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Constraining organic alkalinity in Antarctic sea ice brines containing high concentrations of dissolved organic matter: Current limitations and future directions

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Abstract. Organic alkalinity (OrgAlk), the component of total alkalinity (A_T) arising from non-inorganic species or uncharacterized bases, introduces error into calculated carbonate system parameters when A_T is used as an input. OrgAlk has been identified in Arctic sea ice brines with elevated dissolved organic carbon (DOC) concentrations, suggesting organic contributions to A_T may also be important in other sea ice environments. Antarctic sea ice brines are reported to contain higher DOC concentrations, yet estimating carbonate system components in Antarctic sea ice brines has relied on A_T-based calculations although no direct OrgAlk measurements exist for Antarctic sea ice brines and the potential magnitude of organic contributions to Antarctic brine A_T remains unknown. This study assesses potential OrgAlk contributions in Antarctic sea ice brines using published OrgAlk:DOC relationships as boundary conditions. Applying published OrgAlk:DOC relationships spanning 0.06-0.44 to Antarctic sea ice brine DOC concentrations produced a wide range of possible OrgAlk values, reinforcing the uncertainty of transferring DOC relationships across environments. These values are not interpreted as quantitative estimates of Antarctic sea ice brine OrgAlk, but rather as a sensitivity framework for evaluating plausible conditions. Sensitivity analyses indicate that unaccounted OrgAlk of this magnitude could affect calculated carbonate system parameters, including pCO_2, when A_T is used as an input parameter. These findings establish current uncertainty boundaries for OrgAlk in Antarctic sea ice brines, highlight a significant gap in Antarctic sea ice biogeochemistry and demonstrate the need for direct OrgAlk measurements to reduce uncertainty in Antarctic sea ice carbonate system calculations.

1 Introduction

The marine carbonate system is commonly characterized using four measurable parameters: Total alkalinity (A_T), dissolved inorganic carbon (C_T), partial pressure of CO_2 (pCO_2) and pH. Although A_T and C_T are frequently used parameters due to their quasi-conservative behavior with respect to temperature and pressure, measured A_T can be affected by the presence of conjugate bases of organic acids. These species interfere with titration measurements and lead to internal inconsistencies in

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carbonate system calculations when A_T is used as an input parameter because they are not typically accounted for in conventional carbonate system calculations (Kim and Lee, 2009). When A_T is used as an input parameter, unaccounted OrgAlk can bias calculated carbonate parameters including pH, pCO_2, and calcium carbonate ($CaCO_3$) mineral saturation states (Song et al., 2020; Hunt et al., 2011; Kuliński et al., 2014; Yang et al., 2015; Kerr et al., 2023a; Hu et al., 2020; Ko et al., 2025). This organic alkalinity (OrgAlk) component has been increasingly recognized as an important, but often poorly constrained, component across aquatic systems globally (Kerr et al., 2021; Song et al., 2020; Fong and Dickson, 2019; Song et al., 2023).

The contribution of OrgAlk varies widely among aquatic systems, reflecting spatial and temporal variability as well as differences in dissolved organic matter (DOM) and dissolved organic carbon (DOC) concentration, composition and biogeochemical processing. Efforts to measure OrgAlk have resulted in a range of published OrgAlk:DOC values spanning 0.06 to 0.44 across aquatic environments, including estuarine, coastal, tidal, marsh, groundwater and marine systems. Although OrgAlk:DOC values overlap among environments, the variability demonstrates that the relationship between DOC and OrgAlk is not universal globally and reflects differences in DOM source, transformation, seasonality and acid-base properties (Song et al., 2020). Consequently, OrgAlk:DOC relationships developed in one environment may not be directly transferable to other systems.

Recent measurements in Arctic sea ice brines and under-ice waters, nevertheless, provide the first direct constraints on OrgAlk in a sea ice environment. Rush et al. (2026) reported an average OrgAlk:DOC ratio of approximately 0.13 for brine from direct OrgAlk measurements (ranges: 0.10-0.17 in brine; 0.03-0.27 in under-ice water; 0.08-0.17 in open ocean water). These measurements demonstrated that unaccounted OrgAlk could contribute to uncertainty in carbonate system calculations in high-DOM sea ice environments, with calculated pCO_2 differences of up to 84 µatm when A_T was used as an input parameter and OrgAlk was not considered. These observations indicate that OrgAlk may represent an important component of carbonate system uncertainty in high-DOM sea ice environments. The extent to which Arctic-derived OrgAlk:DOC relationships apply to Antarctic sea ice, however, remains uncertain because differences in DOM sources, biological processes and physical conditions may influence organic acid-base composition.

Antarctic sea ice is a chemically distinct environment where OrgAlk may also be important. Although Arctic sea ice brines contain elevated DOC (Vancoppenolle et al., 2013 and therein such as Riedel et al., 2008), Antarctic sea ice brines can be considerably higher in DOC, with concentrations reaching up to 23.3 mmol L^{-1} (Thomas et al., 2001). Such high DOC concentrations within the Antarctic sea ice system result from its predominantly first-year ice (FYI) regime (Maksym and Stammerjohn, 2025) that is thinner, warmer, more saline and more mobile than Arctic sea ice (Thomas, 2025). Because most Antarctic sea ice is also not land bound, it contains larger, more connected, and more porous brine channels that promote microbial activity and facilitate autochthonous DOM accumulation. In contrast to the Arctic, Antarctic sea ice receives little terrestrial-derived DOM due to the absence of major riverine inputs (Stedmon et al., 2011). These differences in DOM source

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and composition suggest that Antarctic sea ice may possess organic acid-base characteristics distinct from those observed in Arctic, coastal and estuarine systems where most OrgAlk studies have been conducted. Despite these characteristics, OrgAlk has not been directly measured in Antarctic sea ice brines. Existing Antarctic carbonate chemistry datasets were primarily collected to characterize the inorganic carbonate system in a major CO_2 sink region (Delille et al., 2014; Yasunaka et al., 2023) rather than constrain OrgAlk.

This study assesses the potential contribution of OrgAlk in Antarctic sea ice to place this unknown measurement into the broader context of potential uncertainties in carbonate system calculations, including pCO_2 estimates and, ultimately, carbon fluxes. The Winter Weddell Outflow Study (WWOS) and Ice Station Polarstern (ISPOL) field campaigns provide a rare set of DOC together with A_T measurements from Antarctic sea ice brines, representing an exceptionally limited dataset for this highly concentrated organic matter environment. Because OrgAlk in Antarctic sea ice remains unknown, this study uses published OrgAlk:DOC relationships to establish boundary conditions for the potential magnitude of OrgAlk and evaluate the possible implications for pCO_2 calculations in Antarctic sea ice systems. The limitations associated with constraining OrgAlk in Antarctic sea ice brines are also assessed, highlighting the current uncertainty surrounding organic contributions to alkalinity in this environment. Rather than providing a quantitative estimate of Antarctic OrgAlk, this study establishes the range of potential OrgAlk conditions that need to be considered when interpreting carbonate system calculations, including pCO_2. The results identify key observational needs for future measurements required to better constrain OrgAlk and improve representation of Southern Ocean carbon cycling in regional and global climate models.

2 Methods

2.1 Study Site, Data Acquisition, and Calculations

The data used in this study were obtained from two Antarctic field campaigns, as shown in Fig. 1: Ice Station Polarstern (ISPOL) and Winter Weddell Outflow Study (WWOS). The objectives and findings of both expeditions have been extensively documented in the literature (see cruise reports: El Naggar et al., 2007; Lemke, 2009). Briefly, ISPOL involved a northward drift with a 10×10 km ice floe, comprised of first- and second-year ice in the western Weddell Sea during the spring to summer transition (November-January) of 2004-2005 (El Naggar et al., 2007). In contrast, WWOS collected samples from discrete ice stations consisting of first- and second-year ice in the northern and northwestern Weddell Sea during the winter to spring transition (August-October) of 2006 (Lemke, 2009). For both WWOS and ISPOL, the sea ice was generally greater than 70 cm thick and often greater than 100 cm thick.

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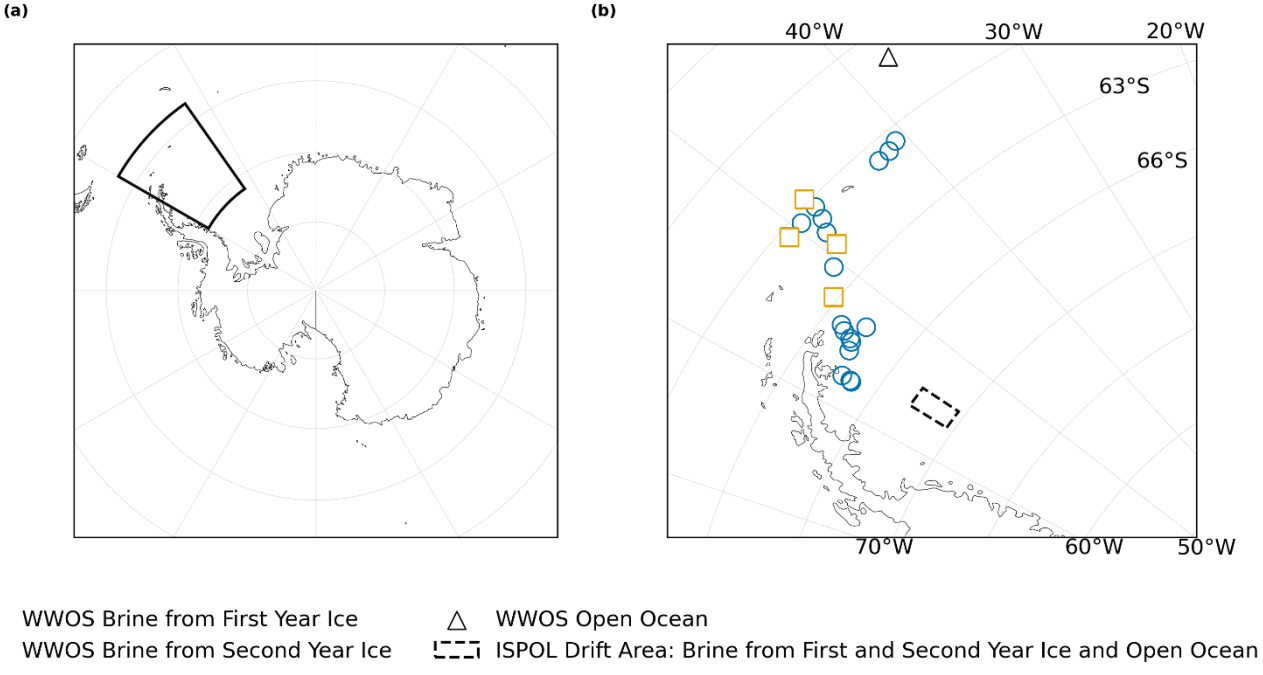

Figure 1. Study sites and labelled sample locations from the WWOS and ISPOL Antarctica field campaigns in the Weddell Sea area. Panel (a) is an Antarctic overview map showing the approximate location of the sampling region of both WWOS and ISPOL campaigns outlined with the black box. Panel (b) is a zoomed-in map of the sampling region. It shows WWOS brine sampling sites from first- and second-year ice, a CTD site, and the ISPOL drift area (dashed black box) that includes brine samples from first- and second-year ice and CTD casts. Details of sampling expeditions can be found in published literature and cruise reports (El Naggar et al., 2007; Lemke, 2009).

