



Silicate weathering in anoxic marine sediment as a requirement for authigenic carbonate burial

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ABSTRACT

We emphasize the importance of marine silicate weathering (MSiW) reactions in anoxic sediment as fundamental in generating alkalinity and cations needed for carbonate precipitation and preservation along continental margins. We use a model that couples thermodynamics with aqueous geochemistry to show that the CO₂ released during methanogenesis results in a drop in pH to 6.0; unless these protons are buffered by MSiW, carbonate minerals will dissolve. We present data from two regions: the India passive margin and the active subduction zone off Japan, where ash and/or rivers supply the reactive silicate phase, as reflected in strontium isotope data. Offshore India and Korea, alteration of continent-derived silicates results in pore water enriched in radiogenic ⁸⁷Sr, with ⁸⁷Sr/⁸⁶Sr ratios as high as 0.7095 and 0.7104, respectively. Off Japan, strontium in pore water influenced by ash alteration is depleted in ⁸⁷Sr, with ⁸⁷Sr/⁸⁶Sr as low as 0.7065. Carbonate minerals formed by alkalinity and cations generated through MSiW carry these strontium isotopic signals, and are typically dolomite, siderite, and Fe-rich calcite. These contrast with the aragonite and high-magnesium calcite that form during anaerobic oxidation of methane and incorporate the coeval seawater ⁸⁷Sr/⁸⁶Sr signal. We show that MSiW is necessary for authigenic carbonate formation and preservation along continental margins, which remove carbon from Earth's surface at rates previously estimated to be at least 10¹² mol yr⁻¹. In addition, these authigenic carbonates are of relevance to studies of the deep biosphere, fluid flow, seismogenesis, slope stability, and reservoir characteristics.

1. Introduction

Burial of organic carbon and calcium carbonate are the main pathways for carbon removal from the atmosphere and hydrosphere reservoirs (Milliman, 1993). Whereas biogenic carbonate has long been included in global carbon budgets, recent studies have demonstrated that precipitation of authigenic carbonate constitutes a carbon sink that, although not previously considered, can be critical in carbon cycling over Earth's history (e.g. Schrag et al., 2013). Authigenic carbonate, i.e. a carbonate mineral precipitated inorganically at the sediment-water interface or within the sediment, is normally attributed to alkalinity produced from microbially-mediated organic matter

metabolic pathways that reduce sulfate or ferric iron, or by anaerobic oxidation of methane (AOM). Sun and Turchyn (2014) show this removal term to be highest along continental margins, where primary production and rates of particulate organic carbon burial are particularly high. Continental margins are also the regions of highest microbial methane generation (Wallmann et al., 2012) and are typically characterized by shallow sulfate-methane transition (SMT) zones (Egger et al., 2018). Whereas alkalinity is enhanced during AOM, the organic carbon disproportionation reaction that generates methane below the SMT, also releases CO₂ (Wallmann et al., 2008; Solomon et al., 2014). Therefore, methanogenesis leads to a decrease in pH that drives carbonate dissolution. The fundamental question we must ask is how can

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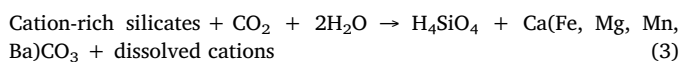
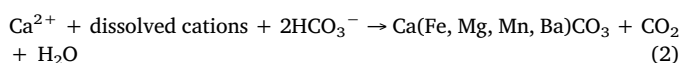
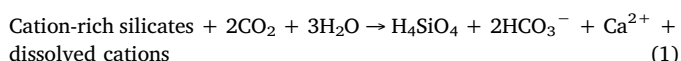
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carbonate minerals be preserved along continental margins when sediments below the SMT are exposed to low pH conditions. Another outstanding question regarding formation of large authigenic carbonate deposits is the source of cations needed for their formation, as reflected in the various potential magnesium sources debated for dolomitization in marine sediment (e.g. Baker and Burns, 1985; von Breymann et al., 1990).

The missing fundamental piece in the budgets that call for alkalinity and cation removal via carbonate mineral formation along continental margins is the role that silicate weathering plays in marine sediment. Incongruent weathering of silicate minerals exposed on land generates alkalinity and dissolved ions; and has long been established as the main sink of atmospheric CO₂ over geologic times (Garrels, 1983). Although less recognized, this reaction also takes place in marine sediment when both reactive silicates (either volcanic ash or continentally-derived material) and protons are present. As proposed by Aloisi et al. (2004), Wallmann et al. (2008) and Solomon et al. (2014), CO₂ generated during methanogenesis induces weathering of reactive silicate phases in the sediment (Eq. [1]) and promotes carbonate formation (Eq. [2]), leading to a net reaction shown in Eq. [3].



In this review we call attention to the formation of authigenic carbonates triggered by marine silicate weathering (MSiW) coupled with methanogenesis. We describe a numerical model coupling mineral thermodynamics and aqueous chemistry to illustrate predicted changes in inorganic carbon speciation below the SMT. Simulated scenarios, with and without MSiW reactions, are shown to document the fundamental role that silicates play in carbonate mineral formation. Using data collected by drilling in two regions (the India passive margin and the active subduction zone off Japan), we show that both continental and volcanic-sourced minerals can act as the reactive silicate phase. We review evidence in support of MSiW reactions, illustrate the role of strontium isotopes to trace silicate alteration, and show how this valuable isotopic fingerprint is preserved in the resulting carbonate minerals. We compare mineralogy and isotopic characteristics of carbonate minerals formed by alkalinity generated via MSiW with the methane-derived authigenic carbonate (MDAC) that forms at the SMT during AOM, and examine the conditions that led to the formation of organogenic dolomites. The global extent of the carbon-silica coupling highlights its significance as a driver for the major carbon sink in sedimentary reservoirs.

2. Conceptual and numerical simulation of dissolved carbonate chemistry changes below the SMT

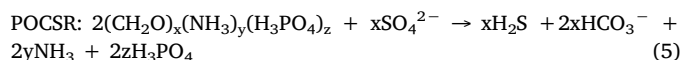
Total alkalinity (TA) is a measure of the acid-neutralising capacity of water, defined by Stumm and Morgan (2012) as the equivalent sum of the bases that are titratable with strong acid. In other words, TA corresponds to the number of moles of hydrogen ion equivalent to the excess of proton acceptors (i.e. bases formed from weak acids with a dissociation constant K_a less than or equal to $10^{-4.5}$ at 25 °C and zero ionic strength) over the proton donors (acids with $K_a > 10^{-4.5}$) in one kilogram of sample, such that:

$$\text{Alkalinity} = \text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{NH}_3] + [\text{H}_3\text{SiO}_4^-] + 2[\text{H}_2\text{SiO}_4^{2-}] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{OH}^-] + [\text{HS}^-] + 2[\text{S}^{2-}] + [\text{Org. Acids}] - [\text{H}^+] - [\text{H}_3\text{PO}_4] \quad (4)$$

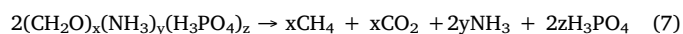
In seawater and pore water systems this buffering capacity comes

from seven weak inorganic acid-base pairs and organic acids, with carbonate alkalinity ($\text{CALK} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$) making up most of the total alkalinity. Alkalinity (TA) is commonly and reliably measured in natural waters (e.g. Millero et al., 1993; Sauvage et al., 2014), so we compare our results with literature values that report total (rather than carbonate) alkalinity (for more details see supplementary information).

Since alkalinity is given in equivalents, for every mole of double-charged bases (such as carbonate) being consumed, alkalinity has to increase by two moles to satisfy the charge balance. During early organic matter diagenesis, particulate organic carbon sulfate reduction (POCSR) and AOM consume sulfate, generating both alkalinity and dissolved inorganic carbon ($\text{DIC} = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$) at a maximum ratio of 2:1 (Equations [5] and [6]).



Below the SMT organic matter is consumed through diverse metabolic pathways of fermentation and methanogenesis. As carbohydrates are metabolized in the methanogenesis zone, one mole of CO₂ is produced for every mole of CH₄ (Equation [7])



The molar ratio of [CO₂]/[CH₄] will vary slightly if proteins and lipids are metabolized; however, as shown in Equation [7], methanogenesis leads to an increase in DIC, but there is no net change in CALK (Aloisi et al., 2004; Wallmann et al., 2008; Solomon et al., 2014). Total alkalinity changes in methanogenic sediments depend on concentration changes of the non-carbonate weak acid-base pairs (e.g. [NH₄⁺]/[NH₃]), which are significantly smaller than the change in DIC.

From the discussion above it follows that in no instance can the alkalinity produced solely from sulfate-coupled organic carbon metabolic pathways exceed 58 mM plus the amount of dissolved inorganic nitrogen/phosphate released from organic matter and the amount of protons consumed (i.e., $2x + 2y$ in Equation [5]). Assuming a Redfield ratio for the organic matter (i.e., $x:y:z = 106:16:1$ in Equation [5]), the maximum increase of TA with the complete consumption of seawater sulfate (~29 mM) will be 67 mM. However, as noted by Wallmann et al. (2008), in many locations along continental margins the alkalinity does exceed 67 mM at the bottom of the sulfate reduction zone, reaching values that are in some instances over 100 mM. Such high alkalinity points to silicate weathering reactions that consume CO₂ and generate CALK, analogous to weathering of silicates exposed on land (Eq. [1]). Locations of significant MSiW identified by Wallmann et al. (2008) based on excess alkalinity are illustrated by red symbols in Fig. 1.

