Erosion of carbonate-bearing sedimentary rocks may close the alkalinity budget of the Baltic Sea and support atmospheric CO₂ uptake in coastal seas

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High alkalinity values observed in coastal seas promote the uptake of CO₂ from the atmosphere. However, the alkalinity budget of coastal areas and marginal seas is poorly understood, even though some of the recently observed alkalinity enhancement can be ascribed to riverine fluxes and anaerobic processes in shelf sediments. Here, we investigate the alkalinity budget of the Baltic Sea to identify previously unrecognized alkalinity sources. We quantify the generation of alkalinity and dissolved calcium (Ca) in this marginal sea applying simple mass balance calculations. Using this approach, we identify alkalinity and Ca sources of approximately 324 Gmol yr^{-1} and 122 Gmol yr^{-1}, respectively, that cannot be ascribed to the riverine input. The magnitude of the Ca source suggests that a major fraction of the excess alkalinity (244 Gmol yr^{-1}) is induced by the dissolution of calcium carbonate (CaCO₃). A review of available field data shows that carbonate-bearing rocks at the coast and the seabed of the Baltic Sea are rapidly eroded and may provide sufficient CaCO₃ to close the Ca budget. Hence, dissolution of eroded CaCO₃ is the most likely source for the Ca enrichment observed in Baltic Sea water. This hypothesis is supported by mass accumulation rates of sediments derived from radioisotope data that are evaluated to derive a basin-wide rate of mud to muddy sand accumulation at the bottom of the Baltic Sea. The resulting value (139 Tg yr^{-1}) exceeds current estimates of riverine particle fluxes into the Baltic Sea by more than one order of magnitude and confirms that rates of till erosion are sufficiently high to account for the Ca and most of the alkalinity excess in Baltic Sea water. Finally, we show that deliberate addition of CaCO₃ to

sediments deposited in the Baltic Sea could neutralize significant amounts of CO_2 and help to achieve net-zero greenhouse gas emissions in the Baltic region.

Introduction

The global ocean takes up a significant fraction of anthropogenic CO_2 emissions (IPCC, 2021). Coastal seas contribute to CO_2 removal from the atmosphere by absorbing large amounts of CO_2 (Tsunogai et al., 1999; Thomas et al., 2005; Chen et al., 2013). Prior to the onset of industrialization, CO_2 was released from coastal seas (Bauer et al., 2013). However, the increase in atmospheric pCO_2 and coastal eutrophication induced a reversal of this flux such that coastal seas are now a major sink for anthropogenic CO_2 (Chen et al., 2013). The Baltic Sea shows a similar behavior. It released CO_2 prior to the onset of eutrophication (Omstedt et al., 2009), mainly driven by the mineralization of terrigenous organic matter, and has apparently acted as a net sink for atmospheric CO_2 over the last decades, even though the strong seasonal, interannual and spatial variability complicates the assessment of a basin-wide CO_2 budget (Thomas et al., 2010; Schneider et al., 2014; Gustafsson et al., 2015). Eutrophication in the widely stratified marginal sea led to enhanced CO_2 removal from the atmosphere and organic carbon deposition at the seabed while increasing atmospheric CO_2 levels amplified the air-sea disequilibrium (Kulinski et al., 2022).

Total alkalinity (A_T) of seawater provides buffering capacity and, therefore, supports CO_2 uptake from the atmosphere (Zeebe and Wolf-Gladrow, 2001). Many marginal seas are enriched in A_T with respect to normal seawater. The A_T enrichment has been ascribed to riverine A_T inputs and anaerobic degradation processes in shelf sediments that produce large amounts of A_T (Thomas et al., 2009). An A_T balance for the Baltic Sea, set up using the Baltic Sea Long-Term Large-Scale Eutrophication Model (BALTSEM), showed a mismatch between inflow and outflow and an A_T excess that could not be assigned to riverine A_T fluxes (Gustafsson et al., 2014; Gustafsson et al., 2019). This excess A_T (380 Gmol yr^{-1}) was partly attributed to pelagic and benthic redox processes generating internal A_T sources (40 Gmol yr^{-1}). However, a large unresolved A_T source remained (340 Gmol yr^{-1}) that could not be ascribed to any known process occurring in the Baltic Sea (Gustafsson et al., 2019, corrigendum). Moreover, A_T in Baltic Sea water has increased over the last decades for reasons that are largely unknown (Schneider et al., 2015; Müller et al., 2016). Müller et al. (2016) further showed that the A_T increase between 1995 and 2014 could compensate half of the expected pH change and almost all of the change in carbonate saturation which would be induced by the increase in atmospheric pCO_2 over the same period. Unidentified sources of A_T in the Baltic Sea and other coastal areas are major knowledge gaps in our understanding of the marine carbon cycle.

The poorly defined A_T balance of coastal seas is also relevant with respect to carbon dioxide removal (CDR) approaches such as enhanced weathering that have been proposed to mitigate global climate change and achieve net-zero CO_2 emissions (IPCC, 2018). In one of these techniques, olivine and other alkaline minerals are added to the coastal ocean and the shallow seabed where they dissolve and convert the greenhouse gas CO_2 into climate-neutral A_T (Hartmann et al., 2013; Feng et al., 2017; Montserrat et al., 2017; Fuhr et al., 2022). However, accounting of A_T production induced by alkaline mineral addition is only possible when natural source and sink terms are fully constrained. Hence, a better understanding of A_T dynamics is also required to validate future marine CDR approaches.

Here, we propose a new mechanism that can account for missing A_T sources in the Baltic Sea. We hypothesize that the erosion of carbonate-bearing sedimentary rocks at the coast and the bottom of the Baltic Sea provides $CaCO_3$ that is subsequently dissolved in surface sediments to deliver most of the unaccounted A_T. $CaCO_3$ dissolution is induced by corrosive bottom waters that are undersaturated with respect to aragonite and calcite in the deep basins of the Baltic Sea (Tyrrell et al., 2008) and by high rates of metabolic CO_2 production in Baltic surface sediments (Nilsson et al., 2019) that lower the pH and promote $CaCO_3$ dissolution close to the sediment-water interface. We also discuss how benthic $CaCO_3$ dissolution can be amplified by deliberate $CaCO_3$ addition and used as a new CDR approach.

In the following, we first set up A_T and Ca mass balances for the Baltic Sea. Subsequently, we review the available literature to assess possible $CaCO_3$ sources at the coast and at the seabed. Finally, we evaluate mass accumulation rates of muddy sediments across the Baltic Sea to validate our estimates on coastal and seabed erosion of $CaCO_3$-bearing glacial till.

Alkalinity and Ca balance of the Baltic Sea

In this section, we assess water and salinity fluxes for the Baltic Sea. Subsequently, these fluxes are applied to estimate sources for dissolved A_T and Ca in Baltic Sea water. Finally, we evaluate whether the derived Ca release can account for the previously observed unresolved A_T excess.

Water and salinity budget

The hydrography of the Baltic Sea depends on the water exchange with the Skagerrak and Kattegat (Figure 1), which is restricted by narrows and sills, and on river runoff into the Baltic Sea. Inflow of saline waters, riverine water fluxes and the mean salinity of brackish Baltic Sea water all show strong decadal variability with a cycle length of about 25 – 30 years (Meier and Kauker, 2003a; Meier and Kauker, 2003b; Meier, 2007; Mohrholz, 2018). However, no long-term trends in these water flows and salinities have been observed over the last century (Meier and Kauker, 2003a; Mohrholz, 2018). In the following, we, hence, calculate steady state mass balances for the Baltic Sea using fluxes and salinities averaged over the last 100 years (Table 1). The Baltic Sea is defined as the entire Baltic Sea basin excluding the Kattegat and Skagerrak. The seaward boundary is located between the Kattegat and the Baltic Sea where water is exchanged across the shallow Danish straits and the Øresund (Figures 1, 2).