This study uses published measurements of A_T, DOC, and salinity from both expeditions (ISPOL: Papadimitriou et al. 2007 and 2009; WWOS: Norman et al. 2011; Papadimitriou et al. 2012). For both field campaigns, data were filtered to include only samples containing A_T and DOC. The resulting WWOS dataset comprised 103 brine samples from first year ice, 16 from second year ice, and 8 open ocean samples collected during CTD casts. The ISPOL dataset comprised 33 brine samples from first year ice, 2 from second year ice, and 18 open ocean samples collected during CTD casts. Although melt ponds and gaps were explored (ISPOL: Papadimitriou et al. 2009), they were excluded from the present analysis due to the markedly different physical and chemical properties. Rather this study focuses exclusively on sea ice brines obtained with the sack hole technique (described in detail in Papadimitriou et al. 2007).

Python was used for data processing and visualization of the observational data presented in this paper particularly with the pandas, cartopy, NumPy, Matplotlib, SciPy, and Seaborn packages.

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2.2 OrgAlk:DOC Sensitivity Analysis Approach

Potential OrgAlk was explored using a sensitivity analysis based on published OrgAlk:DOC ratios reported across diverse aquatic environments, including open ocean, estuarine, coastal, tidal, marsh and Arctic Ocean sea ice brine waters (Kuliński et al., 2014; Ulfsbo et al., 2015; Hammer et al., 2017; Lee et al., 2024; Song et al., 2020; Song et al., 2023; Rush et al., 2026). Reported OrgAlk:DOC ratios span a wide range across these environments, including 0.12-0.17 in the Baltic Sea (Kuliński et al., 2014; Ulfsbo et al., 2015; Hammer et al., 2017), an average of 0.09 in coastal surface waters of the East Sea (Lee et al., 2024), 0.07-0.28 in tidal and marsh waters of Waquoit Bay, Massachusetts (Song et al., 2020), 0.06-0.44 in estuarine waters of the southeastern China Sea (Song et al., 2023), 0.03-0.27 in Arctic Ocean waters and sea ice brines (Rush et al., 2026), and 0.08-0.12 in humic and fulvic acids (Hammer et al., 2017). The variability across these studies reflects differences in location, seasonality, and DOM composition. Here, the full published OrgAlk:DOC range was used to constrain the influence of OrgAlk in carbonate system studies in Antarctic sea ice brines. Specifically, sensitivity analysis in this investigation included the lower and upper bounds of published estuarine observations (0.06 and 0.44), the average Arctic sea ice brine relationship (0.13; Rush et al., 2026), and two intermediate values (0.25 and 0.35) to represent potential relationships within the published range.

3 Results

3.1 Existing Data- DOC Concentrations

Brine samples collected from first- and second-year ice on the WWOS and ISPOL campaigns had elevated DOC concentrations relative to seawater (Fig. 2; Table 1), consistent with previous observations of organic carbon enrichment within sea ice brine systems (Thomas et al., 2001). As reported for the WWOS and ISPOL campaigns, brine DOC concentrations ranged from 114 to 970 µmol kg^{-1} and from 23 to 343 µmol kg^{-1}, respectively. Comparatively, surface seawater DOC concentrations ranged from 14 to 76 µmol kg^{-1} during WWOS and from 29 to 66 µmol kg^{-1} during ISPOL (Papadimitriou et al. 2007; Norman et al. 2011). These seawater DOC values were within the typical ranges for Wedell Sea summer and winter conditions (Norman et al. 2011, and references therein).

Brine DOC varied substantially across salinity, ice type, and sampling location between the WWOS and ISPOL campaigns. WWOS generally exhibited higher DOC concentrations and higher values of associated biogeochemical parameters (see Norman et al., 2011) compared to ISPOL. Nevertheless, across both campaigns, brine DOC concentration ranges were elevated relative to surface seawater, indicating an accumulation of organic matter within sea ice brine systems, and overlapped with the DOC concentration range reported for estuarine systems where OrgAlk has been previously investigated.

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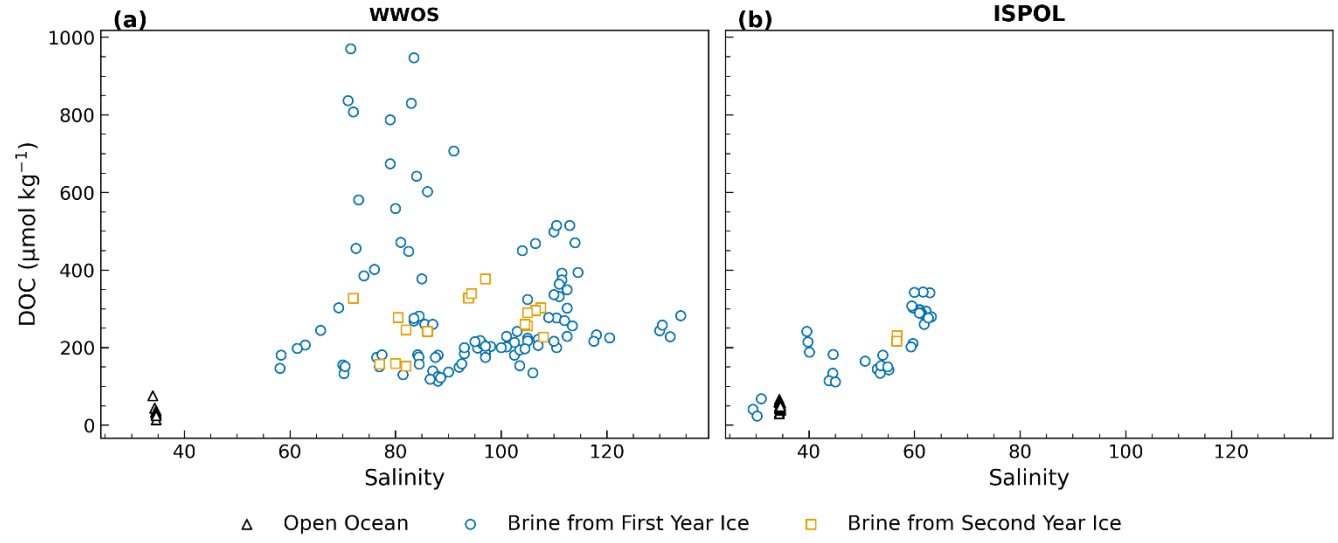

Figure 2. Dissolved organic carbon as a function of salinity in open ocean and brine samples from the WWOS and ISPOL Antarctica field campaigns in the Weddell Sea area.

Table 1. Measured salinity, DOC, and A_T in sea ice brine and open ocean samples from the WWOS and ISPOL Weddell Sea field campaigns, reported as mean ± standard deviation (range).

Campaign	Sample Type	n	Salinity	DOC (µmol kg^{-1})	A_T (µmol kg^{-1})
WWOS	Brine from First Year Ice	103	94.3±17.0 (58.1-134.0)	307±192 (114-970)	6081±1164 (3912-9054)
	Brine from Second Year Ice	16	92.6±12.6 (72.0-108.0)	265±67 (152-377)	5724±1100 (4091-7133)
	Open Ocean	8	34.5±0.2 (34.1-34.7)	36±18 (14-76)	2322±19 (2287-2338)
ISPOL	Brine from First Year Ice	33	52.7±10.4 (29.4-63.2)	212±90 (23-343)	3668±738 (1925-4369)
	Brine from Second Year Ice	2	56.7±0.1 (56.6-56.7)	224±11 (216-231)	3513±62 (3469-3556)
	Open Ocean	18	34.5±0.1 (34.3-34.6)	47±11 (29-66)	2336±14 (2293-2357)

3.2 Parameterized estimates of OrgAlk

The high DOC concentrations measured in these Antarctic sea ice brines suggest the potential for substantial OrgAlk contributions. Therefore, published OrgAlk:DOC ratios (0.06-0.44) spanning diverse marine environments were applied to

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parameterize OrgAlk as outlined in Sect. 2.2 (Fig. 3; Table 2). This range was originally determined in estuarine systems in a single study (Song et al., 2023) but encompasses values or ranges from other aquatic environments, including river, ground, marsh, tidal, coastal waters and Arctic sea ice brines (Rush et al., 2026; Lee et al., 2024, Song et al., 2020; Hammer et al., 2017; Ulfsbo et al., 2015; Kuliński et al., 2014). Given the limitations of OrgAlk:DOC relationships (*see* Sect. 4.2.1 below), these calculations provide sensitivity bounds rather than direct estimates of OrgAlk in Antarctic sea ice brines.