To better illustrate and visualize these changes, we constructed a numerical simulation to follow changes in pore water composition as organic matter is metabolized below the SMT. The simulation includes all seven weak acid-base pairs that contribute to the alkalinity in sediment, with and without the presence of reactive silicate phases. Details of the reaction network, initial pore water conditions and solid phase components used in the simulation are given in the supplementary material (Appendix A). Briefly, methanogenesis is allowed to proceed in “typical” marine sediment below the SMT (i.e. pore water devoid of sulfate), using initial conditions typically observed at the SMT along continental margins (Table A1), and monitor the reaction progress through time. Whereas several inferences can be derived from such an exercise (see examples in supplementary materials), we focus our discussion on changes in carbonate speciation, alkalinity, ammonium, calcium, and magnesium.

DIC is produced during microbial methanogenesis (ME) but any increase in alkalinity is limited to the generation of weak acid-base pairs (green symbols in Fig. 2A; Table A2). However, upon addition of silicate minerals (in this example albite, anorthite, and biotite), the DIC

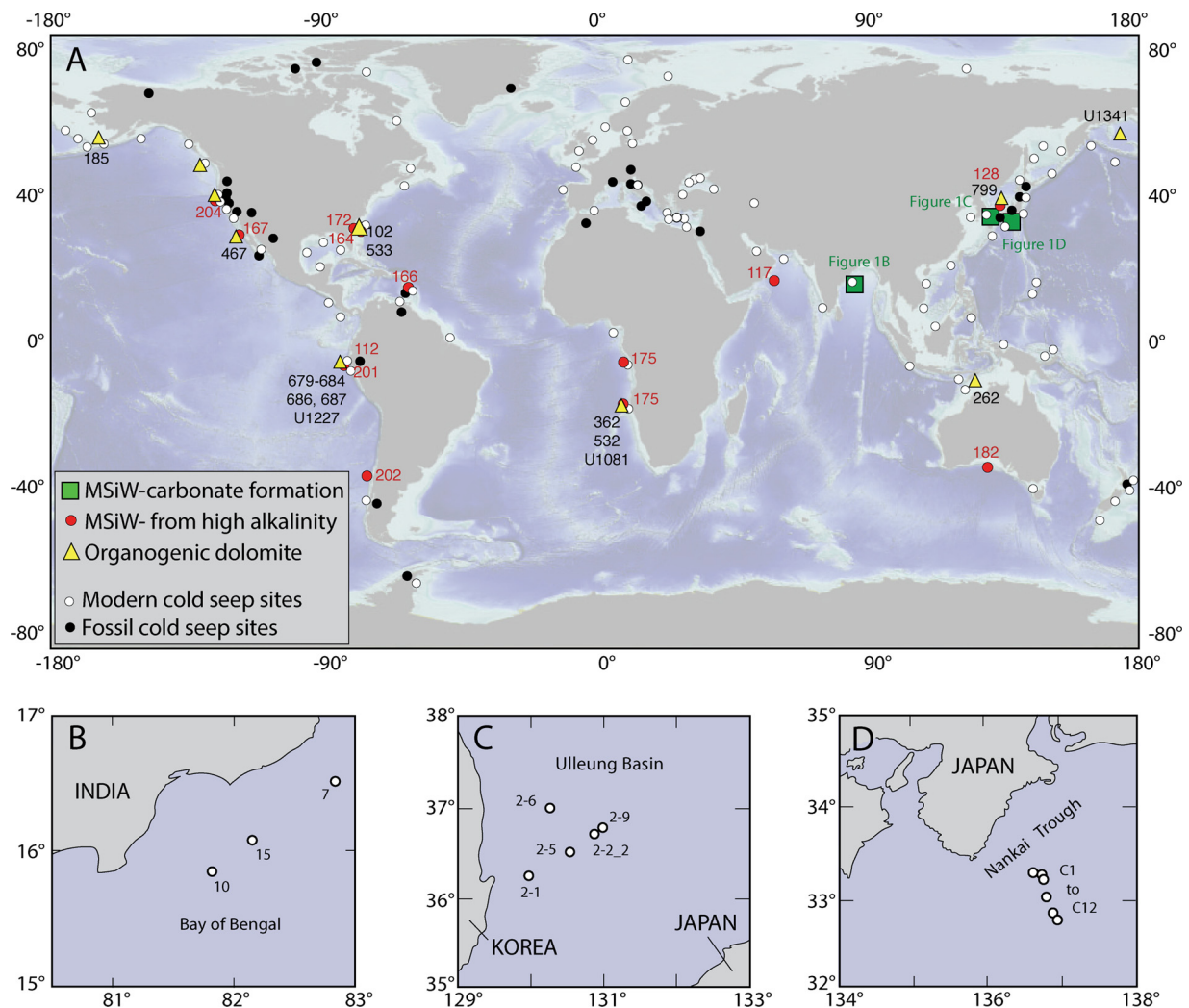


Fig. 1. A. Locations of known authigenic carbonate formation associated with cold seeps (white and black circles; from [Bohrmann and Torres, 2015](#)) and organogenic dolomite (yellow triangles); when the dolomite was described in ocean drilling proceedings, the site numbers are shown in black. Locations of inferred MSiW reactions based on excess alkalinity are shown in red (circles), and the numbers associated indicate drilling expedition numbers (from [Wallmann et al., 2008](#)). Green squares designate locations in the Indian margin and the Nankai subduction zone system, where carbonate formation associated with MSiW has been documented. B. Site locations in the Krishna-Godavari Basin, India. C–D. Sites drilled in the Nankai system from the incoming section on the Philippine Sea Plate (D) to the back-arc Ulleung Basin (C). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

increase is matched by an increase in alkalinity, which illustrates the conversion of CO_2 to HCO_3^- during silicate weathering reactions (Eq. [1]). A plot of alkalinity (TA) against dissolved inorganic nitrogen ($\text{DIN} = [\text{NH}_3] + [\text{NH}_4^+]$) below the SMT shows the release of DIN from organic matter degradation, but the increase in alkalinity in the absence of silicate weathering is much less than that observed when reactive silicates are present (Fig. 2B). In the absence of silicate weathering the main DIN species is NH_4^+ , because of the predicted decrease in pH during methanogenesis.

Using results from the simulation exercise, we depict the changes in carbonate speciation to illustrate the predicted response of the system as CO_2 is generated via methanogenesis (Fig. 3). As methanogenesis proceeds, the continued production of CO_2 in the absence of silicates (green symbols) will lower the pore water pH to values as low as 6, i.e. the carbonate speciation will shift towards the carbonic acid field, with the bicarbonate species (HCO_3^-) decreasing to less than 40% of the total DIC pool (Fig. 3A and 3B). In such acidic conditions any solid carbonate phase in the sediment will dissolve, as shown, for an example, by the drastic drop in calcite and dolomite saturation (green symbols Fig. 3D and 3H). This is clearly not occurring in marine sediment. It then follows that carbonate precipitation below the SMT is

not possible unless MSiW reactions convert CO_2 to bicarbonate (blue, red and purple symbols in Fig. 3).

In addition to alkalinity production, MSiW reactions also contribute a significant fraction of cations to the pore water inventories. For example, [Kim et al. \(2016\)](#) attribute the source of potassium needed for smectite-illite reactions to MSiW in the anoxic sediment of the Ulleung Basin, illustrating that MSiW impacts the diagenetic evolution of both carbonate and silicate phases. The simulation exercise shows this to be the case (Table A2); whereas organic matter diagenesis alone results in no concentration change for potassium, silicate weathering can increase of dissolved potassium by up to a factor of 2 (Fig. 3E).

Calcium concentration changes show that alteration of silicate minerals contribute ~50% of the calcium in the calcite formed after 2000 years (blue versus green symbols in Fig. 3F). Our simulation does not include downward fluxes from the overlying seawater, nor any cation exchange reactions, and it is shown here only with the purpose to illustrate the significance of silicate mineral contributions relative to available dissolved calcium in a closed system below the SMT.