In the long-term mean, saline water from the Kattegat enters the Baltic Sea (Figure 2) and low-saline water leaves the Baltic because of the freshwater surplus (Meier and Kauker, 2003a). Saltwater entering the Baltic Sea has a reduced salinity since saline North Sea water and brackish water masses leaving the Baltic Sea are mixed in the Skagerrak and Kattegat (Hordoir and Meier, 2010; Hordoir et al., 2013). The water flowing into the Baltic Sea from the Kattegat has a mean salinity of 17 (HELCOM, 1986) while the water flux has been estimated as 481 km^3 yr^{-1} (HELCOM, 1986). The mean freshwater flux into the Baltic Sea averaged over the period 1902 – 1998 amounts to 508 km^3 yr^{-1} where 444 km^3 yr^{-1} are delivered by continental runoff (rivers) and 64 km^3 yr^{-1} by net precipitation (precipitation - evaporation) across the Baltic Sea/atmosphere interface (Meier and Kauker, 2003a). Analysis of 78 rivers draining into the Baltic Sea shows that the mean salt content (total dissolved solids) of river water entering the Baltic is 0.15 g kg^{-1} as measured over the period 1996 – 2000 (Sun et al., 2017). The mean outflow of brackish water from the Baltic into the Kattegat corresponds to the sum of the water inflows ($F_W^{out} = 989 \ km^3 yr^{-1}$, Table 1). The mean salinity of this outflowing water mass (S_{out}) is calculated applying a salinity balance where the salt outflow is equal to the sum of salt inflows ($F_S^{out} = 8244 \ Tg \ yr^{-1}$):

$$S_{out} = F_S^{out} / F_W^{out} = 8.3 \tag{1}$$

The calculated salinity of brackish surface water leaving the Baltic Sea falls into the range of surface water salinities (<6 - 14) measured in the Danish straits and the Øresund (Hordoir et al., 2013).
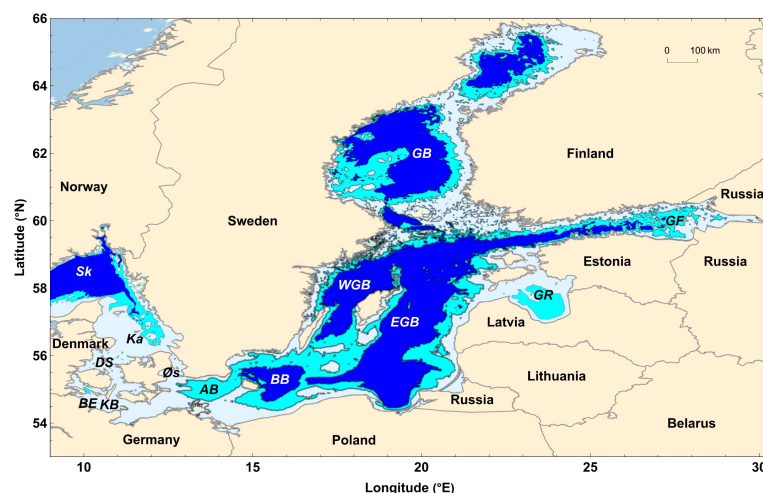
FIGURE 1
Map of the Baltic Sea and bordering countries. The map includes the Skagerrak (Sk), Kattegat (Ka), Danish straits (DS), Øresund (Øs), Kiel Bight (KB), Boknis Eck (BE), Arkona Basin (AB), Bornholm Basin (BB), Western Gotland Basin (WGB), Eastern Gotland Basin (EGB), Gulf of Riga (GR), Gulf of Finland (GF), and Gulf of Bothnia (GB). Colors indicate water depths (blue: > 65 m, cyan: 65 – 30 m, light blue: 0 – 30 m). The map was produced using Mathematica 13.

TABLE 1 Long-term mean budget of salinity, alkalinity and Ca in the Baltic Sea.

	F_W in km^3 yr^{-1}	S in g kg^{-1}	A_T in mmol kg^{-1}	Ca in mmol kg^{-1}	F_S in Tg yr^{-1}	F_A in Gmol yr^{-1}	F_{Ca} in Gmol yr^{-1}
Water inflow	481	17	1.91	5.37	8177	919	2583
Water outflow	989	8.3	1.71	3.00	8244	1691	2967
River water	444	0.15	1.01	0.59	67	448	262
Net precipitation	64	0	0	0	0	0	0
Outflow - inflow	0	–	–	–	0	324	122

Fluxes of water (F_W), salinity (F_S), alkalinity (F_A) and dissolved Ca (F_{Ca}) are calculated to determine the mass balances (outflow - inflow) for alkalinity and dissolved Ca in the Baltic Sea.

Alkalinity balance

A_T in mean river water (A_T^{riv}) entering the Baltic Sea is calculated as 1.01 mmol kg^{-1} applying bicarbonate concentrations and river water fluxes reported in Sun et al. (2017). A_T of brackish outflow water (A_T^{out}) is derived from the linear relation between A_T and S measured in the saline part of the central Baltic Sea (Gustafsson et al., 2014):

$$A_T^{out} = 25.966\ S_{out} + 1492.5 = 1708\ \mu mol\ kg^{-1}$$

$$= 1.71\ mmol\ kg^{-1} \qquad (2)$$

Water entering the Baltic Sea is assumed to be composed of seawater with a salinity of 35 ($S_{sw} = 35$) and brackish outflow waters ($S_{out} = 8.3$) that are mixed in the Skagerrak and Kattegat. The seawater fraction (f_{sw}) of this two-component mixture is calculated as:

$$f_{sw} = \frac{S_{in} - S_{out}}{S_{sw} - S_{out}} = 0.326 \qquad (3)$$

Seawater with $S_{sw} = 35$ entering the Skagerrak and Kattegat has an alkalinity of $A_T^{sw} = 2.33\ mmol\ kg^{-1}$ (Anderson and Dyrssen, 1981). A_T of the inflowing water results as:

$$A_T^{in} = f_{sw}A_T^{sw} + (1 - f_{sw})\ A_T^{out} = 1.91\ mmol\ kg^{-1} \qquad (4)$$

A_T fluxes are calculated by multiplying A_T concentrations and the corresponding water fluxes (Table 1). The A_T source derived from the difference of A_T outflow and inflow fluxes results as $O–I–A_T = 324\ Gmol\ yr^{-1}$ (Table 1). This value is rather close to the A_T excess derived from the BALTSEM model (380

Gmol yr^{-1}, Gustafsson et al., 2019). This correspondence suggests that the simple geochemical mass balance approach applied above yields realistic estimates for the long-term mean of O-I-A_T even though the real physical system simulated in BALTSEM is far more complex and dynamic than our simple modeling approach (Figure 2, Table 1).

Ca balance

In the following, the mass balance approach developed above is applied for Ca dissolved in Baltic Sea water. The dissolved Ca concentration in mean river water (Ca_{riv}) entering the Baltic Sea is calculated as 0.59 mmol kg^{-1} applying Ca concentrations and river water fluxes reported in Sun et al. (2017). Ca of brackish outflow water (Ca_{out}) is derived from the linear relation between Ca (in g kg^{-1}) and chlorinity (Cl in g kg^{-1}) reported for the saline part of the central Baltic (Kremling and Wilhelm, 1997):

$$Ca_{out} = 0.0202\ Cl_{out} + 0.0279 \qquad (5)$$

where salinity and chlorinity (Cl in g kg^{-1}) of Baltic Sea water are related as (Millero, 1978):

$$S = 0.045 + 1.8042\ Cl \qquad (6)$$

Applying Eq. (5) and (6) results in a Ca_{out} value of 3.0 mmol kg^{-1}. Ca in seawater with S = 35 entering the Skagerrak and Kattegat is set to $Ca_{sw} = 10.28\ mmol\ kg^{-1}$ (Chester, 2000). The Ca concentration in water flowing into the Baltic Sea from the Kattegat results as:
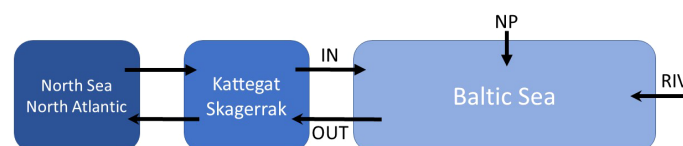