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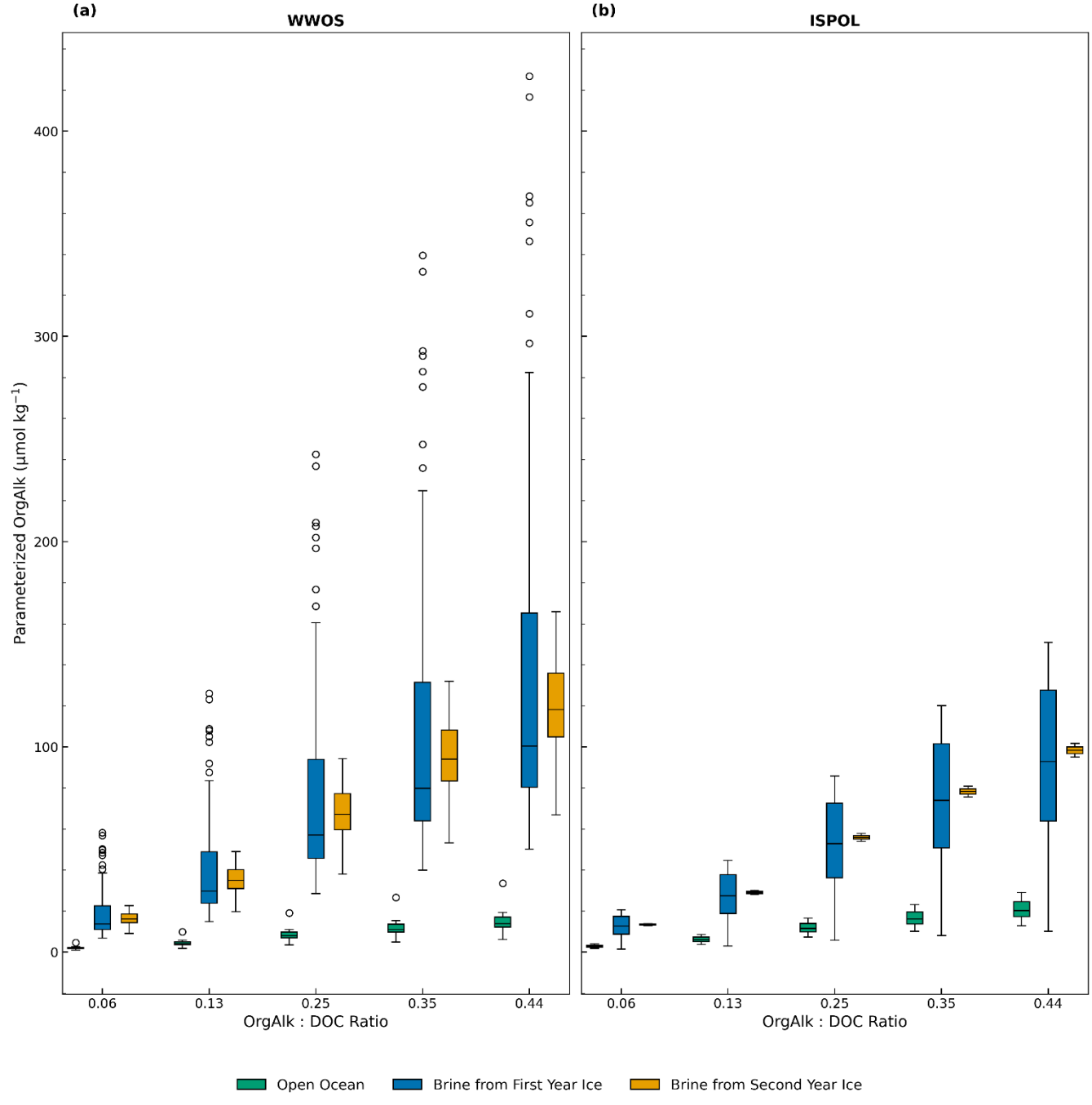

Figure 3. Parameterized OrgAlk across the OrgAlk:DOC ratio range reported in previous studies, applied to sea ice brine and open ocean samples from the WWOS and ISPOL Antarctica field campaigns. The horizontal line inside the box represents the median and the open circles represent outliers.

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Higher OrgAlk values were calculated for brines relative to seawater, directly reflecting elevated DOC concentrations in brine compared to seawater. At the lowest applied ratio (0.06), parameterized OrgAlk ranged from 1 to 58 µmol kg^{-1} in sea ice brine and 1 to 5 µmol kg^{-1} in seawater across both campaigns. At the highest applied ratio (0.44), parameterized OrgAlk ranged from 10 to 427 µmol kg^{-1} in sea ice brine and 6 to 33 µmol kg^{-1} in seawater for both campaigns. Across the full ratio range (0.06 v. 0.44), parameterized OrgAlk differed by a factor of approximately 7 to 8.

WWOS exhibited higher parameterized OrgAlk than ISPOL, again, owing to higher DOC concentrations in the WWOS campaign. Within WWOS, mean parameterized OrgAlk was higher in brine from first year ice compared to brine from second year ice, although median values were higher in brine from second year ice compared to brine from first year ice. For example, at the 0.13 OrgAlk:DOC ratio, average parameterized OrgAlk was 40 µmol kg^{-1} in brine from first year ice and 34 µmol kg^{-1} in brine from second year ice whereas median parameterized OrgAlk was 30 and 35 µmol kg^{-1}, respectively. This pattern was true across the range of OrgAlk:DOC relationships applied to WWOS brine samples. For ISPOL, both mean and median parameterized OrgAlk values were higher in brines from second year ice compared to brine from first year ice. ISPOL brine from second year ice, however, is based on a limited number of samples (n=2).

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Table 2. Parameterized OrgAlk across the OrgAlk:DOC ratio range reported in previous studies applied to sea ice brine and open ocean samples from the WWOS and ISPOL Antarctica field campaigns, reported as mean ± standard deviation (range, *median*).

OrgAlk:DOC Ratio			0.06	0.13	0.25	0.35	0.44
Descriptor			Low end of published range	Arctic sea ice brine (Rush et al., 2026)	Intermediate case within published range	Intermediate case within published range	High end of published range
Campaign	Sample Type	n	Parameterized OrgAlk (µmol kg^{-1})				
WWOS	Brine from First Year Ice	103	18±12 (7-58, *14*)	40±25 (15-126, *30*)	77±48 (29-243, *57*)	107±67 (40-340, *80*)	135±85 (50-427, *100*)
	Brine from Second Year Ice	16	16±4 (9-23, *16*)	34±9 (20-49, *35*)	66±17 (38-94, *67*)	93±23 (53-132, *94*)	116±29 (67-166, *118*)
	Open Ocean	8	2±1 (1-5, *2*)	5±2 (2-10, *5*)	9±5 (4-19, *8*)	13±6 (5-27, *11*)	16±8 (6-33, *14*)
ISPOL	Brine from First Year Ice	33	13±5 (1-21, *13*)	28±12 (3-45, *27*)	53±22 (6-86, *53*)	74±31 (8-120, *74*)	93±39 (10-151, *93*)
	Brine from Second Year Ice	2	13±1 (13-14, 13)	29±1 (28-30, *29*)	56±3 (54-58, *56*)	78±4 (76-81, *78*)	98±5 (95-102, *98*)
	Open Ocean	18	3±1 (2-4, *3*)	6±1 (4-9, *6*)	12±3 (7-17, 12)	16±4 (10-23, *16*)	21±5 (13-29, *20*)

3.3 The parameterized OrgAlk contribution to A_T

The resulting parameterized OrgAlk values were combined with measured A_T to assess the potential contribution of OrgAlk to A_T across WWOS and ISPOL samples (Fig. 4; Table 3). Over the range of OrgAlk:DOC ratios and resulting parameterized OrgAlk bounds, OrgAlk could represent a non-negligible fraction of A_T in sea ice brines. At the lowest applied ratio (OrgAlk:DOC = 0.06), the parameterized OrgAlk contribution to A_T ranged from 0.1 to 1.2 % in sea ice brine and 0.0 to 0.2 % in seawater across both field campaigns. At the highest applied ratio (OrgAlk:DOC = 0.44), the parameterized OrgAlk contribution to A_T ranged from 0.5 to 8.5 % in sea ice brine and 0.3 to 1.5 % in seawater for both campaigns. Across the full ratio range (OrgAlk:DOC = 0.06-0.44), the parameterized OrgAlk contribution to A_T differed by a factor of approximately 7 to 9. These differences in scaling between parameterized OrgAlk and its contribution to A_T reflect variability in measured A_T across samples.