The drop in pH during methanogenesis (Fig. 3B) affects saturation of all carbonate minerals. Calcite saturation is controlled by both alkalinity and the availability of the calcium ions (difference in blue and

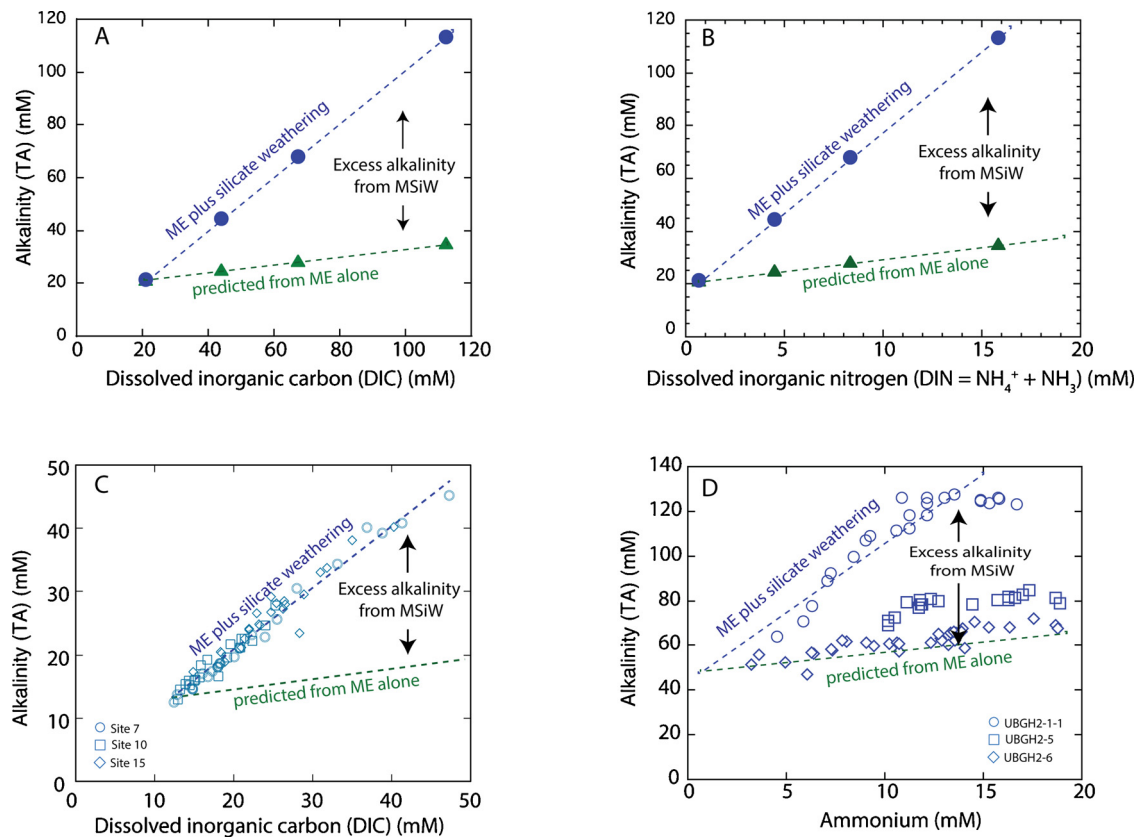


Fig. 2. Changes in total alkalinity (TA) versus (A) dissolved inorganic carbon (DIC) and (B) dissolved inorganic nitrogen ($\text{DIN} = [\text{NH}_3] + [\text{NH}_4^+]$) during methanogenesis (ME) (i.e. system devoid of sulfate below the SMT) in the presence (blue symbols) and absence (green symbols) of reactive silicate (in this example biotite and anorthite). TA, DIC and DIN were chosen as they are the species commonly measured in pore water analytical protocols. The amount of conversion of CO_2 to alkalinity depends on the amount of reactive silicates available, but silicate weathering can buffer up to 100% of the CO_2 generated by methanogenesis. Details of the simulation parameters including reaction network and initial conditions are given in supplementary material. C. TA versus DIC in pore water below the SMT from the Krishna-Godavari Basin for Sites 7, 10 and 15 (from Solomon et al., 2014). The dotted green line denotes the predicted alkalinity from methanogenesis (from Fig. 2A), blue line shows TA when MSiW reactions are included. D. TA versus ammonium for samples from the Ulleung Basin (Sites UBGH2-1_1, UBGH2-5 and UBGH2-6) below the SMT. The dotted green line is the predicted relationship in a system devoid of silicate (green symbols Fig. 2B). The increase in alkalinity observed in samples from UBGH2-1_1 reflects conversion of the CO_2 from methanogenesis to bicarbonate via MSiW (data from Kim et al., 2016). For sites UBGH2-5 and UBGH2-6, alkalinity data also reflect a carbonate precipitation component as discussed by Kim et al. (2016). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

red symbols in Fig. 3C and 3F). Calcite is only stable in systems where the pH and the cation concentration in pore water is regulated through MSiW. This is shown by the rapid decrease below saturation (given as $\log_{10}(\Omega/\text{Ksp})$; where Ω = ion activity product and Ksp = solubility constant) when silicate weathering is not included in the simulation (green triangles in Fig. 3D). Similarly, our simulation also shows that dolomite formation in the methanogenic zone necessitates the co-occurrence of MSiW reactions (Table A2). Dolomite saturation (shown in Fig. 3H as the $\log_{10}(\Omega/\text{Ksp})$) decreases rapidly in a system where only methanogenesis is occurring, leading to unstable conditions shortly after burial in acidic waters. In addition, dolomitization requires a significant supply of Mg, which we show (Fig. 3G) can be released from silicates (in this simulation, biotite). Indeed, extremely high dissolved Mg concentrations (up to 71 mM) were measured in the Ulleung Basin, which have been attributed to biotite alteration (Kim et al., 2016). Carbonate mineral precipitation below the SMT is thus only possible through the supply of ions (Ca and Mg) and the buffering role of MSiW.

We stress that our model set-up was not intended to simulate conditions of any specific sediment system; rather, we designed it to show scenarios that underscore the fact that the cation and alkalinity budgets in the dissolved phase are significantly impacted by silicate alteration. Clearly the resulting geochemical composition of fluids and authigenic phases depends on the nature, abundance, and distribution of the reactive silicate pool. Furthermore, in natural systems other processes

also play a role in the cation and carbonate inventories. For example, basement alteration constitutes a significant calcium source, which results in carbonate formation both within the basement as well as by diffusion into the lower sediment sections (McDuff and Gieskes, 1976; Gieskes and Lawrence, 1981; Sample et al., 2017). Other reactions such as ion exchange, iron-sulfur networks, reverse silicate weathering, smectite to illite conversion, as well as external factors such as the amount and nature of organic carbon and sedimentation rates all influence sediment diagenesis and pore water profiles. A fully coupled model that includes all these reactions in various different settings is beyond the scope of this study. Rather, in the sections below we present data collected by drilling off India, Japan and Korea (Fig. 1), as examples of the fundamental role of MSiW in authigenic carbonate formation.

3. Examples from passive and active margins

We selected the India passive margin and the active subduction zone off Japan (from the input section to its back-arc basin) as examples to illustrate the carbon-silica coupling in systems where the reactive silicate is supplied by both clastic and igneous sources. At these locations there exists a good data set suitable for this review (Figs. 4 and 5); a few additional analyses were conducted in support of this study to complement the available data. All the data sources and methods used to