FIGURE 2
Fluxes considered in the water and dissolved species budgets of the Baltic Sea. IN: Fluxes from the Kattegat into the Baltic Sea across the Danish straits and the Øresund. OUT, Fluxes from the Baltic Sea to the Kattegat; NP, Net precipitation in the Baltic Sea; RIV, Riverine fluxes into the Baltic Sea.

$$Ca_{in} = f_{sw}Ca_{sw} + (1 - f_{sw})\, Ca_{out} = 5.37 \; mmol \; kg^{-1} \qquad (7)$$

Ca fluxes are calculated by multiplying Ca concentrations and the corresponding water fluxes listed in Table 1. The Ca source derived from the difference of outflow and inflow fluxes results as O-I-Ca = 122 Gmol yr^{-1}. Considering that two mol of A_T are generated by the dissolution of one mol of $CaCO_3$, O-I-Ca is sufficiently large to explain a major fraction of O-I-A_T *via* carbonate dissolution (244 Gmol yr^{-1}). The difference between O-I-A_T (324 Gmol yr^{-1}, Table 1) and A_T attributed to $CaCO_3$ dissolution (244 Gmol yr^{-1}) might be largely explained by redox-related processes in the Baltic Sea (e.g. pyrite burial, nitrogen cycling) that may generate significant amounts of A_T (Gustafsson et al., 2014; Gustafsson et al., 2019).

Uncertainties in flux estimates

In the calculations above, we assume for simplicity that the density of all considered water masses is equal to 1 g cm^{-3}. Moreover, we assume that measured salinity values correspond to salt concentrations in g kg^{-1}. Both assumptions are, strictly speaking, not correct (Millero and Kremling, 1976; Millero, 1978). However, the error introduced by these simplifications is probably negligible compared to the more relevant uncertainties discussed in the following paragraph.

In the mass balance calculations above, we apply a water flux of $F_W^{in} = 481 \; km^3 yr^{-1}$ and a salinity of $S_W^{in} = 17$ for the saline water masses entering the Baltic Sea (HELCOM, 1986). However, other estimates are available for these parameter values. Hence, the Arkona Basin can be used to assess the inflow of saltwater, since all saline water masses entering the Baltic Sea pass through this western-most Baltic basin (Figure 1). The mean inflow of saline deep water in the Arkona Basin amounts to 685 km^3 yr^{-1} when averaged over the last century (Gustafsson, 2001). The mean salinity of this water mass is 14.3 and affected by mixing with salt-depleted water masses within the Baltic Sea (Gustafsson, 2001). The inflow into the basin has been estimated as only 598 km^3 yr^{-1} with a mean salinity of 13.9 over the period 1979 – 1990 (Lehmann and Hinrichsen, 2002). The latter inflow and salinity estimates are somewhat lower than the long-term mean since the period 1979 – 1990 was marked by an unusually low inflow intensity (Lehmann and Hinrichsen, 2002). A much higher water influx from the North Sea (1359 km^3 yr^{-1}) has been estimated within the BALTEX program for the period 1979 – 2002 (Omstedt and Nohr, 2004). Unfortunately, the mean salinity of the inflowing water has not been determined in that program. The higher water flux estimated in BALTEX probably includes water fluxes that are not recorded in the Arkona Basin since the saltwater may be rapidly mixed with brackish surface water in the Skagerrak and Kattegat and transported back into the North Sea by outflowing water before it can enter the Baltic Sea.

In the following, we apply $F_W^{in} = 685 \; km^3 yr^{-1}$ and $S_W^{in} = 14.3$ (Gustafsson, 2001) and repeat our mass balance calculations (Eq. 1 - 7) to assess the magnitude of the A_T and Ca imbalance (outflux - influx) for this alternative parameterization. The calculations yield $O–I–A_T = 323 \; Gmol \; yr^{-1}$ and $O–I–Ca = 99 \; Gmol \; yr^{-1}$. The A_T estimate is very close to the value listed in Table 1 while the O-I-Ca value is significantly smaller than the previous estimate (122 Gmol yr^{-1}, Table 1). Hence, the Ca mass balance is more affected by the uncertainty in the saline water influx than the A_T balance which is probably related to the larger contrast in Ca concentrations between seawater and brackish Baltic Sea waters.

The main uncertainty in our flux estimates is related to temporal changes in A_T and Ca concentrations detected over the last decades. A_T in surface water of the central Baltic Sea increased by 100 µmol kg^{-1} over the period 1930 – 2010 (Schneider et al., 2015) and 70 µmol kg^{-1} over the period 1994 – 2014 (Müller et al., 2016). The data that were used to derive Eq. 2 and our A_T^{out} estimate of 1.71 mmol kg^{-1} (Table 1) were measured during the BALTEX II phase in 2003 – 2012. To test how an A_T change by 100 µmol kg^{-1} (0.1 mmol kg^{-1}) may affect our balance calculations, A_T in the water mass leaving the Baltic is decreased from $A_T^{out} = 1.71 \; mmol \; kg^{-1}$ (Table 1) to 1.61 mmol kg^{-1}. Calculations with this updated A_T^{out} value yields O-I-A_T = 259 Gmol yr^{-1} which is still significant, but smaller than the standard value (324 Gmol yr^{-1}, Table 1).

The Ca data that were used to derive Eq. 5 and our Ca$_{out}$ estimate of 3.0 mmol kg^{-1} (Table 1) were measured in 1994 – 1995 (Kremling and Wilhelm, 1997). Ca measurements conducted in 1989 and salinity-Ca relationships reported for 1989 (Dyrssen, 1993) yield a Ca$_{out}$ estimate of 3.1 mmol kg^{-1} while Ca concentrations measured over the period 1966 - 1970 (Kremling, 1969; Kremling, 1970; Kremling, 1972) and Ca-Cl relationships derived for this period (Anderson and Dyrssen, 1981) yield Ca_{out}= 2.9 mmol kg^{-1}. Ca concentrations measured in 1935 were apparently close to those measured over the period 1966 - 1970 (Gripenberg, 1937; Anderson and Dyrssen, 1981).

Taken at face value, these estimates would imply that Ca concentrations in the Baltic Sea peaked in 1989. Such a peak was, however, not observed in the A_T data (Müller et al., 2016). One may speculate that the Ca peak was induced by acid rain precipitation accelerating $CaCO_3$ dissolution in the Baltic Sea drainage area (Kremling and Wilhelm, 1997) that is not recorded in the A_T data since A_T may have been consumed by sulfuric acid addition. However, it is also possible that the different Ca$_{out}$ estimates reflect the uncertainty in Ca data and observed Ca-salinity and Ca-Cl relationships. The error in O-I-Ca (122 Gmol yr^{-1}) can be estimated as ± 70 Gmol yr^{-1} by applying Ca_{out}= 2.9 mmol kg^{-1} and 3.1 mmol kg^{-1} in our budget calculations. According to this approach, our O-I-Ca estimate is associated with a large error. Nevertheless, our budget calculations suggest that a significant fraction of the unaccounted A_T source in the Baltic Sea can be attributed to $CaCO_3$ dissolution.