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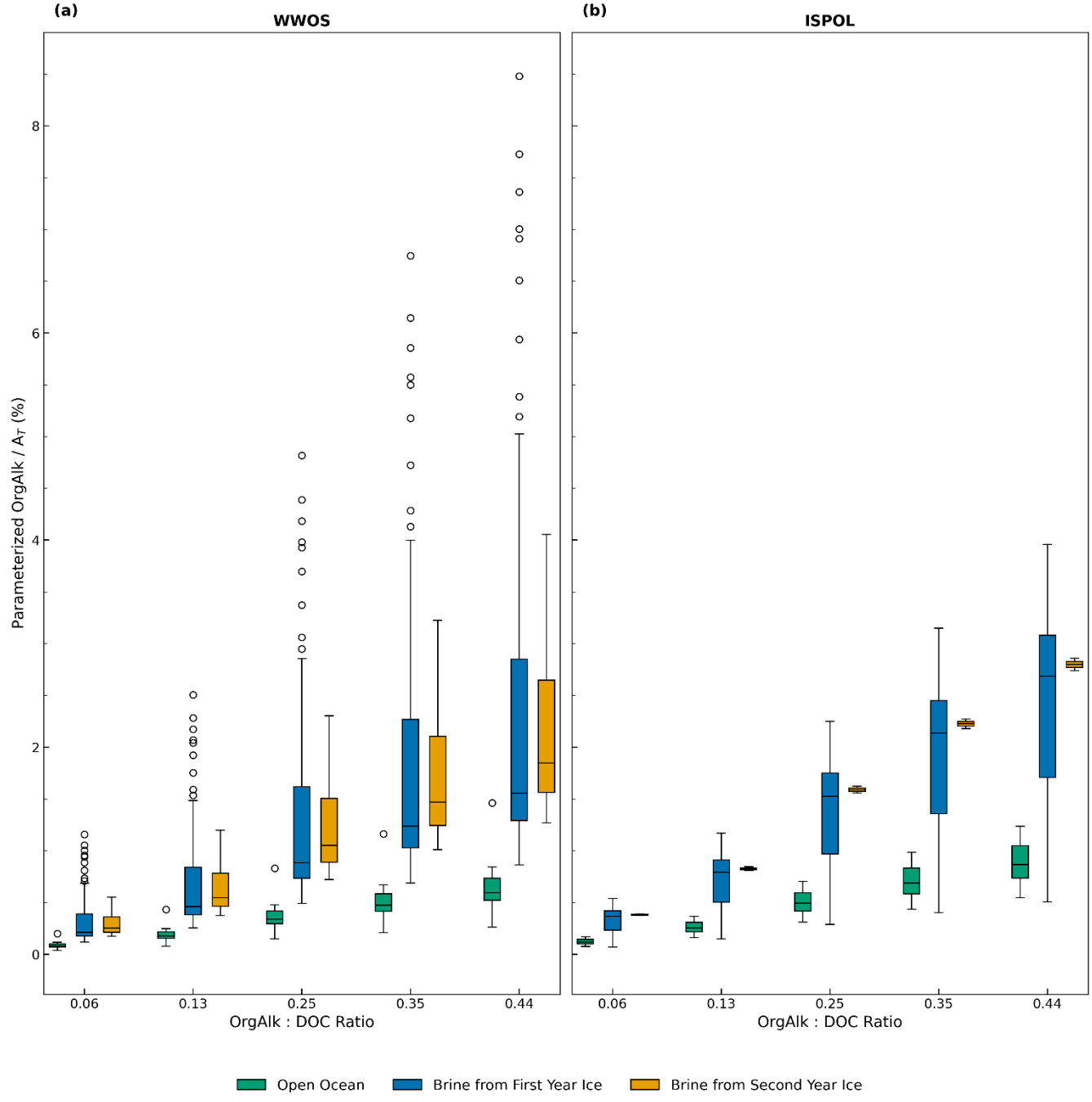

Figure 4. Parameterized OrgAlk as a fraction of total alkalinity across the OrgAlk:DOC ratio range reported in previous studies, applied to open ocean and brine samples from the WWOS and ISPOL Antarctica field campaigns. The horizontal line inside the box represents the median and the open circles represent outliers.

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Table 3. Parameterized OrgAlk as a fraction of A_T across the OrgAlk:DOC ratio range reported in previous studies applied to sea ice brine and open ocean samples from the WWOS and ISPOL Antarctica field campaigns, reported as mean ± standard deviation (range).

OrgAlk:DOC Ratio			0.06	0.13	0.25	0.35	0.44
Descriptor			Low end of published range	Arctic sea ice brine (Rush et al., 2026)	Intermediate case within published range	Intermediate case within published range	High end of published range
Campaign	Sample Type	n	Parameterized OrgAlk/ A_T (%)				
WWOS	Brine from First Year Ice	103	0.3±0.2 (0.1-1.2)	0.7±0.5 (0.3-2.5)	1.3±0.9 (0.5-4.8)	1.9±1.3 (0.7-6.7)	2.3±1.7 (0.9-8.5)
	Brine from Second Year Ice	16	0.3±0.1 (0.2-0.6)	0.6±0.2 (0.4-1.2)	1.2±0.5 (0.7-2.3)	1.7±0.6 (1.0-3.2)	2.1±0.8 (1.3-4.1)
	Open Ocean	8	0.1±0.0 (0.0-0.2)	0.2±0.1 (0.1-0.4)	0.4±0.2 (0.1-0.8)	0.5±0.3 (0.2-1.2)	0.7±0.4 (0.3-1.5)
ISPOL	Brine from First Year Ice	33	0.3±0.1 (0.1-0.5)	0.7±0.2 (0.1-1.2)	1.4±0.5 (0.3-2.2)	2.0±0.7 (0.4-3.1)	2.5±0.8 (0.5-4.0)
	Brine from Second Year Ice	2	0.4±0.0 (0.4-0.4)	0.8±0.0 (0.8-0.8)	1.6±0.0 (1.6-1.6)	2.2±0.1 (2.2-2.3)	2.8±0.1 (2.7-2.9)
	Open Ocean	18	0.1±0.0 (0.1-0.2)	0.3±0.1 (0.2-0.4)	0.5±0.1 (0.3-0.7)	0.7±0.2 (0.4-1.0)	0.9±0.2 (0.5-1.2)

4 Discussion

4.1 DOC Sources and Variability Considerations

Although DOC and other measured biogeochemical parameters (not shown) were higher in WWOS than ISPOL, Norman et al. (2011) detailed that the organic matter sources were likely the same for both campaigns: the initial parent seawater, the underlying seawater and the in-situ production from the sea ice biological assemblages. The higher parameters during WWOS are likely a function of seasonal ice growth and decay, with ISPOL sampling the spring to summer transition and WWOS sampling the winter to spring transition (Norman et al., 2011).

The organic matter composition of Antarctic sea ice differs from many environments where OrgAlk has previously been investigated: In contrast to the Arctic Ocean, where DOC often contains a substantial terrigenous (allochthonous) component

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associated with the large volume of riverine inputs (Stedmon et al., 2011), the Southern Ocean receives relatively little terrestrial organic matter and lacks a strong freshwater-derived organic carbon source. Antarctic sea ice is, therefore, dominated by autochthonous organic matter produced within the ice that delivers fresh, labile DOC and colored dissolved organic matter (CDOM) to surface waters (Norman et al., 2011; Fig. 2).

These characteristics distinguish the Antarctic sea ice brines from the coastal and estuarine environments where OrgAlk has been most extensively investigated. Even compared to the Arctic sea ice brine OrgAlk study, Antarctic sea ice brine represents a chemically distinct and largely unconstrained OrgAlk environment. Because OrgAlk depends not only on DOC concentration but also on the abundance and chemical properties of organic acid functional groups, the composition of Antarctic sea ice DOM represents a key uncertainty when applying existing approaches to constrain OrgAlk.

4.2 Limitations of Typical Methods to Constrain OrgAlk

Efforts to constrain the magnitude of OrgAlk and its influence on the carbonate system are challenging in Antarctic sea ice brines because existing approaches rely on assumptions that may not be applicable to this environment. Although OrgAlk has been investigated using multiple approaches, including DOC-based parameterizations and carbonate system overdetermination, each method requires information or relationships that are currently poorly constrained for Antarctic sea ice brines. Therefore, existing datasets cannot uniquely resolve the magnitude of OrgAlk or its influence on carbonate system calculations in this environment.

4.2.1 Limitations of OrgAlk:DOC Ratio Approaches

OrgAlk can be parameterized from DOC using published OrgAlk:DOC ratios. These relationships, however, vary spatially and temporally because chemical composition, not solely DOC concentration, controls the OrgAlk. Variability in DOM source, composition, degradation, and mixing produces differences in OrgAlk:DOC ratios among environments (Song et al., 2020). Seasonal variability in these relationships has also been observed in estuarine environments, demonstrating that even within a single system, a single OrgAlk:DOC ratio may not be representative across different conditions. Given the extreme seasonality of Antarctic sea ice, it is unlikely a single OrgAlk:DOC ratio would adequately address or represent the potential OrgAlk contribution. Therefore, as discussed by Song et al. (2020), accounting for OrgAlk contributions through DOC alone is inadequate.

These limitations are particularly relevant in Antarctic sea ice, where the DOC pool is dominated by autochthonous rather than allochthonous organic matter. Although previous OrgAlk studies have established OrgAlk:DOC ratios in high-DOC environments, most OrgAlk studies have focused on coastal, ground, marsh, tidal, estuarine, and oceanic waters (Kuliński et al., 2014; Ulfsbo et al., 2015; Hammer et al., 2017; Lee et al., 2024; Song et al., 2020; Song et al., 2023). The only existing

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investigation of high-DOC sea ice brines were examined in annual Arctic sea ice (Rush et al., 2026), where terrestrial organic matter is presumed to have had a strong influence.

Moreover, the salinity conditions of Antarctic sea ice brines differ substantially from those represented in previous OrgAlk studies. WWOS and ISPOL sea ice brine samples span a salinity range of 29-134 that extends well beyond the range investigated in Arctic sea ice brines (29-59) (Rush et al., 2026) and greatly exceeds the salinity conditions examined in estuarine and coastal environments (0-38) (Cai et al., 1998, Kuliński et al., 2014; Hernández-Ayon et al., 2007; Yang et al., 2015; Hammer et al., 2017; Song et al., 2020; Song et al., 2023; Kerr et al., 2023a; Kerr et al., 2023b; Hunt et al., 2025; Ko et al., 2016; Lee et al., 2024; Ko et al., 2025; Hunt et al., 2011). Therefore, applying OrgAlk relationships derived from these systems to Antarctic sea ice brines requires extrapolation beyond the environmental conditions in which those relationships were established.

Although Arctic sea ice brine provides the closest available comparison by sample type, transferring Arctic organic acid charge group concentrations, pKa distributions and OrgAlk:DOC relationships to Antarctic brines assumes similar relationships between DOC concentration, organic matter composition and proton-binding capacity. These assumptions remain untested, and thus, the markedly different DOC composition and salinity range of Antarctic sea ice brines limits the direct transferability of those relationships. Differences in organic matter source, molecular composition, and microbial production may influence the abundance and reactivity of the proton-binding functional groups that contribute to OrgAlk.

Furthermore, DOC concentration alone does not necessarily translate into a proportional contribution of reactive functional groups relevant to OrgAlk. Smaller particles and DOM can aggregate into colloidal structures via a variety of mechanisms (Kepkay, 1994) that can reduce the capacity of DOC to contribute to the OrgAlk pool. Consequently, estimating OrgAlk solely from DOC may over- or under-estimate the contribution of organic matter to A_T depending on the structure of the DOC pool.