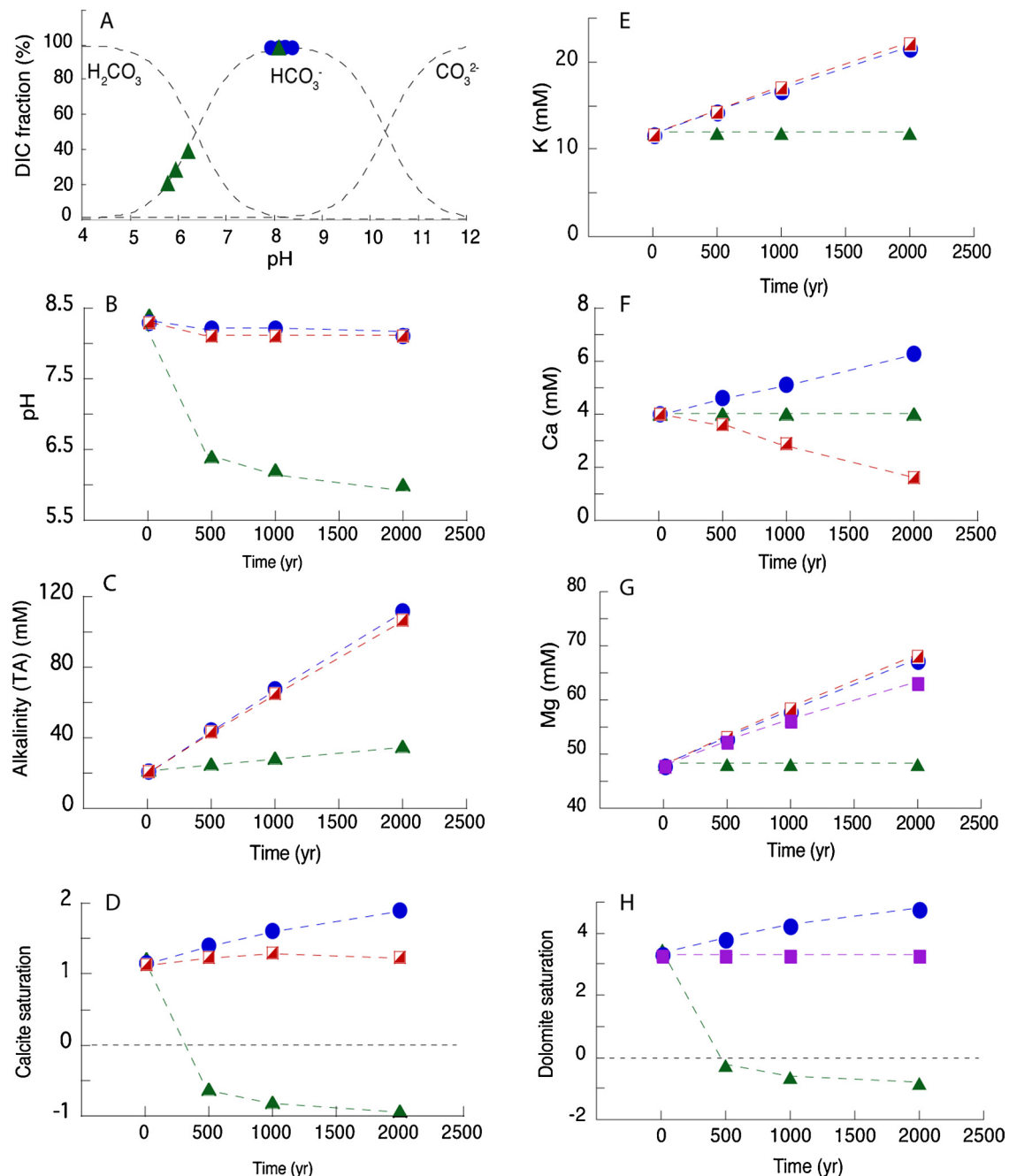
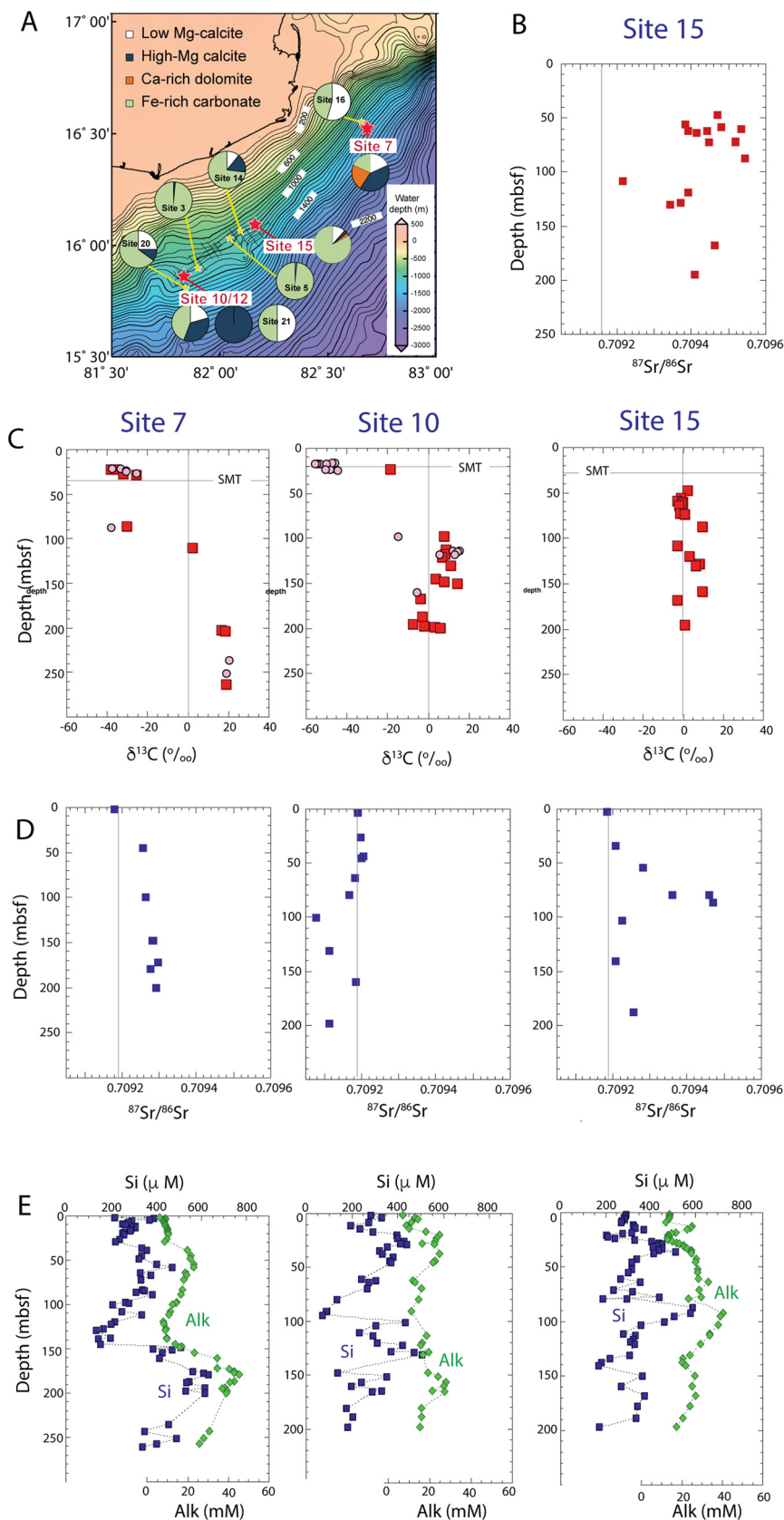


Fig. 3. Simulated response of a marine sediment system undergoing methanogenesis (below the SMT) in the presence (blue and purple symbols) and absence (green symbols) of reactive silicate (in this example biotite and anorthite). The effect of calcite precipitation is shown by the red symbols, the effect of dolomite formation is shown by purple symbols. A. Change in carbonate speciation predicted as a function of changing pH (green symbols = absence of reactive silicates, blue symbols = organic matter and silicate alteration). B. As methanogenesis progresses, CO_2 is produced, which would lower the pH from seawater value of 8.1 to 6.0 in 2000 yr; buffering by silicate weathering consumes CO_2 and generates bicarbonate (Eq. [1] in text), so that the resulting fluid will maintain a pH above 8 (red and blue symbols). C. Changes in total alkalinity in the absence (green symbols) and presence (blue symbols) of reactive silicates, alkalinity is removed by formation of authigenic carbonates (red symbols). D. Calcite saturation (expressed as the $\log_{10}(\Omega/K_{sp})$) illustrating how anoxic sediment undergoing methanogenesis will rapidly become undersaturated with respect to calcite as the pH drops (green symbols), unless the system is buffered by MSiW (blue symbols); as calcite is produced calcium ions are consumed and calcite saturation decreases (red symbols). E. Changes in potassium concentration in pore water, showing the contribution from silicate weathering (red and blue symbols) compared with green symbols that denote no MSiW. F. Changes in calcium concentration in the pore water. The only sources considered are dissolved calcium, which at the SMT we assigned a value of 4 mM (due to carbonate formation above the SMT) and calcium supplied from silicate phases. This plot illustrates the role of silicate phases in supplying cations for carbonate precipitation, which in this scenario shows that ~50 % of the calcium is supplied by a calcium aluminosilicate (anorthite). G. Change in magnesium concentration that results from MSiW reactions, purple symbols denote magnesium uptake by dolomite formation. H. Dolomite saturation (expressed as the $\log_{10}(\Omega/K_{sp})$) illustrating how anoxic sediment undergoing methanogenesis will rapidly become undersaturated with respect to dolomite as the pH drops (green symbols), unless the system is buffered by MSiW (blue symbols); as dolomite is produced, calcium and magnesium ions are consumed, and dolomite saturation decreases (purple symbols). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).



Carbonates

Pore Water

Fig. 4. A. Mineralogy of carbonates recovered at sites drilled in the Krishna-Godavari Basin overlaid on the regional bathymetry (from [Teichert et al., 2014](#)). B. Strontium isotopic composition of carbonates from Site 15. C. Carbon isotopic composition of carbonate samples ($\delta^{13}\text{C}$ VPDB) from Sites 7, 10 and 15. The circles designate MDAC and the squares show Fe-rich carbonates or dolomites indicative of MSiW reactions, vertical line denotes seawater value and horizontal line marks location of the SMT (data from [Solomon et al., 2014](#)). D. Strontium isotopic composition of pore water from Sites 7, 10 and 15, vertical line denotes seawater value (data from [Solomon et al., 2014](#)). E. Dissolved silica and alkalinity in of pore water from Sites 7, 10 and 15 (data from [Solomon et al., 2014](#)).