Another uncertainty is related to the composition of mean river water entering the Baltic Sea and the riverine fluxes of A_T and Ca that may have changed over the past decades. The samples used to derive the mean alkalinity and Ca concentrations in river water (A_T^{riv} = 1.01 $mmol\ kg^{-1}$, Ca_{riv}= 0.59 $mmol\ kg^{-1}$, Table 1) were taken in 1996 – 2000 (Sun et al., 2017). Ca concentrations in river water entering the Baltic Sea were previously estimated by plotting Ca as a function of chlorinity (Cl) or salinity (S) and determining the concentration at the axis intercept (Cl = 0, S = 0) by linear regression (Gripenberg, 1937). For deep water sampled below the halocline in the Baltic Proper (BP) in 1935, this approach yielded a Ca concentration in fresh water of 0.56 mmol kg^{-1} (Gripenberg, 1937). Resampling of saline BP waters yielded intercept values of 0.62 mmol kg^{-1} in 1967, 0.54 mmol kg^{-1} in 1968, 0.57 mmol kg^{-1} in 1969, 0.50 mmol kg^{-1} in 1970, 0.98 mmol kg^{-1} in 1989 and 0.70 mmol kg^{-1} in 1994 - 1995 (Kremling, 1969; Kremling, 1970; Kremling, 1972; Dyrssen, 1993; Kremling and Wilhelm, 1997). The values recorded over the period 1935 – 1970 indicate a mean intercept value of 0.56 ± 0.04 mmol kg^{-1} which is close to the mean Ca concentration measured in modern river water (0.59 mmol kg^{-1}, Sun et al., 2017). A peak value is reported for 1989 and a decline from this peak in 1994 – 1995 that is also reflected in a peak of the calculated Ca concentration in brackish seawater leaving the Baltic Sea (Ca_{out}). The Ca peak was attributed to an increase in carbonate weathering in the Baltic Sea catchment area induced by acid rain precipitation (Kremling and Wilhelm, 1997). It is, however, questionable whether these intercept values do indeed reflect the composition of river water since this simple two-endmember-approach neglects net precipitation of freshwater and Ca release from carbonate rocks eroded at the coast and the seabed. Moreover, time-series data on Ca concentrations in river waters entering the Baltic Sea indicate a stable Ca baseline over the past decades (Sun et al., 2017). It is, hence, more likely that the dynamic intercept values reflect other processes such as decadal variations in water fluxes (net precipitation, salt water inflow, run-off) and, potentially, changes in $CaCO_3$ erosion/dissolution at the seabed.

Some of the dissolved Ca generation in the Baltic Sea might also be explained by processes other than carbonate dissolution that could e.g. be related to cation-exchange within varved clay formations deposited in the Baltic basins during late glacial freshwater phases (Suess, 1976). Porewater studies clearly show that dissolved Ca is released into the porewater of Baltic Sea sediments when brackish seawater penetrates into lacustrine clays deposited during these freshwater periods (Suess, 1976). Most of the exchange sites on the lacustrine clays are occupied by Ca^{2+} ions that are exchanged with Mg^{2+}, K^+ and Na^+ when the modern brackish water diffuses into the lacustrine clays (Suess, 1976). The diffusive Ca flux from these lacustrine sediments induced by cation exchange can be calculated from porewater data reported in Suess (1976). Dissolved Ca concentrations in sediments deposited in the Bornholm Basin typically increase from about 6 mM (mM = mmol dm^{-3} = mol

m^{-3}) at the surface to about 14 mM at 5 m sediment depth which corresponds to a concentration gradient of 1.6 mol m^{-4}. Applying a mean porosity of 80% and a molecular diffusion coefficient in sediments of 0.014 $m^2\ yr^{-1}$ (Boudreau, 1997), the diffusive Ca flux into bottom waters results as 18 mmol $m^{-2}\ yr^{-1}$. Integrated over the entire Baltic Sea floor (about 400 000 km^2), this flux would yield a maximum Ca release of up to 7 Gmol yr^{-1} which may account for some of the calculated Ca imbalance (122 Gmol yr^{-1}, Table 1). More recently, lacustrine clays were drilled during IODP Leg 347 (Andrén et al., 2015) at the Bornholm Basin and an estuary on the east coast of northern Sweden. Increasing Ca-gradients were observed (1.1 and 1.5 mol m^{-4}, respectively), that may be attributed to cation exchange. Even though, it should be noted that the real flux is probably smaller than the maximum estimate of 7 Gmol yr^{-1} since these deposits are remnants that have been identified only over parts of the Baltic Sea floor. Hence, we will discuss in the following sections only whether the erosion and dissolution of carbonate-bearing rocks at the coast and seabed may account for the calculated O-I-Ca and O-I-A_T values.

Carbonate sources

Coastal erosion

Carbonate-bearing rocks such as limestone and chalk as well as till are found along the coast of the Baltic Sea (Łabuz, 2015). Limestone and chalk occur mostly along the coast of Estonia, on a number of Danish and German islands (e.g. Sjælland, Rügen) and along parts of the Swedish coast (Gotland, Öland and Scania) even though most of the Swedish coast is composed of igneous rocks and sandstone (Łabuz, 2015). These carbonate rocks can form cliff coasts that are subject to erosion (Łabuz, 2015). The chalk cliff coast of Rügen, where cliff heights often exceed 100 m, retreats at an average rate of 0.29 – 0.41 m yr^{-1} (Wziatek et al., 2019). Chalk cliffs on the Estonian Osmussaar Island have a mean height of 5 m. They retreat at a mean rate of only 0.07 m yr^{-1} and produce 0.5 m^3 of carbonate sediment per m of shoreline and per year (Orviku et al., 2013). Cliffs on the Estonian Pakri Peninsula, that are mostly composed of limestone and have a mean height of 25 m, retreat at a rate of 0.25 m yr^{-1} and produce carbonate debris at a rate of 6 m^3 $m^{-1}\ yr^{-1}$ (Orviku et al., 2013). The total length of the Baltic coast composed of limestone and chalk and the mean erosion rates of these pure carbonate rocks are presently unknown. Assuming a length of 100 km, a mean cliff height of 20 m, a retreat rate of 0.2 m yr^{-1}, and a dry bulk density of 2 tons m^{-3}, our best guess for the $CaCO_3$ flux induce by erosion of chalk and limestone cliffs results as 0.8 Tg yr^{-1} (8 Gmol yr^{-1}).

Till deposited from ice sheets is very common along the entire southern coast of the Baltic Sea extending from Germany to Latvia (Łabuz, 2015). The external Baltic Sea coastline of Germany, Poland, Lithuania and Latvia has a total length of

about 2000 km (Figure 1). In this region, the coastline retreats by more than 1 m per year (Weisse et al., 2021). The erosive coast is characterized by a series of sandy barrier islands and dunes connected with till cliffs (Weisse et al., 2021). The till contains about 3 - 27 wt-% $CaCO_3$ (Averes et al., 2021) with a mean $CaCO_3$ content of about 17.5 wt-% in the southern Baltic Sea (Healy and Werner, 1987). Studies on coastal cliff erosion indicate that about 2 - 7 m^3 of till are eroded along the German coast of the Baltic per meter cliff length per year (Schwarzer et al., 2003; Averes et al., 2021). The total length of cliffs bordering Germany is 276 km corresponding to 27% of the coastline (Łabuz, 2015).

Till cliffs cover 65 km or 13% of the Polish coast (Łabuz, 2015). Cliff erosion rates were measured on Wolin Island where cliffs are up to 93 m high (Kolander et al., 2013). The mean retreat rate averaged over a period of 30 years amounts to 0.14 m yr^{-1} in this area (Kolander et al., 2013). The corresponding volume flux of till can be estimated as 2 - 10 m^3 m^{-1} yr^{-1} applying a cliff height of 15 - 71 m (Kolander et al., 2013). The volume fluxes are, hence, similar to those observed at the German coast.

Assuming that 20% of the 2000 km long erosive southern coastline of the Baltic Sea is composed of till (Averes et al., 2021) and that the till is eroded at an average rate of 5 m^3 m^{-1} yr^{-1}, the total till erosion rate can be estimated as 2 x 10^6 m^3 yr^{-1}. Applying a till bulk density of 2 tons m^{-3} (Healy and Werner, 1987), the mass flux amounts to 4 Tg yr^{-1}. The corresponding fine-grained lithic sediment flux is 2 Tg yr^{-1} for a mud (clay and silt) content of 50 wt-% (Healy and Werner, 1987). This flux is consistent with a recent study that estimated an annual flux of 1.5 – 3.6 Tg of fine-grained sediment produced by cliff erosion along the Danish, Swedish, German and Polish coasts of the Baltic Sea (Porz et al., 2021). The $CaCO_3$ flux results as 0.7 Tg yr^{-1} for a mean $CaCO_3$ content of 17.5 wt-% (Healy and Werner, 1987).

The dissolution of $CaCO_3$ released by the erosion of carbonate-bearing rocks (0.8 Tg yr^{-1} derived from limestone and chalk, 0.7 Tg yr^{-1} from till) would induce a Ca release of 15 Gmol yr^{-1} and an A_T production of 30 Gmol yr^{-1}. These fluxes are significantly smaller than the O-I-Ca and O-I-A_T values estimated above (Table 1).