With the available Antarctic sea ice brine historical data, however, the OrgAlk relationship with DOC was the only approach to explore first-order, potential OrgAlk contributions to titration alkalinity in this environment. To this end, we combined the range of published OrgAlk:DOC values with the historical data for DOC concentrations in Antarctic sea ice brines. Depending on the selected OrgAlk:DOC value, parameterized OrgAlk differed substantially (Fig. 3; Table 2). All OrgAlk:DOC values suggest that there should be substantial OrgAlk which could represent a significant component of A_T in Antarctic sea ice brines (Fig. 4; Table 3). Because DOC alone cannot uniquely constrain OrgAlk in Antarctic sea ice brines (Song et al. 2020), the above evaluation represents only potential scenarios. Direct measurements of OrgAlk to determine the concentrations of specific organic acid functional groups and characterize their acid-base properties are required to constrain the magnitude and variability of OrgAlk in Antarctic sea ice environments.

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4.2.2 Limitations to Applying the Carbonate System Overdetermination Approach

OrgAlk can also be estimated from the overdetermination of the carbonate system when measurements of more than the two carbonate system parameters are available. Under this approach, measured A_T is compared with A_T calculated from C_T and pH ($A_{T,calc}$). As formulated, $A_{T,calc}$ does not account for the contribution of organic proton acceptors, only for the inorganic protolytes in solution (Dickson et al., 2007). Any positive difference of measured A_T from $A_{T,calc}$ is termed excess alkalinity and is attributed to non-inorganic species. Excess alkalinity is considered conceptually identical to OrgAlk because both correspond to uncharacterized bases contributing to A_T during the A_T titration process (Ko et al., 2025).

Application of this approach to Antarctic sea ice brines, however, is limited by several uncertainties. First, historical Antarctic datasets rarely contain three or more high-quality carbonate system parameters required for overdetermination, and historical measurements are often accompanied by analytical limitations that complicate their ability to resolve OrgAlk assessments. In principle, reliable measurements of C_T and pH would be sufficient to accurately calculate pCO_2 and $CaCO_3$ saturation state, eliminating the need to rely on the A_T-C_T pair. High-quality pH measurements, however, are generally unavailable for Antarctic sea ice brines. Instead, A_T and C_T are the carbonate system parameters most commonly measured in sea ice brines. As reported in Brown et al. (2014), many Antarctic sea ice brine studies report only two measured carbonate parameters. Even in studies where three parameters were measured, the additional parameter was often excluded because of analytical uncertainty or used only for internal consistency checks. For example, ISPOL (Papadimitriou et al. 2007) and WWOS (Papadimitriou et al. 2012) described analytical methods for the measurement of A_T, C_T, and pH, but the pH data was not published due to measurement uncertainty. Any attempt to use these pH measurements for an overdetermination approach would only add additional uncertainty that would be propagated across calculations and confound the OrgAlk signal, further limiting the reliability of an OrgAlk overdetermination estimate. Consequently, existing datasets cannot uniquely constrain OrgAlk using overdetermination. Compared to other studies with more than two measured parameters, Fransson et al. (2011) and Delille et al. (2007) used A_T and pH carbonate system measurements to evaluate C_T or pCO_2 internal consistency, respectively. Where direct pCO_2 measurements have been compared with calculated values in Antarctic sea ice brines (Delille et al., 2007; Geilfus et al., 2014), differences of approximately ±25 and ±50 µatm, respectively, were reported. These discrepancies demonstrate that the uncertainty associated with poorly constrained carbonate system parameters is not negligible.

Second, carbonate system calculations for Antarctic sea ice brines require extrapolation beyond the validity ranges of commonly used acid-base equilibrium constants. The carbonic acid dissociation constants have been extended to -6 °C and a salinity of 100 in seawater-derived brines (Papadimitriou et al., 2018), but some sea ice brine samples from WWOS remain outside these ranges. An additional consideration is also the natural brine composition in-situ in comparison with that of the experimental brines, which preserved the seawater molar ratios of major ions. There is additional uncertainty from the dissociation constants of the other inorganic acid-base systems pertinent to A_T (borate, silicate, phosphate, ammonium), which

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have not been determined in brine matrices. These uncertainties introduce additional limitations into calculated carbonate system parameters. Ultimately, even if historical Antarctic datasets contained three high-quality carbonate parameters for overdetermination, the thermodynamic carbonate system calculations would still not be well-defined for sea ice brine conditions.

Finally, overdetermination provides only an estimate of the potential impact of OrgAlk on calculated carbonate system parameters and relies on a simplified representation of organic acid chemistry. The overdetermination approach indirectly estimates the potential contribution of OrgAlk from the difference between measured total alkalinity ($A_{T,meas}$) and alkalinity calculated from C_T and pH ($A_{T,calc}$). This excess alkalinity, however, cannot be interpreted as a direct measurement of OrgAlk because the magnitude of the residual depends on uncertainty in $A_{T,calc}$. As a result, comparing carbonate system calculations based on C_T-$A_{T,meas}$ and C_T-$A_{T,calc}$ provides a useful estimate of the potential influence of OrgAlk on calculated carbonate variables, but it remains only a hypothetical partitioning of inorganic and organic A_T pools rather than a direct representation of OrgAlk or its effect on carbonate system variables.

OrgAlk, however, does not act as an independent alkalinity pool that can be removed from, or added to, measured A_T. Rather, organic acid-base groups participate in proton-transfer reactions that proportionally alter the distribution of A_T among all contributing acid-base systems (Ko et al., 2016; Kerr et al., 2021). Therefore, within the current CO2SYS framework, the most appropriate approach for assessing the effects of OrgAlk on calculated carbonate system variables is to leave $A_{T,meas}$ unchanged and explicitly incorporate OrgAlk as an additional acid-base system inside the equilibrium calculations using the relevant organic acid charge group concentrations and associated pKa values. This approach differs from treating OrgAlk as an alkalinity contribution that can simply be added to or subtracted from $A_{T,meas}$ as in the hypothetical partitioning described above. Ultimately, however, a complete treatment of OrgAlk would require it to be explicitly defined and included within the A_T equation and parameterized in the same way as the inorganic acid-base systems in seawater, as a function of pH with the total concentration and pKa of the relevant organic acid-base systems. Organic acid concentrations and pKa distributions, however, remain largely unconstrained in Antarctic sea ice brines. The broad range of pKa values associated with OrgAlk across aquatic systems highlights this complexity (Hunt et al., 2025) and further limits the ability to uniquely quantify OrgAlk contributions to Antarctic sea ice carbonate system calculations.

4.3 An illustrative sensitivity analysis using an Arctic sea ice brine OrgAlk:DOC relationship

Because Antarctic OrgAlk cannot be constrained directly for these field campaigns, quantitative estimates of its effect on other carbonate system variables are not possible. Nevertheless, an illustrative sensitivity analysis provides context for why resolving OrgAlk is highly pertinent. Numerous studies have demonstrated that OrgAlk can influence carbonate system calculations when A_T is used as an input parameter. In systems with unaccounted OrgAlk, calculations using A_T and C_T will underestimate pCO_2 and overestimate pH. Calculations using A_T and pH as the input parameters can overestimate both pCO_2 and C_T. In

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Antarctic sea ice brine studies, A_T has frequently been employed as a carbonate parameter measurement in campaigns due to its quasi-conservative nature, compared to pH. It is, therefore, critical to ascertain the accuracy of calculated carbonate system variables given the reliance on A_T. Although this assessment is impossible with the Antarctic sea ice brine datasets, it is useful to perform a sensitivity analysis as context for the potential magnitude of these effects. This exercise does not represent an estimate of carbonate system measurements; rather, it demonstrates the range of possible carbonate system responses under a hypothetical OrgAlk scenario to inform future research.

For Arctic sea ice brines, Rush et al. (2026) reported directly measured OrgAlk values averaging approximately 16 µmol kg^{-1} (range: 10 to 22 µmol kg^{-1}). Correspondingly, the ΔpCO_2 (difference between OrgAlk adjusted A_T and non-OrgAlk adjusted A_T) values ranged from -8 to -24 µatm. For both Arctic brine and under-ice water, the directly measured OrgAlk average value was 12 µmol kg^{-1} (range: 2-24 µmol kg^{-1}) with corresponding ΔpCO_2 values ranging from -4 to -84 µatm. As a hypothetical scaling exercise, applying the Arctic sea ice OrgAlk relationship reported by Rush et al. (2026) of 0.13 µmol kg^{-1} μM^{-1} to Antarctic sea ice brine DOC concentrations would yield parameterized OrgAlk values averaging approximately 37 µmol kg^{-1} across WWOS and ISPOL samples (39 and 28 µmol kg^{-1} for WWOS and ISPOL, respectively) with a range of 3-126 µmol kg^{-1} (Table 2). These values are not interpreted as Antarctic OrgAlk estimates, as the transferability of Arctic OrgAlk relationships remains uncertain. Instead, they provide an illustrative range of potential OrgAlk magnitudes at one OrgAlk:DOC ratio that can be used to evaluate carbonate system sensitivity (Fig. 5).