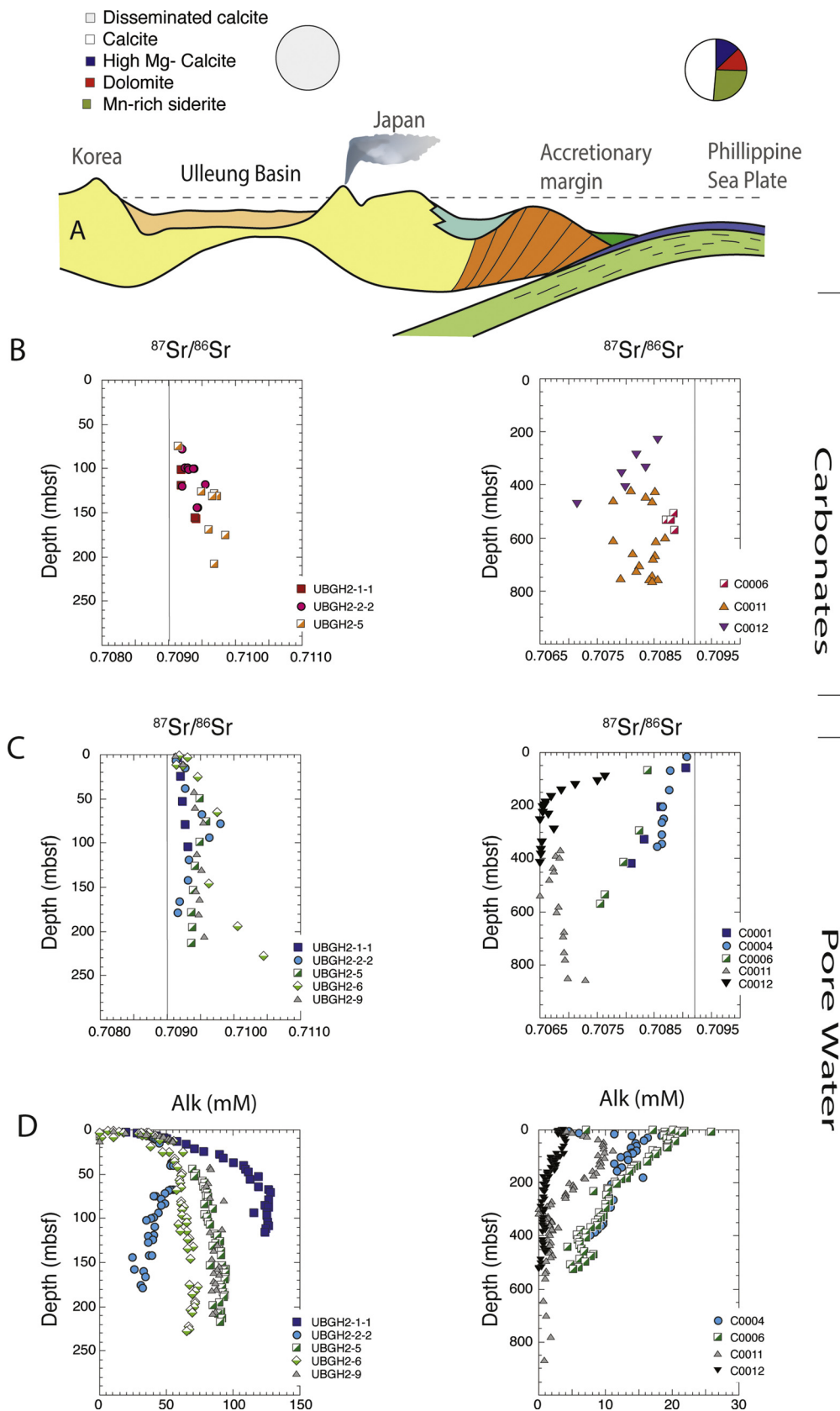


Fig. 5. A. Diagram indicating location of samples in the Philippine Sea Plate (IODP Expeditions 322 and 333), the accretionary prism (IODP Expeditions 315 and 316), and the Ulleung Basin (Expedition UBGH2). Pie diagrams indicate mineralogy of the carbonate samples. B. Strontium isotopic composition of carbonates from the Philippine Sea Plate (right panel; [Sample et al., 2017](#)); the accretionary margin and the Ulleung Basin (left panel; this study). C. Strontium isotopic composition of pore water from the Philippine Sea (right panel; [Sample et al., 2017](#)), the accretionary margin and the Ulleung Basin (left panel; [Kim et al., 2016](#)). Vertical lines denote present seawater value of 0.70917 ([Paytan et al., 1993](#)), for the Nankai samples coeval values range from present day to 0.7089 (see text). D. Left panel shows alkalinity data for the Ulleung Basin ([Kim et al., 2016](#)), right panel shows alkalinity in pore water from the Philippine Sea ([Saito et al., 2010](#); [Henry et al., 2012](#)) and the Nankai accretionary margin ([Kinoshita et al., 2009](#)).

Table 1

Location, water depth and depth to the SMT of sites discussed in this review.

Site	Location	Water depth (m)	SMT depth (mbsf)	Sources
NGHP01-7	KG Basin	1284	36	Solomon et al., 2014
NGHP01-10		1039	18	
NGHP01-15		926	31.5	
UBGH2-1_1	Ulleung Basin	1529	7.8	Kim et al., 2016
UBGH2-2_2		2092	7.5	
UBGH2-5		1969	8.3	
UBGH2-9		2106	6.6	
C0001	Nankai accretionary margin	2190	14	Kinoshita et al., 2009
C0004		2635	16-20	
C0006		3873	8-12	
C0011	Shikoku Basin, input sites	4079	80	Henry et al., 2012
C0012		3539	300	

generate new data are listed in the supplementary material (Table B1). The site locations discussed herein, and their SMT depths are listed in Table 1.

3.1. The Indian margin

The Bengal Fan, the largest submarine fan on Earth, results from the uplift and erosion of the Himalayas and Tibetan Plateau. Currently this margin receives sediment loads in excess of 1.2 billion tons a year from rivers draining the Himalayas (Milliman and Meade, 1983; Subramanian and Ramanathan, 1996). Bengal Fan sediments along the eastern passive Indian margin were sampled by drilling during the Indian-funded National Gas Hydrate Program (NGHP) in 2006. The Krishna and Godavari rivers deliver suspended sediment loads rich in smectite, feldspar, quartz, kaolinite, and illite (Subramanian, 1980; Phillips et al., 2014) to the offshore sediment. Solomon et al. (2014) provide a detailed analysis of an extensive suite of pore water data from the ten sites cored in the Krishna-Godavari (KG) Basin. They describe processes affecting concentration and isotopic ratios of various components in the dissolved phase, and discuss in detail how the CO₂ produced through microbial methanogenesis is effectively neutralized by silicate weathering, which is most prominent between approximately 50 to 300 mbsf. Here (Fig. 4) we only show the subset of the data that reveal MSiW reactions.

Intense organic matter degradation is typical of this margin, with SMT depths ranging from 10 to 30 mbsf (Table 1). This depth range is consistent with global average estimates of SMT depths in shelf and slope sediments (Egger et al., 2018), and corresponds to regions characterized by high methane flux to the SMT. Methane production continues below ~130 mbsf at several of the KG Basin sites. AOM leads to a dissolved inorganic carbon pool depleted in ¹³C, with values of −40 ‰ and −58 ‰ (VPDB) at the SMT of Sites 7 and 10, respectively

Table 2

Examples of strontium isotopic ratios indicative of weathering of continentally-derived and volcanogenic silicates, here reported as the maximum of minimum values in pore fluid samples.

	Location	Site	Depth (mbsf)	⁸⁷ Sr/ ⁸⁶ Sr	Reference
Continental margin sources	Krishna Godavari Basin (India)	NGHP1-15	87	0.7095	Solomon et al., 2014
	Ulleung Basin (Korea)	UBGH2-6	227	0.7104	Kim et al., 2016
	Sumatra (input section)	IODP U1480	325	0.7137	McCarthy et al., 2019
Volcanogenic sources (tephra)	Nankai (input section)	IODP C0011	539	0.7065	Joseph et al., 2013
	Nankai (input section)	IODP C0012	386	0.7065	Joseph et al., 2013
	Nankai (accretionary margin)	IODP C0006	571	0.7076	This study
	Sulu Sea	ODP 768	383	0.7072	von Breyman et al., 1991
	Costa Rica northern forearc	ODP 1040	357	0.7075	Kastner et al., 2006
	Costa Rica southern forearc	IODP 1378	400	0.7076	Ross et al., 2015

(circles in Fig. 4C).

As shown by Solomon et al. (2014), the alkalinity increase below the SMT is associated with MSiW reactions, which also impact the dissolved silica profiles (Fig. 4E). The 1:1 relationship between DIC and TA (shown in Fig. 2C) indicates that in this margin, all the CO₂ generated by methanogenesis was fully converted to alkalinity (Eq. [1]; Solomon et al., 2014). The full conversion of methanogen-produced CO₂ to alkalinity, as observed in the KG sites is only possible when there are enough reactive silicate phases to fully buffer the newly generated CO₂; this may not always be the case.

Even though MSiW generates alkalinity, in the eastern Indian margin alkalinity is not extremely high (< 45 mM; Fig. 4E), because here the excess alkalinity produced by MSiW is sequestered by carbonate precipitation favored by the abundant release of cations through silicate weathering (Solomon et al., 2014). Authigenic carbonates were indeed recovered from these sediments and analyzed by Teichert et al. (2014), who identified two distinct populations: 1) methane-derived aragonite, calcite and high-magnesium calcite depleted in ¹³C, formed by AOM reactions at the SMT; and 2) dolomite and Fe-rich carbonates enriched in ¹³C, attributed to weathering of silicates in the methanogenic zone (Solomon et al., 2014).

Pore water ⁸⁷Sr/⁸⁶Sr (Fig. 4D) shows distinct deviations from the modern seawater value of 0.70917 (Paytan et al., 1993). These deviations and the resulting signature in the strontium isotopic composition of the carbonates (Fig. 4B) are an excellent tracer for MSiW reactions, as discussed in more detail in Section 4.

