sea ice relative to POC from the water column. Photosynthetic enrichment in $\delta^{13}\text{C}_{\Sigma\text{CO}_2}$ of up to 7.5‰ can explain some but not all of the isotopic enrichment of sea ice algal POC in the Ross Sea. Another significant factor may be much lower ε_p values for sea ice algae compared to ε_p for open water Ross Sea phytoplankton. The estimated average $\varepsilon_{\text{pCO}_2(\text{aq})}$ of 11‰ at biologically active sea ice stations presumably reflects the response of the sea ice algal community to greater levels of carbon drawdown than observed in the open water column. The source of this reduction may also be related to a shift from utilization of $\text{CO}_2(\text{aq})$ to active uptake of HCO_3^- [*Tortell et al.*, 1997, 2008; *Cassar et al.*, 2004] and/or the cell surface/volume ratio of sea ice algae relative to open water communities.

[31] Our results suggest that: (1) abiotic carbon system transformations related to the initial formation of sea ice as well as the continued cooling of brine-containing sea ice during the austral winter may result in precipitation of solid CaCO_3 phases and CO_2 release; (2) photosynthetic drawdown of brine ΣCO_2 contributes significantly to the overall enrichment observed in sea ice algal $\delta^{13}\text{C}$ values; (3) net photosynthetic fractionation factors for sea ice algae are lower and more variable than ε_p values for open water algal communities; and (4) extreme POC $\delta^{13}\text{C}_{\text{POC}}$ enrichments ($> -20\%$) are associated with, and limited to, sea ice environments, suggesting a strong utility for paleoenvironmental assessment of the presence/absence of sea ice.

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