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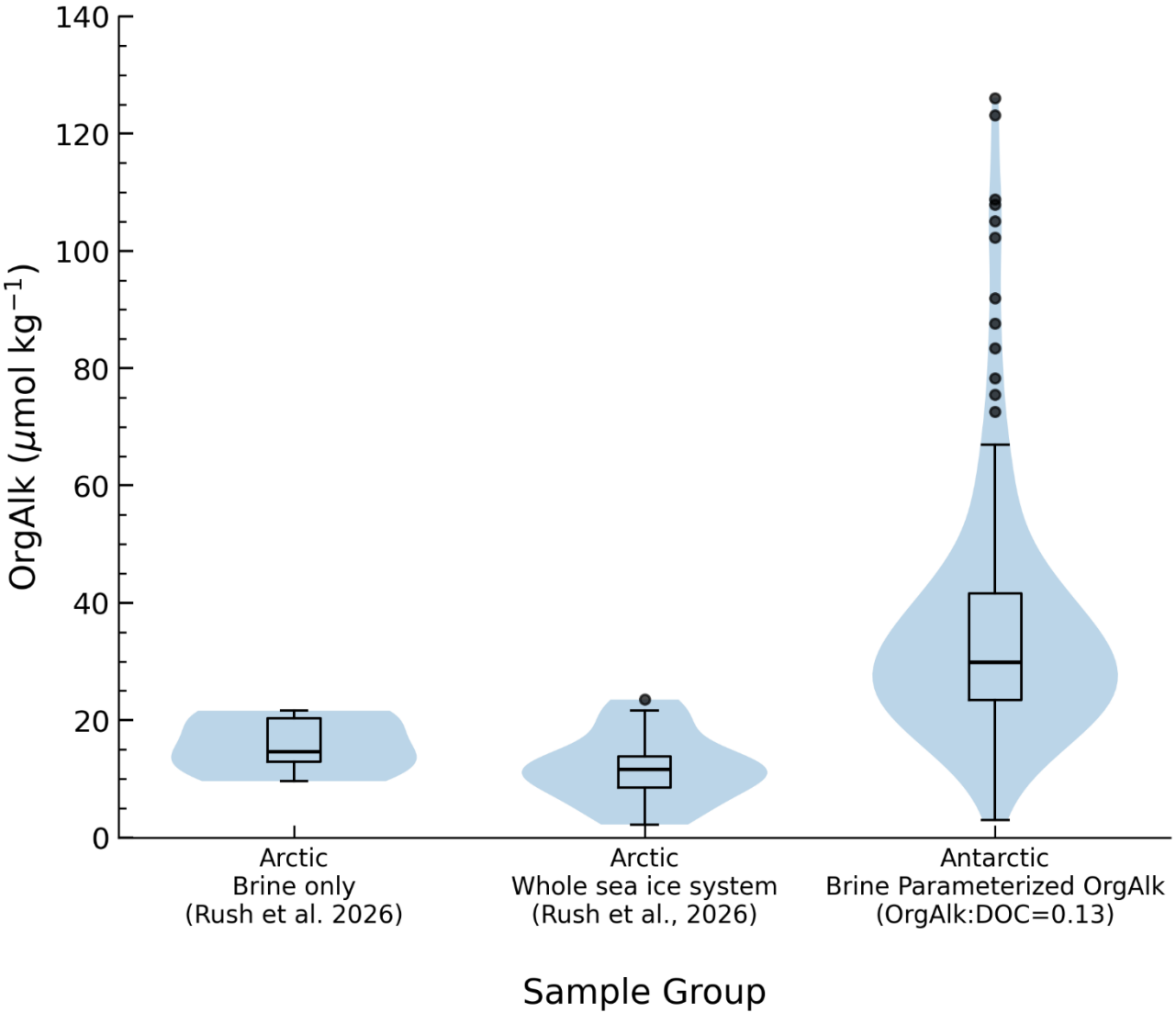

Figure 5. Distribution of measured Arctic and parameterized Antarctic sea ice OrgAlk values. Violin plots show the distribution of measured Arctic OrgAlk values from brines and the whole sea ice system (brine and under-ice water) and potential Antarctic brine OrgAlk values parameterized using an Arctic sea ice OrgAlk:DOC relationship of 0.13 (Rush et al., 2026). The boxplot horizontal line indicates the median and black dots indicate outliers. Arctic brine OrgAlk values (n = 5) had a mean of 16 ± 5 µmol kg⁻¹, median of 15 µmol kg⁻¹, and range of 10-22 µmol kg⁻¹. The Arctic sea ice system (n = 19) had a mean of 12 ± 6 µmol kg⁻¹, median of 12 µmol kg⁻¹, and range of 2-24 µmol kg⁻¹. Parameterized Antarctic brine OrgAlk values (n = 154) had a mean of 37 ± 22 µmol kg⁻¹, median of 30 µmol kg⁻¹, and range of 3-126 µmol kg⁻¹. Antarctic values represent one hypothetical sensitivity scenario and should not be interpreted as direct estimates of Antarctic sea ice OrgAlk.

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When comparing Arctic and Antarctic brines, the average parameterized OrgAlk in Antarctic brines was approximately 2.3 times the measured Arctic mean, with individual Antarctic values ranging from approximately 0.3 to 5.7 times the Arctic brine values. Comparing the broader sea ice system (brine and under-ice water), the average parameterized OrgAlk in Antarctic brines was approximately 3.1 times the Arctic mean, with individual values ranging from approximately 1.5 to 5.3 times the Arctic brine values (Fig. 5). Scaling the corresponding ΔpCO_2 from Arctic sea ice observations suggests that an unaccounted OrgAlk contribution of this magnitude will produce measurable shifts in calculated carbonate-system parameters. For brine only comparisons, the illustrative scaling corresponds to ΔpCO_2 ranges of approximately -2 to -7 µatm based on minimum scaling, -19 to -56 µatm based on average range scaling and -46 to -137 µatm based on maximum range scaling (Fig. 6). For the broader sea ice system, the corresponding illustrative ΔpCO_2 ranges extend from approximately -6 to -126 µatm (minimum-based), -12 to -259 µatm (average-based) and -21 to -441 µatm (maximum-based).

These calculations should not be interpreted as quantitative predictions of ΔpCO_2 in Antarctic sea ice brines. The applied OrgAlk:DOC relationship represents a first-order evaluation that requires validation because the relationship between DOC and OrgAlk in Antarctic sea ice remains unknown. The true OrgAlk contribution could vary depending on organic matter composition and its acid-base characteristics. These results solely demonstrate that uncertainty in uncharacterized OrgAlk may propagate into appreciable uncertainty in carbonate system parameter estimates derived from typical A_T-C_T input. Ultimately, this sensitivity analysis demonstrates that even modest OrgAlk contributions have the potential to influence carbonate system calculations and highlights the importance of directly constraining organic acid chemistry in Antarctic sea ice brines to quantify its potential effect on such calculations.

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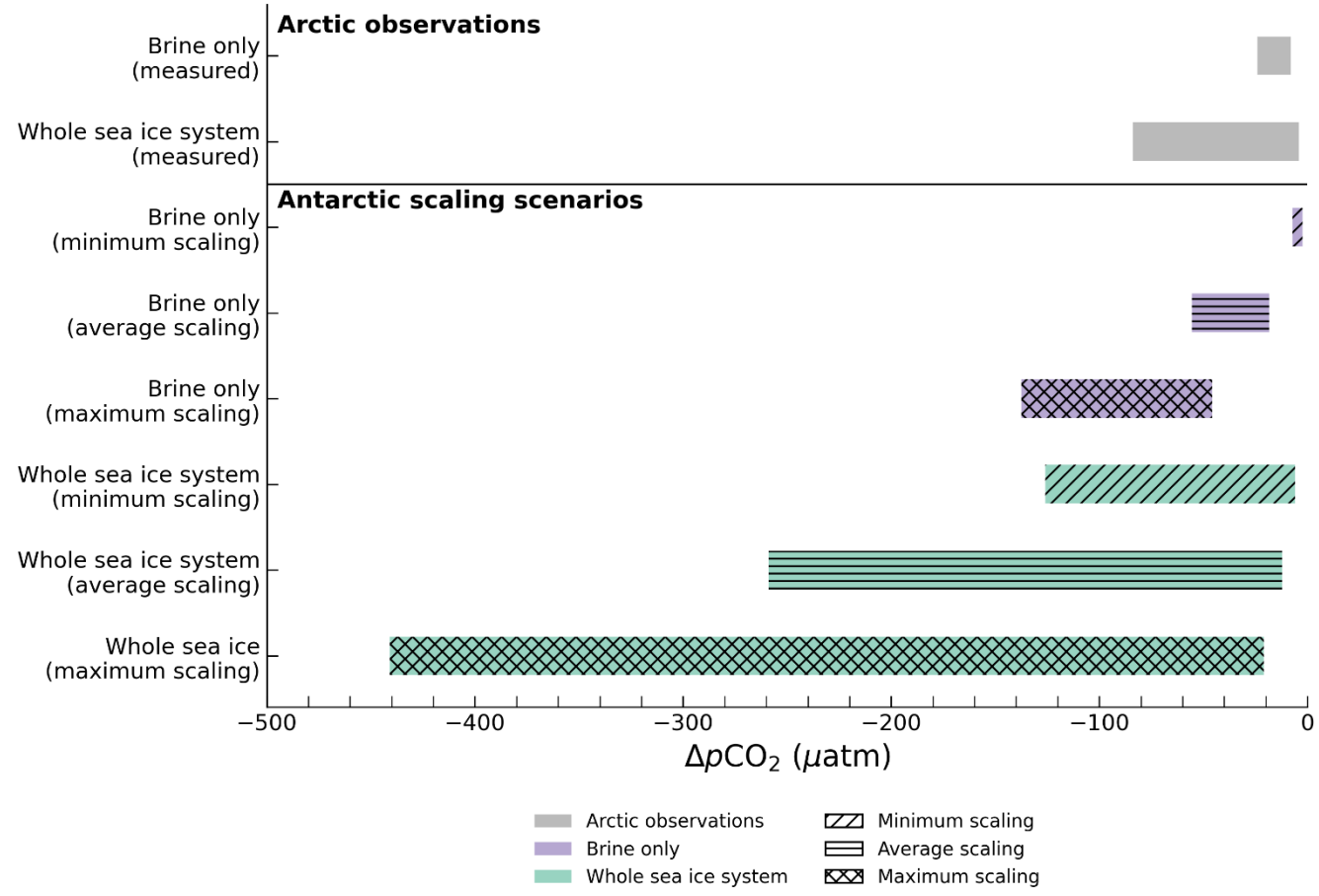

Figure 6. Potential ΔpCO_2 ranges applying the Arctic sea ice brine OrgAlk:DOC ratio to the Antarctic sea ice system. Shading and hatching patterns indicate solely brine and whole sea ice system extrapolations with minimum, average, and maximum range scaling.