3.2. Margins off Japan and Korea

Abundant clastic silicates are also present offshore Korea in the back-arc setting sampled during the second Gas Hydrate Expedition to the Ulleung Basin (UBGH2) in 2010 (Figs. 1 and 5). The > 4 km of sediment that fills this basin reflects the large sediment load of rivers draining the Asian continent, which include the Nakdong, Yangtze, and Yellow rivers (Meng et al., 2008; Shin et al., 2011), coupled with intensive mass transport events since the Pleistocene (Chough et al., 2000; Kim et al., 2013). The organic content of the sediment is ~1%, typically of marine origin (KIGAM, 2011). This set of conditions has led to a basin characterized by high methane fluxes and shallow SMT depths (Table 1). The extremely high alkalinity (up to 130 mM; Fig. 5D) in the pore water was put forward as evidence for weathering of clastic silicate minerals within methanogenic sediments (Kim et al., 2016). Ammonium is released below the SMT as organic matter is metabolized by methanogens, but the high alkalinity values at Site UBGH2-1_1 cannot be explained solely by organic metabolic pathways (green dotted line in Fig. 2B and D). Rather, the excess alkalinity (blue symbols Fig. 2B and D) must reflect a contribution from MSiW reactions. The strontium in the pore water is enriched in ⁸⁷Sr, as observed offshore India and further discussed in Section 4.

In contrast to passive margins that receive a significant detrital silicate input, volcanic ash is a common constituent of active margin

sediments (Table 2) and the alteration products of this highly reactive silica phase have long been documented (e.g. Gieskes and Lawrence, 1981). Not surprisingly, sediment from the Nankai subduction zone recovered by drilling on the incoming Philippine Sea Plate (IODP Expeditions 322 and 333) and on the accretionary prism (IODP Expedition 316) contains tuffaceous layers with 25 to 75 vol% volcanic glass, originating from the Japan and Izu-Bonin-Mariana volcanic arcs (Scudder et al., 2014). Sites C0001 and C0004 sampled the youngest sediments on the slope overlying the accretionary prism, which consist of slowly deposited hemipelagic clay and clayey silt with intercalations of volcanic ash. The SMT at these sites is shallower than 20 mbsf, below which there are clear indications of biogenic methane generation (Kinoshita et al., 2009). At Site C0006, drilled on the seaward edge of the accretionary prism, sulfate depletion and a concomitant increase in methane concentration at ~8 mbsf place the SMT to ~8–12 mbsf (Kinoshita et al., 2009). At these sites, alkalinity only reaches 25 mM (Fig. 5D).

The sediment input to the subduction zone was sampled at Sites C0011 and C0012 on the Shikoku Basin (Saito et al., 2010; Henry et al., 2012). Sediment here was deposited at relatively low sedimentation rates, and is dominated by hemipelagic sequences with < 0.5 wt% total organic carbon (TOC). Consequently, the SMT at Sites C0011 and C0012 is considerably deeper than at sites drilled on the accretionary prism. The alkalinity in pore water recovered from the incoming sediments to the Nankai subduction zone range from ~20 mM to values below seawater concentrations in the deeper sediments cored (Fig. 5; Sample et al., 2017). These alkalinity values by themselves would not suggest a component of MSiW, however, as shown by Sample et al. (2017) and discussed below, the $^{87}\text{Sr}/^{86}\text{Sr}$ data in pore water and the composition of authigenic carbonate minerals recovered at depth are indicative of a MSiW pathway. Pore water in the input sites shows a marked increase in dissolved silica suggestive of ash alteration, consistent with observations in smear slide samples (Henry et al., 2012). The $^{87}\text{Sr}/^{86}\text{Sr}$ profiles show a distinct and marked depletion of the radiogenic ^{87}Sr (Fig. 5), also reflecting the alteration of volcanogenic silicates (Joseph et al., 2013). Sites drilled in the accretionary margin (Sites C0001, C0004 and C0006; Fig. 5) also have a strontium isotopic fingerprint of ash alteration reactions (see Section 4).

3.3. Evidence for marine silicate weathering (MSiW) in methanogenic marine sediment

The data collected across the distinct provinces outlined above provide solid evidence for coupling of methanogenesis with marine weathering of reactive silicates (both clastic and volcanogenic). As shown by Wallmann et al. (2008) and illustrated by our simulation results in Section 2, alkalinity values > 67 mM attest to ongoing MSiW reactions in the methanogenesis zone. In the Ulleung Basin, alkalinity reaches 130 mM (Figs. 5, 2D). Plots of alkalinity vs. DIC and alkalinity vs. DIN (Fig. 2) can also be used as diagnostics of these coupled carbon-silica reactions (e.g. Solomon et al., 2014). However, the examples discussed in Sections 3.1 and 3.2 highlight the fact that, whereas in some margins the excess alkalinity is a definite indicator of MSiW, removal of carbonate ions via authigenic carbonate phases can significantly consume the excess alkalinity, masking the silicate weathering contribution. Similarly, whereas an increase in dissolved silica is suggestive of MSiW, biogenic silica phases also release dissolved silica to the pore water. A better diagnostic for MSiW is provided by $^{87}\text{Sr}/^{86}\text{Sr}$ data, which in pore water reflects input of strontium from the mineral phase undergoing alteration.

Old continental rocks (granites) have a larger Rb/Sr ratio than basaltic melts. Their enrichment in the radiogenic ^{87}Sr arises from the emission of a negative β -particle as ^{87}Rb decays through time (Veizer, 1989). In contrast, low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios characterize the upper mantle and rocks derived from it (basalts). When marine sedimentary material is deposited, its pore water reflects the seawater composition.

Currently, the ocean has a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70917 (Paytan et al., 1993), but this value has varied through time due to changes in relative inputs from continental weathering and hydrothermal sources (Veizer, 1989). After deposition, changes in the concentration and isotopic composition of dissolved strontium reflect remobilization of reactive Sr-bearing phases superimposed on the coeval seawater signal. Potential source materials that can modify the strontium isotopic composition of the pore water are continental detritus ($^{87}\text{Sr}/^{86}\text{Sr} = \sim 0.7119\text{--}0.7133$), volcanogenic material ($^{87}\text{Sr}/^{86}\text{Sr} = \sim 0.7065$), and/or exchange with the oceanic crust ($^{87}\text{Sr}/^{86}\text{Sr} = \sim 0.703$) (Elderfield, 1986).

Margins that receive continent-derived reactive silicate minerals, reveal their alteration as enrichment in the radiogenic ^{87}Sr in pore water relative to coeval seawater; as shown by values as high as 0.7104 and 0.7095 for the Ulleung and KG basins, respectively (Figs. 4 and 5; Table 2). Similar ^{87}Sr -enriched fluids have been reported for sites drilled offshore Sumatra, indicating the long-range effect of the continentally-derived minerals from the denudation of the Himalayas (McCarthy et al., 2019; Table 2). Such radiogenic values are in stark contrast with the dissolved strontium isotopic ratio in the input section and accretionary prism of the Nankai subduction system (Fig. 5), where tephra deposits constitute the reactive silica source (Joseph et al., 2013). The $^{87}\text{Sr}/^{86}\text{Sr}$ values in the pore water are lower than in seawater, reaching a value of 0.7065. Such strong depletions in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in marine pore water have been observed globally along convergent margins that are influenced by input from volcanic sources (Table 2).

3.4. Carbonate formation triggered by MSiW

Authigenic minerals record the composition of the formation fluids from which they precipitated, thus the carbonates recovered offshore India display an enrichment in ^{87}Sr over seawater values (Fig. 4). Along the transect shown in Fig. 5, the strontium isotopic composition of carbonate minerals ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7015$ to 0.70891) recovered from the input sequence to the Nankai subduction zone (Sites C0011 and C0012) plots between coeval seawater and pore water values. As demonstrated by Sample et al. (2017) these data are indicative of a mixture of inorganic carbon, strontium, and other cation reservoirs.

The strontium isotopic tracer thus constitutes an excellent tool to fingerprint the effect of MSiW during carbonate formation. These authigenic carbonates also have other distinctive characteristics. For example, in contrast with MDAC, which are typically aragonite and high-magnesium calcite, below the SMT authigenic carbonates commonly include siderite and dolomite, as well as elevated Fe, Mn and Ba values in the calcite structure, as observed both in offshore India and in the Nankai subduction zone (Teichert et al., 2014; Sample et al., 2017; Kocherla et al., 2015). In addition to mineralogy, the carbonate minerals formed in the methanogenic zone are typically enriched in ^{13}C , reflecting the isotopic composition of the residual DIC pool generated during preferential uptake of ^{12}C by methanogens (Solomon et al., 2014; Teichert et al., 2014). However, this signal can be masked when the carbonate sample has components of both MSiW as well as an early MDAC phase.