It should, however, be noted that cliff erosion rates are difficult to assess and that rates depend critically on the time period considered and the method applied. For instance, a short term study (1.5 years) on moraine cliff erosion using terrestrial laser technology (Terefenko et al., 2019) yielded volume fluxes for German and Polish sites (12 – 45 m^3 m^{-1} yr^{-1}) that clearly exceed the mean value applied here (5 m^3 m^{-1} yr^{-1}). Moreover, the $CaCO_3$ content of till may vary along the erosive coast of the Baltic Sea extending from German to Latvian coastal areas. Hence, till deposited in Finland has no significant $CaCO_3$ content even though some of the Finnish bedrock formations (e. g. Muhos sedimentary rock) contain large amounts of carbonate (Lintinen, 1995). It is, hence, possible that the high $CaCO_3$ content measured in German till samples (17.5 wt-%, Healy and Werner) is not representative for the entire erosive coast of the Baltic Sea. In any case, our review of cliff erosion rates implies that additional $CaCO_3$ sources are required to explain the O-I-Ca and O-I-A_T fluxes (Table 1).

Seabed erosion

Much of the shallow seafloor area of the Baltic Sea is dominated by erosion rather than sediment deposition. Net sedimentation occurs only on about one third of the Baltic seabed (Kaskela et al., 2012) mostly at greater water depths below the halocline (Almroth-Rosell et al., 2011). In the remaining area, sediments are transported (50% of the seabed) or eroded (17%, Kaskela et al., 2012). Most of the eroded and transported fine-grained sediments are ultimately delivered to the deep basins, which serve as depocenters for fine-grained material. The underlying bed rock that is exposed and possibly eroded in the erosive regions is composed of sedimentary rocks (Kaskela et al., 2012). Only in the northern parts of the Baltic, crystalline rocks are exposed at the seabed. In the remaining area, the exposed seabed is partly composed of till, i.e. the same material that forms large parts of the coastal cliffs (Schwarzer, 2010). In the southern Baltic Sea off the coast of Mecklenburg-Vorpommern (Germany), the erosive seafloor is covered by till up to water depths of 50 m (Gingele and Leipe, 1997). In the south-western Baltic Sea, the seafloor at 5 – 15 m water depth is covered by a thin layer of lag sediments that are formed by the erosion of the underlying till (Schwarzer, 2010). These lag sediments are composed of pebbles, cobbles and boulders while the fine sediment components (sand, silt, clay) of the till are transported away by bottom currents (Schrottke et al., 2006). Carbonate deposited in the till is physically eroded and ultimately dissolved at the seabed.

The erosion rate of till exposed at the bottom of Kiel Bight located in the south-western Baltic Sea (Figure 1) was determined as 2.1 – 2.4 cm yr^{-1} at 2 – 3 m water depths and 0.16 cm yr^{-1} at 10 m water depth (Wefer et al., 1976). Additional measurements conducted in front of three active cliffs provided till erosion rates of 0.7 – 3.6 cm yr^{-1} (Schwarzer et al., 2014). The erosive region covers 17% (Kaskela et al., 2012) of the total Baltic Sea floor area (about 400 000 km^2) which corresponds to an erosive area of about 68 000 km^2 (Almroth-Rosell et al., 2011). If 25% of this area would be covered by till and if till erosion would proceed at a rate of 0.1 – 1.0 cm yr^{-1}, a total till volume of 17 x 10^6 m^3 to 170 x 10^6 m^3 would be eroded each year. Applying a till bulk density of 2 t m^{-3} (Healy and Werner, 1987), the mass fluxes provided by seabed erosion would result as 34 – 340 Tg yr^{-1}. For a clay/silt content of 50 wt-% (Healy and Werner, 1987), the flux of fine sediment results in 17 - 170 Tg yr^{-1}. Applying the full range of observed carbonate contents in till (3 - 27 wt-% $CaCO_3$, Averes et al., 2021), results in possible $CaCO_3$ fluxes of 1 - 92 Tg yr^{-1} for seabed erosion.

The total $CaCO_3$ flux from coastal and seabed erosion would amount to 2 - 94 Tg yr^{-1} for till-$CaCO_3$ contents of 3 - 27 wt-% $CaCO_3$ (Averes et al., 2021). Dissolution of the eroded carbonate would yield Ca fluxes of 20 - 940 Gmol yr^{-1} that may be high enough to explain the O-I-Ca value derived above (122 Gmol yr^{-1}, Table 1). It is, however, not possible to conclude at this stage that erosion of carbonate-bearing sedimentary rocks delivers sufficient $CaCO_3$ to close the Ca budget of the Baltic Sea since, both, erosion rates and $CaCO_3$-contents of eroded till are poorly constrained. In the following section, we, hence, set up a mass balance for fine-grained sediments in the Baltic Sea to better constrain the basin-wide erosion rate and estimate the mean $CaCO_3$ content of the eroded material.

Fine-grained sediment balance of the Baltic Sea

Rivers transport fine-grained suspended solids to the Baltic Sea. The corresponding riverine particle flux into the Baltic Sea has been estimated as 4.5 Tg yr^{-1} (Lajczak and Jansson, 1993). Suspended particles are also exchanged between the Baltic Sea and the North Sea across the Danish straits. High kaolinite contents in muddy surface sediments deposited in the southern basins of the Baltic Sea may indicate that a fraction of this clay mineral is imported from the North Sea where kaolinite-rich deposits may be eroded and transported into the Baltic during saltwater inflow events (Gingele and Leipe, 1997; Gingele and Leipe, 2001; Porz et al., 2021). The mean annual influx of North Sea sediments caused by these events has been estimated as 0.1 Tg yr^{-1} (Porz et al., 2021). This flux is very small compared to the riverine particle input. Moreover, the particle export associated with the outflow of brackish water from the Baltic into the North Sea may exceed the particle import (Porz et al., 2021). Hence, the particle exchange with the North Sea can be neglected from a mass balance perspective.

The first comprehensive map of modern sedimentation rates (SR in cm yr^{-1}) in the Baltic Sea was recently provided by Mitchell et al. (2021). The authors used a total of 430 stations from the Baltic Sea for which ^{137}Cs-based SRs are reported and compiled in the EMODnet-Geology data base. The ^{137}Cs enrichment used for the SR calculation is assumed to reflect the deposition of ^{137}Cs emitted during the Chernobyl accident in April 1986. The reported values, hence, present SRs averaged over the time period from 1986 to the date of sampling. A machine-learing approach was applied (Random forest) to produce a SR map from these ^{137}Cs-dated cores covering almost the entire Baltic Sea (Mitchell et al., 2021).

The following equation was applied to transform the reported SR values into mass accumulation rates (MAR in g cm^{-2} yr^{-1}):

$$MAR = d_S (1 - P_{mean}) SR \qquad (8)$$

where d_S is the average grain density and P_{mean} the mean porosity (as a unitless fraction) of sediments deposited above the Chernobyl peak. We applied $d_S = 2.5\ g\ cm^{-3}$ which corresponds to the value previously employed for surface sediments deposited in the Baltic Sea (Ilus et al., 2001; Mattila et al., 2006).

A total of 963 porosity values measured by GEOMAR in muddy surface sediments from the Southern Baltic Sea (Kiel Bight) and the Gotland Basin were used to estimate the mean porosity of sediments deposited above the Chernobyl peak (see Supplement S1 for further details). This data base yields the following mean porosities (± 1 standard deviation): 0 – 5 cm: 0.920 ± 0.038, 0 – 10 cm: 0.905 ± 0.040, 0 – 15 cm: 0.899 ± 0.042, 0 – 20 cm: 0.894 ± 0.043. Since the Chernobyl peak typically occurs at 5 – 20 cm (Ilus et al., 2001; Kotilainen et al., 2021), we applied P = 0.90 for the MAR calculation. The corresponding dry bulk density (DBD = d_S (1 - P)) amounts to 0.25 g cm^{-3}. This DBD value is close to values previously reported for the Arkona Basin (Leipe et al., 2011). It should, however, be noted that much lower DBD values (DBD ≈ 0.05 g cm^{-3}) were reported for extremely water- and POC-rich surface sediments deposited of the Eastern Gotland Basin at water depths larger than 200 m (Leipe et al., 2011, Supplement S1).