4.4 Implications for constraining OrgAlk in Antarctic sea ice brine systems and recommendations for future work

There is a lack of information required to characterize the unique organic acid-base chemistry within Antarctic sea ice brines. Closing this gap requires direct measurements of organic acid concentrations and acid-base properties rather than additional parameterizations. Therefore, we recommend that future efforts prioritize direct measurements of OrgAlk in Antarctic sea ice brines. Direct measurements using the back titration approach will provide the ability to constrain OrgAlk and resolve the responsible organic acid charge groups. Coupling these measurements with molecular and chemical characterization of Antarctic sea ice brines would further elucidate the components of the DOC pool contributing to A_T. Although considerable work has investigated the role of extracellular polymeric substances (EPS) within the DOM pool in Antarctic sea ice (Underwood et al., 2010; Underwood et al., 2013; Deming and Collins, 2017), its contribution to, or its potential to correlate with, OrgAlk remains unknown. The EPS pool consists of high-molecular weight polymers containing proton-binding carboxyl

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and amino groups that could contribute to OrgAlk as they are released by sea ice bacteria and microalgae-binding microbial aggregates. Establishing whether EPS quantity or composition can serve as a more precise proxy for OrgAlk than bulk DOC could complement direct OrgAlk measurements by helping constrain historical data and improve parameterized OrgAlk values.

Direct OrgAlk measurements should also be integrated with observations that will allow overdetermination of the carbonate system of the Antarctic sea ice brine environment. Combining measured OrgAlk with three or more high-quality carbonate system input parameters would allow for a carbonate consistency assessment and provide a more rigorous evaluation of how OrgAlk influences A_T-based calculated carbonate parameters, such as pCO_2 and $CaCO_3$ mineral saturation states, in sea ice environments. Moreover, projected shifts from multiyear ice to first-year ice in the Arctic (Maslanik et al., 2011) suggest that Antarctic sea ice may serve as an important analog for future Arctic sea ice conditions, further emphasizing the need to constrain OrgAlk effects in Antarctic brine systems. To this end, additional work is also needed to improve carbonate system calculations under the extreme sea ice brine conditions. Although carbonic acid dissociation constants have been extended for sea ice brine salinity and temperature ranges (Papadimitriou et al., 2018), other equilibrium constants and salinity-dependent relationships remain insufficiently defined at such conditions. Improving these parameterizations would reduce uncertainty in carbonate system calculations to support an overdetermination approach.

5 Conclusions

OrgAlk represents a potentially important but poorly constrained and neglected component of the Antarctic sea ice carbonate system. This study establishes boundary conditions for potential OrgAlk contributions in Antarctic sea ice brines and demonstrates that existing approaches cannot uniquely resolve its magnitude. DOC-based parameterization of OrgAlk is limited because OrgAlk:DOC relationships vary with organic matter source, composition, environmental conditions, time, and space. Additionally, the ability to constrain OrgAlk in Antarctic sea ice brines remains limited by the scarcity of carbonate system measurements and the uncertainties associated with carbonate system calculations under extreme brine conditions.

Applying a full range of published OrgAlk:DOC relationships to historical Antarctic sea ice brine DOC concentrations provides useful sensitivity scenarios but does not provide a direct estimate of Antarctic sea ice brine OrgAlk. These scenarios illustrate that plausible OrgAlk contributions could represent a non-negligible fraction of A_T in sea ice brines and could influence calculated carbonate system parameters, such as pCO_2, when A_T is used as an input parameter. Accordingly, this analysis supports the idea that it is highly pertinent to consider and directly measure OrgAlk in Antarctic sea ice brines. Advancing our understanding of CO_2 uptake requires addressing such unresolved factors to constrain OrgAlk, refine our understanding of polar carbon cycling and enhance the biogeochemical models used to simulate CO_2 fluxes in the Southern Ocean and beyond.

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Data availability

This study's data is accessible as Thomas and Papadimitriou (2026) https://doi.org/10.1594/PANGAEA.990321 for ISPOL and Thomas and Papadimitriou (2026) https://doi.org/10.1594/PANGAEA.990477 for WWOS.

Author contributions

Samantha Glass: Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Visualization, Writing-original draft, Writing- reviewing and editing. **David Thomas:** Conceptualization, Data curation, Supervision, Writing-reviewing and editing. **Stathys Papadimitriou:** Data curation, Supervision, Writing-reviewing and editing. **Penny Vlahos:** Supervision, Writing-reviewing and editing.

Competing interests

The authors declare that they have no conflict of interest.

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References

Brown, K. A., Miller, L. A., Davelaar, M., Francois, R., and Tortell, P. D.: Over-determination of the carbonate system in natural sea-ice brine and assessment of carbonic acid dissociation constants under low temperature, high salinity conditions, Mar. Chem., 165, 36-45, http://dx.doi.org/10.1016/j.marchem.2014.07.005, 2014.

Cai, W.-J., Wang A, Y., and Hodson, R. E.: Acid-base properties of dissolved organic matter in the estuarine waters of Georgia, US, Geochim. Cosmochim. Acta., 62, 473-483, https://doi.org/10.1016/S0016-7037(97)00363-3, 1998.

Delille, B.: Inorganic carbon dynamics and air-ice-sea CO_2 fluxes in the open and coastal waters of the Southern Ocean (PhD Thesis), Univ. de Liège, Liège, France, 296 pp., 2006.

Delille, B., Jourdain, B., Borges, A. V., Tison, J.-L., and Delille, D.: Biogas (CO_2, O_2, dimethylsulfide) dynamics in spring Antarctic fast ice, Limnol. Oceanogr. 52, 1367-1379, https://doi.org/10.4319/lo.2007.52.4.1367, 2007.

Delille, B., Vancoppenolle, M., Geilfus, N.-X., Tilbrook, B., Lannuzel, D., Schoemann, V., Becquevort, S., Carnat, G., Delille, D., Lancelot, C., Chou, L., Dieckmann, G. S., and Tison, J.-L.: Southern Ocean CO_2 sink: The contribution of sea ice, J. Geophys. Res. Oceans., 119, 6340-6355, https://doi.org/10.1002/2014JC009941, 2014.

Deming, J. W., and Collins, R. E.: Sea ice as a habitat for Bacteria, Archaea, and viruses, in: Sea Ice, third ed., edited by: Thomas, D. N., John Wiley & Sons, Hoboken, NJ, 326-369, 2017.

Dickson, A. G., Sabine, C. L., and Christian, J.R. (Eds.): Guide to Best Practices for Ocean CO2 Measurements, PICES Special Publication 3, 2007.

El Naggar, S. E. D., Dieckmann, G., Haas, C., Schröder, M., and Spingler, M. (Eds): The Expeditions ANTARKTIS-XXII/1 and XXII/2 of the Research Vessel "Polarstern" in 2004/2005, Berichte zur Polar- und Meeresforschung (Reports on Polar and Marine Research), Bremerhaven, Alfred Wegener Institute for Polar and Marine Research, 551, 1-259, https://doi.org/10.2312/BzPM_0551_2007, 2007.

Fong, M. B., and Dickson, A. G.: Insights from GO-SHIP hydrography data into the thermodynamic consistency of CO_2 system measurements in seawater, Mar. Chem., 211, 52-63, https://doi.org/10.1016/j.marchem.2019.03.006, 2019.

https://doi.org/10.5194/egusphere-2026-5346
Preprint. Discussion started: 16 September 2026

Fransson, A., Chierici, M., Yager, P. L., and Smith Jr., W. O.: Antarctic sea ice carbon dioxide system and controls, J. Geophys. Res., 116, C12035, http://dx.doi.org/10.1029/2010JC006844, 2014.

Geilfus, N.-X., Tison, J.-L., Ackley, S. F., Galley, R. J., Rysgaard, S., Miller, L. A., and Delille, B.: Sea ice pCO_2 dynamics and air-ice CO_2 fluxes during the Sea Ice Mass Balance in the Antarctic (SIMBA) experiment- Bellingshausen Sea, Antarctica, The Cryosphere, 8, 2395-2407, https://doi.org/10.5194/tc-8-2395-2014, 2014.

Hammer, K., Schneider, B., Kuliński, K., and Schulz-Bull, D. E.: Acid-base properties of Baltic Sea dissolved organic matter, J. Mar. Syst., 173, 114-121, https://doi.org/10.1016/j.jmarsys.2017.04.007, 2017.

Hernández-Ayon, J. M., Zirino, A., Dickson, A. G., Camiro-Vargas, T., and Valenzuela-Espinoza, E.: Estimating the contribution of organic bases from microalgae to the titration alkalinity in coastal seawaters, Limnol. Oceanogr.: Methods, 5, 225-232, https://doi.org/10.4319/lom.2007.5.225, 2007.

Hu, X.: Effects of Organic Alkalinity on Seawater Buffer Capacity: A Numerical Exploration, Aquat. Geochem., 26, 161-178, https://doi.org/10.1007/s10498-020-09375-x, 2020.

Hunt, C. W., Salisbury, J. E., and Vandemark, D.: Contribution of non-carbonate anions to total alkalinity and overestimation of pCO_2 in New England and New Brunswick rivers, Biogeosciences, 8, 3069-3076, https://doi.org/10.5194/bg-8-3069-2011, 2011.

Hunt, C. W., Salisbury, J. E., Liu, X., and Byrne, R. H.: Organic alkalinity distributions, characteristics, and application to carbonate system calculations in estuarine and coastal systems, Limnol. Oceanogr., 70, 319-333, https://doi.org/10.1002/lno.12761, 2025.

Kepkay, P. E.: Particle aggregation and the biological reactivity of colloids, Mar. Ecol. Prog. Ser., 109, 293-304, https://doi.org/10.3354/meps111293, 1994.

Kerr, D. E., Brown, P. J., Grey, A., and Kelleher, B. P.: The influence of organic alkalinity on the carbonate system in coastal waters, Mar. Chem., 237, 104050, https://doi.org/10.1016/j.marchem.2021.104050, 2021.