Sample et al. (2017) used a mass balance approach to constrain possible mixing scenarios of early, high-Sr and late, low-Sr cements from Sites C0011 and C0012. The mass balance relied on various assumptions that include a $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.7089 for late Tertiary seawater (Veizer et al., 1999), and estimates of the strontium content of the various postulated fractions (e.g. Sample and Kopf, 1995). The Sr isotopic composition of the carbonate samples from which clumped oxygen isotopic data were available was used to further constrain the model results. The best fit to the data indicates that deeper cements contain up to 10% relic early carbonate, with Sr concentrations between 500–600 ppm, whereas the dominant portion is a late cement with 25–50 ppm Sr and an isotopic composition reflecting a pore water that has equilibrated with altered ash. Sample et al. (2017) note that the

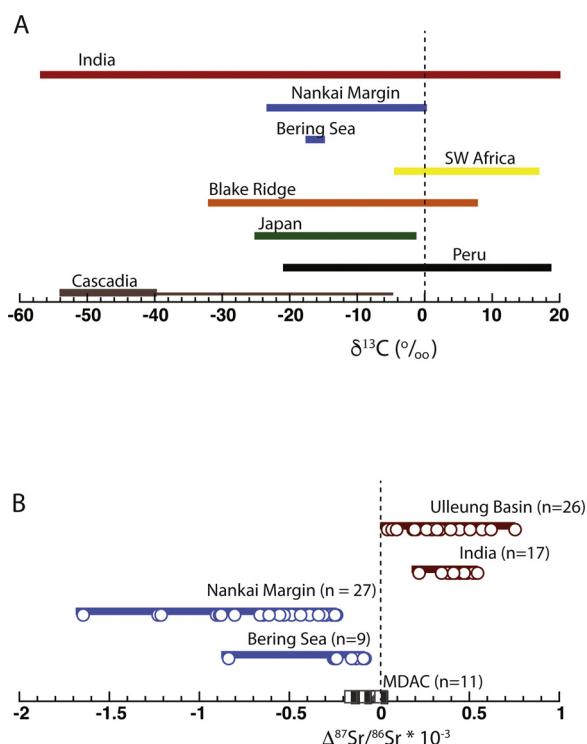


Fig. 6. A. Range of carbon isotopic composition of organogenic dolomite samples ($\delta^{13}\text{C}$ VPDB) (data sources listed in supplementary documents). B. Deviation of the strontium isotopic composition of dolomite samples relative to coeval seawater values, illustrating the wide range of values preserved in carbonates when influenced by alteration of volcanogenic material (blue lines) or continentally-derived silicates (red lines) compared with the narrow range of values in MDAC shown in black (Table S1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

model results are not unique, and could be improved with Sr concentration data from a range of carbonate cements in the Shikoku Basin. Nonetheless, the Sr isotopic data from the carbonate samples revealed continuous cementation of the deep sediment supported by both traditionally recognized carbon cycling mechanisms as well as by the production of bicarbonate from volcanic ash alteration coupled to methanogenesis, such that some of the later-formed carbonates can retain geochemical fingerprints of their early formation history (Sample et al., 2017).

3.4.1. Organogenic dolomites

Dolomites recovered from organic-rich continental margins are characterized by a wide range of carbon isotopic compositions that reveal carbon sources associated with organic matter degradation (Fig. 6; Table 1B). This observation was used in the mid 1980's to postulate an organogenic root for these dolomites (e.g. Kulm et al., 1984; Baker and Burns, 1985; Hennessy and Knauth, 1985). In Fig. 1 we show reported locations of organogenic dolomite and of sites where MSiW is inferred based on alkalinity concentrations > 67 mM, to illustrate the global impact of silicate weathering in carbon sequestration, including authigenic dolomite. Description of the geological settings and geochemical conditions associated with the organogenic dolomites used in Figs. 1 and 6, are given in the supplementary material (Appendix B).

Based on laboratory experiments aimed at establishing chemical controls on dolomitization, Baker and Kastner (1981) show that organogenic dolomite formation is inhibited by the presence of sulfate, and conclude that dolomite can form in nature only where sulfate concentrations are low. Notwithstanding more recent studies that question

the inhibiting role of sulfates (e.g. Warthmann et al., 2000), the fact that some of the dolomites are enriched in ^{13}C points to formation in the methanogenesis zone (Fig. 6; Table B1). No explanation has been provided to date as to how these carbonates form (and are preserved) in a system where CO_2 rather than CaH_2 is produced, with the expected drop in pH during methanogenesis. We argue that it is the buffering role of MSiW that drives organogenic dolomite formation in sulfate-depleted environments.

The wide range of carbon isotope values shown in Fig. 6 attests to the various carbon metabolic pathways involved in sedimentary dolomite formation, which include incorporation of carbon from a DIC pool that is highly enriched in ^{12}C . Such depleted $\delta^{13}\text{C}$ values are typically observed at or above the SMT (Hong et al., 2013, 2014). Because of the wide range of $\delta^{13}\text{C}$ values in these organogenic dolomites, a better diagnostic to establish their potential link to silicate weathering is their strontium isotopic composition (Fig. 6). As shown by Sample et al. (2017), carbonate minerals formed deep in the incoming sediment section to the Nankai subduction zone contain relic signatures from previous carbonates, with carbon isotope values that cannot inconclusively point to formation beneath the SMT. Their strontium isotope composition, however, clearly points to the contribution of ash alteration reactions. The organogenic dolomite examples with depleted $\delta^{13}\text{C}$ values that also have a strontium isotopic signature indicative of MSiW shown in Fig. 6, indicate that either MSiW reactions occurred above or near the SMT (see Section 4.1), and/or that the mineral assemblage that formed below the SMT includes relic carbon from an early MDAC (Sample et al., 2017).

A common challenge in the classic literature on organogenic dolomites that formed below the SMT was the need to identify a source for the Ca and Mg ions needed to sustain dolomitization. Various ideas were postulated to this effect, including dissolution/reprecipitation of biogenic carbonate, diffusive flux from overlying seawater (Baker and Burns, 1985), cation exchange driven by high ammonium concentrations, and various ligand complexation reactions (von Breymann et al., 1990). Whereas all these mechanisms may play some role, we have shown that MSiW constitutes an important source of cations, including Mg (see Fig. 3 and Table A2). For example, in the Ulleung Basin, Kim et al. (2016) report magnesium in the pore water in excess of 70 mM at Site UBGH2-1_1, associated with an alkalinity value of 126 mM. There are no carbonate nodules or concretions reported from this margin, but disseminated calcite has a radiogenic strontium signal (Fig. 5). It is unclear why carbonate mineral formation has not proceeded further in this basin, in a manner analogous to that observed in India and Nankai sites, but the Ulleung Basin data nicely illustrate how silicate weathering generates the cations and alkalinity that is needed for dolomitization.

4. Additional considerations

We have focused this review on the role of MSiW on carbonate formation in anoxic sediments. However, we want to point out that this process may not be limited to the methanogenesis zone, rather it can occur throughout the sediment column. Furthermore, the effects of the carbon-silica coupling described here are also apparent in the geologic record, illustrating the pervasiveness of these reactions.

4.1. Proton sources for MSiW in the oxic and sulfidic zones

Marine silicate weathering can also occur above the SMT. Within the oxic zone, organic matter oxidation via oxygen consumption leads to a decrease in pH that drives carbonate dissolution (e.g. Archer et al., 1989; Emerson and Archer, 1990; Wenzhöfer et al., 2001), and can potentially serve to weather silicates. In the thick oxic zones that occur in deep ocean basins, the organic matter and reactive silicate input to the sediment is low, limiting the effect of the carbon-silica coupling.