Eq. (8) is applied to convert the SR map provided by Mitchell et al. (2021) into a corresponding MAR map and to calculate area-integrated sediment accumulation rates (in Tg yr^{-1}). Since we aim to derive a mud balance, we limit our analysis to those areas where fine-grained sediments dominate (see Supplement S2 for further details). We use the EMODnet-Geology seabed substrate map at a map scale of 1: 1,000,000 (Seabed substrate 1:1M, https://www.emodnet-geology.eu/map-viewer/?p= seabed_substrate). This map provides full coverage of the Baltic Sea at a thematic resolution of five substrate classes (mud to muddy sand, sand, coarse substrate, mixed sediment, and rock and boulders). The mud to muddy sand class is composed of six textural classes (Folk, 1954). However, full coverage of Baltic Sea seabed substrates is neither provided at this detailed thematic resolution nor an intermediate resolution, subdividing the mud to muddy sand class into three textural classes (Kaskela et al., 2019). Hence, our estimates of fine-grained sediment accumulation relate to the mud to muddy sand class without any further differentiation.

The area where mud to muddy sand accumulates (132 955 km^2) accounts for about one third of the total seafloor area and corresponds to the region where sediment accumulation is the dominant process rather than sediment transport and erosion (Kaskela et al., 2012). Our analysis reveals a high accumulation rate of 139 Tg yr^{-1} over this area (Figure 3) that clearly exceeds the riverine particle input (4.5 Tg yr^{-1}, Lajczak and Jansson, 1993) and the particle input from the North Sea. We, hence, conclude that most of the fine-grained particles deposited in the

Baltic Sea are provided by coastal and seabed erosion. Mineralogical studies confirm that fine-grained sediments deposited in major basins of the southern Baltic Sea (Arkona and Bornholm basins) and at the southern coast are mostly derived from glaciogenic material (till) eroded at the coast and at the seabed while riverine signatures are only dominant in sediments deposited close to river mouths (Gingele and Leipe, 1997; Kairytè and Stevens, 2009).

The basin-wide accumulation rate of fine-grained material derived above (139 Tg yr^{-1}) can be used to constrain the erosion rate of fine-grained material along the coast and at the seabed. It should, however, be considered that the muddy sand included in our estimate of fine-grained sediment accumulation may contain sizable fractions of sand and that mud is not only composed of lithic components but contains biogenic material derived from

plankton biomass and the adjacent land area. The mean concentration of particulate organic carbon in muddy Baltic Sea sediments can be estimated as 5 wt-% (Leipe et al., 2011). Considering the elemental composition of marine organic matter (Sarmiento and Gruber, 2006), this carbon content corresponds to an organic matter content of about 10 wt-%. The mean biogenic opal content amounts to about 5 wt-% (Leipe et al., 2011). Carbonate contents in muddy surface sediments deposited in the deep basins are usually <1 wt-% (Leipe et al., 2011) since $CaCO_3$ delivered by erosion is rapidly dissolved in surface sediments by metabolic CO_2 produced by the degradation of plankton biomass deposited at the seabed (Nilsson et al., 2019). Hence, the total content of biogenic matter amounts to about 15 wt-%. The accumulation rate of lithic fine-grained material amounts to 118 Tg yr^{-1}, accordingly.
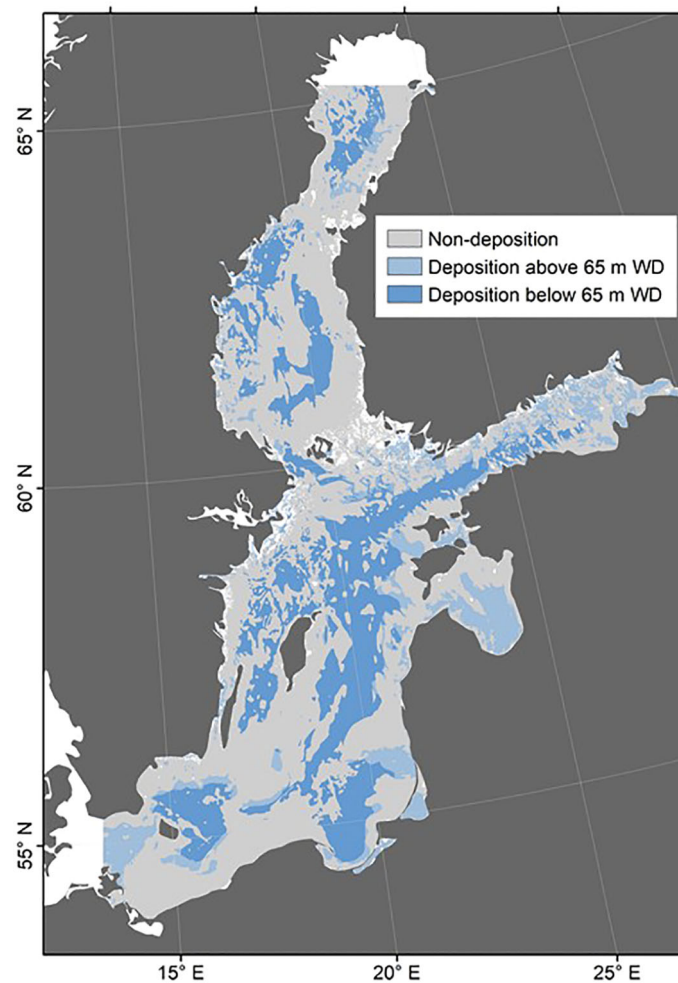

FIGURE 3
Overview of the studied area showing areas of assumed deposition (substrate class mud to muddy sand according to the EMODnet-Geology Seabed Substrate 1:1M map), split into areas shallower and deeper than 65 m water depth (WD) based on EMODnet Bathymetry Consortium (2020). Also shown are areas of assumed non-deposition (substrate classes sand, coarse substrate, mixed sediment, rock and boulders, and no data according to the EMODnet-Geology Seabed Substrate 1:1M map).

Considering that 4.5 Tg yr^{-1} are provided by rivers, the erosion rate of fine-grained material results as 114 Tg yr^{-1}. This value falls into the range of values derived from field observations (19 - 172 Tg yr^{-1}) where most of the material seems to be provided by seabed erosion (17 - 170 Tg yr^{-1}). The high accumulation rate of fine-grained material derived from ^{137}Cs data, hence, supports the hypothesis that the Ca excess in Baltic Sea water may be largely provided by seabed and coastal erosion of $CaCO_3$-bearing till.

The mean bulk $CaCO_3$ content of eroded till (containing 50% coarse material) that is required to reach the Ca flux derived in Table 1 (122 Gmol yr^{-1}) would amount to ca. 5%. This value falls into the lower range of carbonate contents observed in Baltic till (3 - 27 wt-% $CaCO_3$, Averes et al., 2021). It is significantly lower than the mean $CaCO_3$ content in till at the German coast (17.5%) which may suggest that till-$CaCO_3$ contents decline in north-eastern direction along the coast as indicated by the low $CaCO_3$ abundance in Finish till (Lintinen, 1995). It is, however, also possible that other fine-grained material accumulates at the seabed. Hence, erosion of salt marshes and lowlands composed of weathered till and other fine-grained and carbonate-depleted material occurs e.g. along parts of the Danish, Swedish and German coast (Łabuz, 2015). This largely $CaCO_3$-free material may dilute the till-derived sediments and contribute to the low $CaCO_3$ content calculated above.