Kerr, D. E., Grey, A., and Kelleher, B. P.: Organic alkalinity dynamics in Irish coastal waters: Case study in Rogerstown Estuary, Mar. Chem., 254, 104272, https://doi.org/10.1016/j.marchem.2023.104272, 2023a.

Kerr, D. E., Turner, C., Grey, A., Keogh, J., and Brown, P. J.: *OrgAlkCalc*: Estimation of organic alkalinity quantities and acid-base properties with proof of concept in Dublin Bay, Mar. Chem., 251, 104234, https://doi.org/10.1016/j.marchem.2023.104234, 2023b.

Kim, H.-C., and Lee, K.: Significant contribution of dissolved organic matter to seawater alkalinity, Geophys. Res. Lett., 36, L20603, https://doi.org/10.1029/2009GL040271, 2009.

Ko, Y. H., Lee, K., Eom, K. H., and Han, I.-S.: Organic alkalinity produced by phytoplankton and its effect on the computation of ocean carbon parameters, Limnol. Oceanogr., 61, 1462-1471, https://doi.org/10.1002/lno.10309, 2016.

Ko, Y. H., Shin, S.-H., Kim, S.-G., Park, M.-O., Seok, M.-W., Kim, M.-S., Lee, K., and Kim, T.-W.: Excess alkalinity and its impacts on pCO_2 estimation in coastal and estuarine waters of the Yellow Sea, Mar. Chem., 269, 104499, https://doi.org/10.1016/j.marchem.2025.104499, 2025.

https://doi.org/10.5194/egusphere-2026-5346
Preprint. Discussion started: 16 September 2026

Kuliński, K., Schneider, B., Hammer, K., Machulik, U., and Schulz-Bull, D.: The influence of dissolved organic matter on the acid-base system of the Baltic Sea, J. Mar. Syst., 132, 106-115, https://doi.org/10.1016/j.jmarsys.2014.01.011, 2014.

Lee, C.-H., Lee, K., Lee, J.-S., Jeong, K.-Y., and Ko, Y.-H.: Persistent organic alkalinity in the ocean, Geochim. Cosmochim. Acta., 387, 53-62, https://doi.org/10.1016/j.gca.2024.06.010, 2024.

Lemke, P. (Ed): The expedition of the research vessel "Polarstern" to the Antarctic in 2006 (ANT-XXIII/7), Berichte zur Polar- und Meeresforschung (Reports on Polar and Marine Research), Bremerhaven, Alfred Wegener Institute for Polar and Marine Research, 586, 1-147, https://doi.org/10.2312/BzPM_0586_2009, 2009.

Maksym, T., and Stammerjohn, S.: The rise and fall of Antarctic sea ice: Large-scale variability, in: Sea Ice: Its Physics, Chemistry, Biology, Geology and Societal Importance, fourth ed., edited by: Thomas, D. N., John Wiley & Sons, Hoboken, NJ, 215-260, https://doi.org/10.1002/9781394213764.ch06, 2025.

Maslanik, J., Stroeve, J., Fowler, C., and Emery, W.: Distribution and trends in Arctic sea ice age through spring 2011, Geophys. Res. Lett. 38, L13502,https://doi.org/10.1029/2011GL047735, 2011.

Norman, L., Thomas, D. N., Stedmon, C. A., Granskog, M. A., Papadimitriou, S., Krapp, R. H., Meiners, K. M., Lannuzel, D., van der Merwe P., and Dieckmann, G. S.: The characteristics of dissolved organic matter (DOM) and chromophoric dissolved organic matter (CDOM) in Antarctic sea ice, Deep-Sea Res. Part II: Top. Stud. Oceanogr., 58, 1075-1091, https://doi.org/10.1016/j.dsr2.2010.10.030, 2011.

Papadimitriou, S., Kennedy, H., Norman, L., Kennedy, D. P., and Thomas, D. N.: The effect of biological activity, $CaCO_3$ mineral dynamics, and CO_2 degassing in the inorganic carbon cycle in sea ice in late winter-early spring in the Weddell Sea, Antarctica. J. Geophys. Res., 117, C08011, https://doi.org/10.1029/2012JC008058, 2012.

Papadimitriou, S., Loucaides, S., Rérolle, V. M. C., Kennedy, P., Achterberg, E. P., Dickson, A. G., Mowlem, M., and Kennedy, H.: The stoichiometric dissociation constants of carbonic acid in seawater brines from 298 to 267 K, Geochim. Cosmochim. Acta., 220, 55-70, https://doi.org/10.1016/j.gca.2017.09.037, 2018.

Papadimitriou, S., Thomas, D. N., Kennedy, H., Kuosa, H., Krell, A., and Dieckmann, G. S.: Biogeochemical composition of natural sea ice brines from the Weddell Sea during early austral summer, Limnol. Oceanogr., 52, 1809-1823, https://doi.org/10.2307/4502337, 2007.

Papadimitriou, S., Thomas, D. N., Kennedy, H., Kuosa, H., and Dieckmann, G. S.: Inorganic carbon removal and isotopic enrichment in Antarctic sea ice gap layers during early austral summer, Mar. Ecol. Prog. Ser., 386, 15-27, https://doi.org/10.3354/meps08049, 2009.

Riedel, A., Michel, C., Gosselin, M., and LeBlanc, B.: Winterespring dynamics in sea-ice carbon cycling in the coastal Arctic Ocean, J. Mar. Sys., 74, 918e932, 2008

Rush, S., Lee, C.-H., Lee, K., Yoon, S.-H., and Vlahos, P.: Neglecting Organic Alkalinity Introduces Greater Error than Assuming Boron to Salinity Rations in Arctic Sea Ice Brine Carbonate System Calculations, Sci. Reps., 16, 9393, https://doi.org/10.1038/s41598-026-39719-6, 2026.

https://doi.org/10.5194/egusphere-2026-5346
Preprint. Discussion started: 16 September 2026

Song, S., Bellerby, R.G.J., Wang, Z.A., Wurgaft, E., and Li, D.: Organic Alkalinity as an Important Constituent of Total Alkalinity and the Buffering System in River-To-Coast Transition Zones, J. Geophys. Res. Oceans, 128, e2022JC019270, https://doi.org/10.1029/2022JC019270, 2023.

Song, S., Wang, Z.A., Gonneea, M.E., Kroeger, K.D., Chu, S.N., Li, D., and Liang, H.: An important biogeochemical link between organic and inorganic carbon cycling: Effects of organic alkalinity on carbonate chemistry in coastal waters influenced by intertidal salt marshes, Geochim. Cosmochim. Acta., 275, 123-139, https://doi.org/10.1016/j.gca.2020.02.013, 2020.

Stedmon, C. A., Thomas, D. N., Papadimitriou, S., Granskog, M. A., and Dieckmann, G. S.: Using fluorescence to characterize dissolved organic matter in Antarctic sea ice brines, J. Geophys. Res., 116, G03027, https://doi.org/10.1029/2011JG001716, 2011.

Thomas, D. N. (Ed.): Sea Ice: Its Physics, Chemistry, Biology, Geology and Societal Importance, fourth ed., John Wiley & Sons, Hoboken, NJ, https://doi.org/10.1002/9781394213764, 2025.

Thomas, D. N., Kattner, G., Engbrodt, R., Giannelli, V., Kennedy, H., Haas, C., and Dieckmann, G. S.: Dissolved organic matter in Antarctic sea ice, Ann.Glaciol., 33, 297-303, https://doi.org/10.3189/172756401781818338, 2001.

Thomas, D. N., and Papadimitriou, S.: Sea ice brine biogeochemistry measured during RV POLARSTERN cruise ANT-XXII aka ISPOL in 2004/05, PANGAEA [data set], v1, https://doi.org/10.1594/PANGAEA.990321, 2026.

Thomas, D. N., and Papadimitriou, S.: Sea ice brine biogeochemistry measured during RV POLARSTERN cruise ANT-XXIII/7 aka WWOS in 2006, PANGAEA [data set], v1, https://doi.org/10.1594/PANGAEA.990477, 2026.

Ulfsbo, A., Kuliński, K., Anderson, L. G., and Turner, D. R.: Modelling organic alkalinity in the Baltic Sea using a Humic-Pitzer approach, Mar. Chem., 168, 18-26, https://doi.org/10.1016/j.marchem.2014.10.013, 2015.

Underwood, G. J. C., Aslam, S. N., Michel, C., Niemi, A., Norman, L., Meiners, K. M., Laybourn-Parry, J., Paterson, H., and Thomas, D. N.: Broad-scale predictability of carbohydrates and exopolymers in Antarctic and Arctic sea ice, Proc. Natl. Acad. Sci. U.S.A., 110, 15734-15739, https://doi.org/10.1073/pnas.1302870110, 2013.

Underwood, G. J. C., Fietz, S., Papadimitriou, S., Thomas, D. N., and Dieckmann, G. S.: Distribution and composition of dissolved extracellular polymeric substances (EPS) in Antarctic sea ice, Mar. Ecol. Prog. Ser., 404, 1-19, https://doi.org/10.3354/meps08557, 2010.

Vancoppenolle, M., Meiners, K.M., Michel, C., Bopp, L., Brabant, F., Carnat, G., Delille, B., Lannuzel, D., Madec, G., Moreau, S., Tison, J.-L., and van der Merwe, P.: Role of sea ice in global biogeochemical cycles: emerging views and challenges, Quat. Sci. Rev., 79, 207-230, https://doi.org/10.1016/j.quascirev.2013.04.011, 2013.

Yang, B., Byrne, R. H., and Lindemuth, M.: Contributions of organic alkalinity to total alkalinity in coastal waters: a spectrophotometric approach, Mar. Chem., 176, 199-207, https://doi.org/10.1016/j.marchem.2015.09.008, 2015.

Yasunaka, S., Manizza, M., Terhaar, J., Olsen, A., Yamaguchi, R., Landschützer, P., Watanabe, E., Carroll, D., Adiwira, H., Müller, J. D., and Hauck, J.: An Assessment of CO_2 Uptake in the Arctic Ocean From 1985 to 2018, Global Biogeochem. Cy., 37, e2023GB007806, https://doi.org/10.1029/2023GB007806, 2023.