Seafloor areas at shallow water depths above the permanent halocline located at about 65 m water depths are subject to frequent sediment erosion and re-deposition events (Almroth-Rosell et al., 2011). Moreover, Chernobyl ^{137}Cs may be mixed down-core by intense bioturbation which would result in an overestimate of SD and MAR values. An ideal ^{137}Cs depth profile in Baltic Sea sediments should feature a large and sharp ^{137}Cs peak representing the Chernobyl accident in 1986 overlying a smaller and broader peak related to the ^{137}Cs release during nuclear weapons testing that started in 1952 and reached a maximum in the early 1960s (IAEA, 1998). The latter peak is significantly reduced since more than two half-lives of ^{137}Cs have now passed since radionuclides were released during testing. However, many ^{137}Cs profiles measured in coastal sediments do not show these peaks but rather a mixed surface layer enriched in ^{137}Cs (HELCOM, 2007). For these sites, the transition to the largely ^{137}Cs-free sediments below is then assumed to represent either the year 1986 (Mattila et al., 2006) or the early 1950s (Winogradow and Pempkowiak, 2014), i.e. the period when large-scale atomic bomb tests started. ^{137}Cs dating is, hence, ambiguous when surface sediments are mixed by erosion-redeposition cycles and bioturbation.

To address this issue, we also calculated sediment deposition in accumulation areas located at >65 m water depth (Figure 3) where physical and biological sediment reworking is assumed to proceed less frequently (Almroth-Rosell et al., 2011; Virtasalo et al., 2011). The EMODnet bathymetric map was used to define seafloors located at >65 m (EMODnet Bathymetry Consortium,

2020). The resulting accumulation rate of 85 Tg yr^{-1} over an area of 88 063 km^2 still falls into the range of erosion values derived from field observations (19 - 172 Tg yr^{-1}). For this estimate, a correspondingly higher till-$CaCO_3$ content (ca. 8%) would be required to reach the excess Ca flux listed in Table 1. This value still falls into the lower range of carbonate contents observed in Baltic till (3 - 27 wt-% $CaCO_3$, Averes et al., 2021). Hence, the available ^{137}Cs data support our hypothesis that dissolution of $CaCO_3$ provided by till erosion may account for the Ca excess in Baltic Sea water.

Sedimentary $CaCO_3$ balance and dynamics of $CaCO_3$ turnover at the seabed

$CaCO_3$ contents in surface sediments retrieved from the Baltic Sea are reported in Leipe et al. (2011). The authors note that $CaCO_3$ contents in the deep basins are generally low (<1 wt-%) even though the source material (till) contains significant amounts of $CaCO_3$. Only surface sediments deposited in the Gotland Deep (1.1 wt-%), Mecklenburg Bay (1.7 wt-%) and the Gulf of Finland (5.8 wt-%) contain significant amounts of $CaCO_3$ (Leipe et al., 2011). These data confirm that most of the till-$CaCO_3$ is dissolved at the seabed.

However, carbonates are not only dissolved in surface sediments but may precipitate from oversaturated porewaters (Suess, 1979). These authigenic carbonates can be found down to several meters sediment depths (Lepland and Stevens, 1998). They are usually enriched in Mn and can contain significant amounts of Fe and Mg (Suess, 1979; Jakobsen and Postma, 1989). Mn-rich carbonates (Ca-bearing rhodochrosite) may form at high rates after deep basins are flooded with oxygen-bearing and salt-rich bottom waters during major inflow events (Huckriede and Meischner, 1996; Neumann et al., 1997). The highest contents of authigenic carbonates are, however, found in sediment layers that are enriched in organic carbon (Lepland and Stevens, 1998; Virtasalo et al., 2011). This observation can be explain by anoxic degradation processes that provide A_T which is required for authigenic carbonate formation (Lepland and Stevens, 1998). The contribution of these authigenic carbonates to the A_T and Ca balance of the Baltic Sea is largely unknown and neglected in current A_T balances (Gustafsson et al., 2019). The benthic A_T source term considered in these mass balances may be smaller than currently assumed since a significant fraction of the A_T generated via e.g. pyrite and sulfur burial (44 Gmol yr^{-1} Gustafsson et al., 2019) may not be released into ambient bottom waters but bound in authigenic carbonates (Lepland and Stevens, 1998; Wallmann et al., 2008). More till-$CaCO_3$ erosion and dissolution would be required to compensate for authigenic carbonate formation if the latter process fixes significant amounts of seawater A_T and Ca.
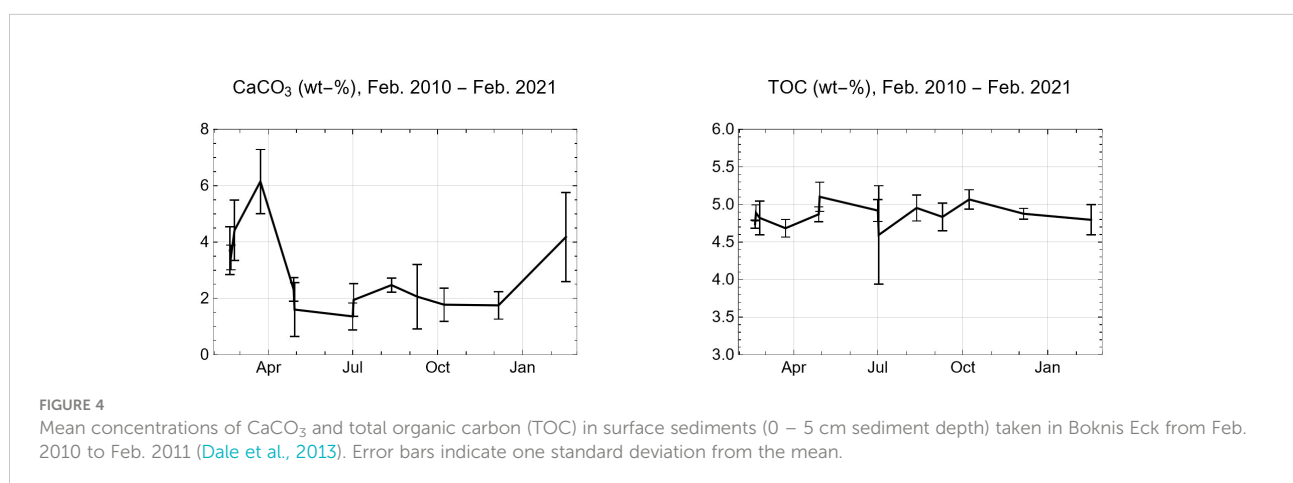
Plankton productivity in the Baltic Sea is dominated by diatoms and dinoflagellates with occasional contributions by mixotrophic ciliates, diazotrophs and dictyochophyceae (Wasmund et al., 2017). The major pelagic $CaCO_3$ producer *Emiliania huxley* occurs in the Skagerrak (Figure 1) where it can form extensive blooms (Van der Wal et al., 1995). In Kiel Bight (Figure 1), *E. Huxley* and other coccolithophores occur only sporadically and at low abundance (Wasmund et al., 2008). Coccolithophores and their coccoliths have not been detected in water column samples taken in the Baltic Proper, Gulf of Riga and Gulf of Bothnia (Tyrrell et al., 2008). Hence, deposition of planktonic carbonate material may not contribute significantly to the sedimentary $CaCO_3$ budget. However, biomarker and DNA analysis indicate the presence of coccolith-producing species belonging to the order Isochrysidales throughout the Baltic Sea (Kaiser et al., 2019). If coccoliths would be buried at a significant rate, even more dissolution of till-$CaCO_3$ would be required to compensate for burial of pelagic $CaCO_3$.

Time-series data are available for Boknis Eck located in Kiel Bight (Figure 1) where surface sediments were taken over a period of one year (Feb. 2010 – Feb. 2011) at approximately monthly resolution (Dale et al., 2013). The data show an interesting seasonal pattern with high $CaCO_3$ contents (4- 6 wt-%) during winter and early spring (Feb. – March) and low values during the rest of the year (around 2 wt-%, Figure 4). These $CaCO_3$ concentrations are significantly lower than those in local till (17.5 wt-%, Healy and Werner) which again confirms that most of the eroded till-$CaCO_3$ is dissolved at the seabed.

The plankton bloom that typically occurs in Kiel Bight during the early spring season (Feb. - March) is clearly dominated by diatoms (Wasmund et al., 2017). Dinoflagellates are present in the bloom (Wasmund et al., 2017) while coccolithophores have not been observed during the spring bloom season (Wasmund et al., 2008). The $CaCO_3$ peak at Feb- March is, thus, not caused by the deposition of planktonic

$CaCO_3$ but can be ascribed to the deposition of $CaCO_3$-rich till that is eroded at the surrounding coast (Averes et al., 2021) and erosive seafloor (Wefer et al., 1976) during the stormy winter season. The marked $CaCO_3$ decline from March to late April 2010 (Figure 4) may be induced by the spring bloom that delivers large amounts of biomass to the seabed (Wasmund et al., 2017). Fast aerobic degradation of this biomass induces high rates of benthic CO_2 release during March-May (Dale et al., 2013) which probably leads to rapid dissolution of till-$CaCO_3$ provided during the winter season. TOC shows, a much lower seasonality (Figure 4) since most of the TOC preserved in surface sediments is refractory and, hence, less reactive than till-$CaCO_3$.

The annual mean rate of till-$CaCO_3$ deposition at Boknis Eck can be estimated as 0.26 mmol cm^{-2} yr^{-1} applying the mean mass accumulation rate (0.15 g cm^{-2} yr^{-1}) reported for this site (Dale et al., 2011) and a local till-$CaCO_3$ content of 17.5 wt-% (Healy and Werner, 1987). The depth-integrated rate of benthic TOC degradation in surface sediments deposited in Boknis Eck has an annual mean value of about 0.5 mmol cm^{-2} yr^{-1} (Dale et al., 2013). Most of the TOC is degraded *via* aerobic respiration and dissimilatory sulfate reduction where sulfide is almost completely re-oxidized to sulfate in surface sediments (Dale et al., 2013). Since, both, aerobic respiration and sulfate reduction coupled to sulfide oxidation yield CO_2 as major metabolic product, the data imply that sufficient CO_2 is produced in surface sediments to dissolve most of the $CaCO_3$ provided by till-erosion. $CaCO_3$ dissolution at Boknis Eck is further aided by metabolic CO_2 that accumulates in oxygen-depleted bottom waters during stagnant summer and autumn periods (Melzner et al., 2013; Lennartz et al., 2014). The example from Boknis Eck and the low $CaCO_3$ contents found throughout the Baltic Sea (Leipe et al., 2011) clearly indicate that most of the $CaCO_3$ delivered by till erosion is rapidly dissolved in surface sediments.

FIGURE 4
Mean concentrations of $CaCO_3$ and total organic carbon (TOC) in surface sediments (0 – 5 cm sediment depth) taken in Boknis Eck from Feb. 2010 to Feb. 2011 (Dale et al., 2013). Error bars indicate one standard deviation from the mean.

Carbon dioxide removal *via* deliberate CaCO$_3$ addition

Our finding that CaCO$_3$ provided by till erosion is rapidly dissolved at the seabed is also relevant for carbon dioxide removal (CDR) approaches that might be employed to mitigate global climate change and achieve net zero CO$_2$ emissions over the coming decades (IPCC, 2018). One of these approaches proposes to use alkaline minerals that are dissolved in the ocean and at the seabed to create alkalinity and promote CO$_2$ uptake from the atmosphere (Hartmann et al., 2013). Olivine is the alkaline mineral that has been most frequently proposed to be applied for this purpose. However, recent experimental studies showed that olivine may not be suitable since the generation of alkalinity during olivine dissolution is compromised by secondary mineral formation (Fuhr et al., 2022). Experiments that are currently conducted at GEOMAR within the framework of the RETAKE project (https://retake.cdrmare.de/en/) confirm that calcite added to muddy Baltic Sea sediments dissolves at the sediment surface and releases alkalinity in ambient bottom waters. Hence, CaCO$_3$ may be a suitable alkaline mineral to remove CO$_2$ from Baltic Sea water and the atmosphere.

CaCO$_3$ addition may also have the beneficial side effect to reduce release of dissolved phosphate from sediments into ambient bottom waters because it may promote formation of authigenic carbonate fluorapatite and other Ca- and phosphate-bearing solids in surface sediments (Ruttenberg and Berner, 1993; Prüter et al., 2020). Since oxygen losses and nutrient accumulation in the Baltic Sea are amplified by benthic phosphate release (Conley et al., 2002), CaCO$_3$ addition may not only mitigate acidification but also eutrophication and deoxygenation of this marginal sea.

The basin-wide rate of benthic DIC (dissolved inorganic carbon) release in the Baltic Sea has been estimated as 1 833 Gmol yr^{-1} (Nilsson et al., 2019). Benthic HCO_3^- release induced by pyrite and sulfur burial has been estimated as 44 Gmol yr^{-1} (Gustafsson et al., 2019) while the ongoing dissolution of 122 Gmol of CaCO$_3$ per year (Table 1) would induce a benthic HCO_3^- flux of 244 Gmol yr^{-1}. The remaining DIC flux is probably composed of CO$_2$ produced during aerobic respiration and sulfate reduction coupled to sulfide oxidation (1 545 Gmol yr^{-1} = 68 million tons of CO$_2$ per year). Neutralization of this large CO$_2$ flux by CaCO$_3$ addition could help to achieve net-zero CO$_2$ emissions in countries along the Baltic coast. Our finding that CaCO$_3$ erosion and dissolution is a natural process in the Baltic Sea may help during the approval process for CaCO$_3$-based CDR measures within existing legal frameworks. However, a better quantification of natural A$_T$ sink and source terms and a full assessment of all side effects of CaCO$_3$ addition are required before this promising CDR approach can be applied at large scale.

Conclusions

Our budget calculations and estimates of till erosion rates indicate that the dissolution of about 12 *Tg CaCO$_3$ yr^{-1}* (Table 1) provided by seabed and coastal erosion can explain the dissolved Ca and most of the A$_T$ excess observed in Baltic Sea water. The apparent increase in A$_T$ and Ca concentrations over the past decades might, hence, be related to a corresponding increase in coastal and seabed erosion induced by e.g. climate change, dredging, and bottom trawling. Moreover, eutrophication, rising temperatures and the increase in CO$_2$ accumulation in oxygen-depleted bottom waters (Kulinski et al., 2022) may have supported further CaCO$_3$ dissolution. It should, however, be noted that more work on erosion rates and an improved reconstruction and understanding of temporal changes in the chemical composition of Baltic Sea water are required to consolidate these findings. A systematic survey of stable calcium isotopic compositions of different water masses in the Baltic Sea and possible Ca sources (till-CaCO$_3$, riverine Ca, Ca dissolved in North Sea water) could be conducted to test our hypothesis that the Ca excess in Baltic Sea water is caused by till-CaCO$_3$ dissolution.

Since our data suggest that CaCO$_3$ provided by till erosion is rapidly dissolved at the seabed, we propose that deliberate addition of CaCO$_3$ may be a suitable carbon dioxide removal approach for the Baltic Sea.

Our results may not only be relevant for the Baltic Sea but also for other coastal seas and shelf areas where internal generation of alkalinity may drive up to 60% of the CO$_2$ uptake from the atmosphere (Thomas et al., 2009). So far, the A$_T$ generation has been ascribed to anaerobic degradation processes of organic matter in anoxic shelf sediments (Thomas et al., 2009). Our results imply that dissolution of eroded CaCO$_3$ may strongly contribute to the A$_T$ generation in regions where sediments and rocks forming the coastline and the seabed contain significant amounts of carbonate. Better quantification and parameterization and, ultimately, inclusion of CaCO$_3$ erosion and dissolution in basin-wide ecosystem models will thus be important for future studies of acidification and CO$_2$ source/sink attribution in coastal seas.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author.

Author contributions

KW initiated the paper by developing the hypothesis that carbonate erosion and dissolution may close the alkalinity budget at the Baltic Sea and contribute to CO_2 uptake in coastal seas. MD provided data on sedimentation rates and calculated basin-wide mass accumulation rates of fine-grained sediments in the Baltic Sea. FS provided insights into coastal erosion of glacial till. GR supported the set-up of the alkalinity budget of the Baltic Sea. AD and MF provided carbonate data for Boknis Eck. ES contributed data and background on cation exchange and authigenic carbonate formation in Baltic Sea sediments. All authors contributed to the paper by drafting, reading, finalizing, and approving the text.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2022.968069/full#supplementary-material

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