The situation is less clear in suboxic and sulfidic sediment. Whereas

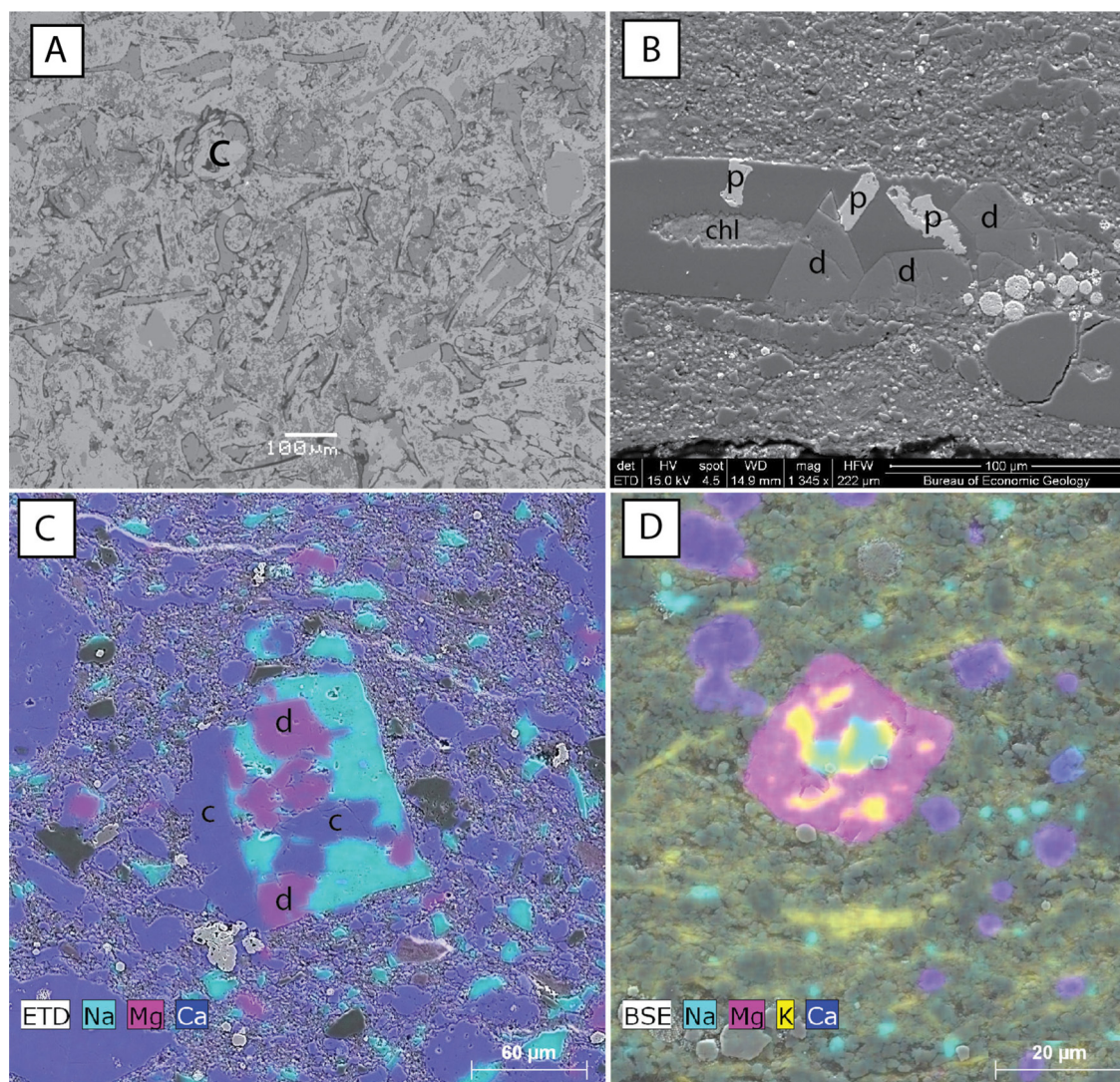


Fig. 7. Examples of carbonate-replaced silicate detritus. A. Partial replacement of volcanic ash and silicates by calcite (c), in IODP Sample 322-C0012A-46R – CC recovered from 474 mbsf in the input sediment sequence to the Nankai Trough; from [Sample et al. \(2017\)](#). B) Fe-dolomite- (d), pyrite- (p) and chlorite- (chl) replaced sponge spicule. Mississippian, Barnett Shale, Fort Worth Basin, Texas, USA. Back-scattered electron image. C. Dolomite- (d) and calcite- (c) replaced plagioclase grain (aqua). Jurassic, Vaca Muerta Formation, Argentina. Energy-dispersive X-ray elemental map. D. Dolomite-replaced plagioclase-K-feldspar grain in an organic-rich mudrock. Devonian Woodford Formation, Permian Basin, west Texas, USA. Energy-dispersive X-ray elemental map.

these redox zones are well developed along continental margins, the pH controls associated with organic matter degradation are complex, as documented by extensive modeling by [Boudreau and Canfield \(1988\)](#). These authors point to the fairly narrow limit of pH in all marine sulfidic pore water, which contrasts with the high variability of protolytic species involved in organic carbon cycling within the ferruginous and sulfidic redox zones. When sulfate reduction leads to sulfide burial, the CO_2 formed from organic matter oxidation is transformed into bicarbonate. In contrast, CO_2 rather than HCO_3^- is produced when sulfide is reoxidized by oxygen. The complex reaction network modeled, which assumes exclusive removal of $\Sigma\text{H}_2\text{S}$ by FeS formation, shows that the pH above the methanogenic zone is highly linked to iron geochemistry and cycling. [Boudreau and Canfield \(1988\)](#) note, however, that the stability of the final pH in sulfidic pore water is likely the result of buffering by silicate reactions that are independent of H_2S , as postulated by [Mackin and Aller \(1984\)](#). As an example, ash alteration within the sulfate-reducing sediment offshore Nicaragua was documented by [Schacht et al. \(2008\)](#), a process that will act to buffer the pH. Furthermore, ash alteration releases iron, which in turn can provide additional buffering capacity by reactions with H_2S .

There is to our knowledge no comprehensive quantitative analyses of the extent to which silicate reactions influence pH above the SMT, nor the degree by which this reaction may impact authigenic carbonate formation. We include this discussion here to illustrate that MSiW is not limited to the anoxic sediments undergoing methanogenesis, but can occur shallower in the sediment column, generating alkalinity and ions for authigenic carbonate precipitation.

4.2. Carbon-silica coupling in the sedimentary record

MSiW coupled with carbonate formation in modern marine sediment serve as an analog system to better understand diagenetic reactions in the deeper subsurface preserved in the geologic record. Carbonate samples from the input sediment to the Nankai subduction zone show textural relationships in which ash is replaced by calcite and rhodochrosite-siderite ([Fig. 7A and B](#)), leading to a cement that is a mixture of clay, carbonate and to a lesser extent silica.

As we have shown here, organogenic dolomite is fundamentally tied to MSiW reactions. Analogies derived from observations of dolomites recovered from organic-rich marine sediment were used to attribute a

diagenetic origin to Miocene dolomites in the Monterey and Drake Formations of California (e.g. Baker and Burns, 1985). The recognition of this diagenetic pathway, which led to a revision of the traditional ideas for the origin of dolomites preserved in the geologic record (e.g. ; Kulm et al., 1984; Hennessy and Knauth, 1985), must now include an understanding of the intimate coupling of carbon-silica reactions necessary for their formation.

The broader significance of coupled carbon-silica reactions is also evident in data reported from clastic sediments that are studied with respect to reservoir quality assessment for oil and gas production, both conventional and unconventional, as illustrated by feldspars and volcanic ash in organic-rich mudstones that display prominent replacement by calcite and dolomite (Fig. 7C and D). A review of some subsurface mudrock and sandstone systems where petrographic evidence for these reactions exists are given by Milliken (2004); the examples presented here are only included to show the widespread occurrence of carbon-silica coupling during diagenesis, as well as the geological consequences that arise from carbonate formation.

In the deeper portions of sedimentary basins, within the zone of hydrocarbon generation, volumetrically significant replacement of detrital feldspars by carbonate (Milliken, 1992; Milliken and Land, 1993) as well as bulk compositional data for rocks and pore water (Smith and Ehrenberg, 1989; Hutcheon et al., 1993; Seewald, 2003; Milliken, 2004; Dutton, 2008) show that linkages between the carbonate and silicate diagenetic systems persist across a wide range of burial conditions. Dissolving silicates appear to be a major control on pH in sedimentary basins (Smith and Ehrenberg, 1989; Hutcheon et al., 1993; Milliken, 2004), whereas the ultimate exhaustion of silicate buffering through near complete loss of the detrital feldspar assemblage appears to correlate with a substantial rise in the $p\text{CO}_2$ of subsurface fluids (Franks and Forester, 1984; Lundegard and Land, 1986; Smith and Ehrenberg, 1989; Milliken, 2004), as predicted from simulation experiments with no reactive silicate (Fig. 3). Proton sources for the deep basinal processes are no doubt different from the ones described here for marine and shallow burial diagenetic systems, but the key point here is that the buffering relationships between silicates and carbonates appear to remain much the same. Similar petrographic relationships between silicates and carbonates are also observed in organic-rich non-marine sediments (Milliken et al., 2017), further attesting to the generality of these observations. To summarize, where reactive silicates are present there is a strong tendency for acid buffering that allows for the precipitation of carbonate minerals.

5. Significance of MSiW in carbon budgets

Carbon is removed from the Earth's surface primarily through burial of calcium carbonate and organic carbon (e.g. Milliman, 1993). Recent studies have shown that quantifying the carbon sequestered in authigenic minerals is critical in unraveling key aspects of the Earth system including carbon flux and reservoir inventories, volatile budgets of the mantle, and redox evolution of Earth's surface (Falkowski et al., 2000; Higgins et al., 2009; Barry et al., 2019).

Following the arguments of Schrag et al. (2013) that highlight the importance of constraining the authigenic component, Sun and Turchyn (2014) used the extensive IODP database to quantify the degree of calcium carbonate precipitation in marine sediments using dissolved calcium and alkalinity data. Assuming a 1:1 Ca:C stoichiometry, their analyses return a minimum rate for carbon removal of $\sim 1 \times 10^{12}$ mol yr^{-1} , with an uncertainty of ~ 50 %. Several interesting observations stem from their analyses. The highest rates of authigenic carbonate formation occur along the eastern margins of ocean basins, where rain of organic carbon to the seafloor is highest. Here, the alkalinity flux out of continental margin sediments is approximately 15 % of the global riverine flux. They associate the alkalinity generation exclusively to organic carbon oxidation, and note that this flux in the deep ocean is lower than along continental margins (Sun and Turchyn, 2014).

Our results add a fundamental missing piece to their analyses by providing the mechanism needed for enhanced alkalinity generation along the ocean margins. In a simple view of carbon cycling in high productivity zones, the biological pump removes CO_2 from the atmosphere. In high productivity regions the redox ladder is compressed, so that coupled fermentation and methanogenesis regenerate CO_2 at depths that may be as shallow as a few tens of meters (Egger et al., 2018). However, instead of this process resulting in a CO_2 flux back into the ocean-atmosphere system, MSiW consumes CO_2 and generates the excess alkalinity that is measured in pore water and was used by Sun and Turchyn (2014) to estimate the alkalinity fluxes. The numerical and field data we present in this review demonstrate that the buffering effect of silicate weathering reactions is necessary to generate alkalinity in the slope and shelf regions, where SMT depths are in the order of tens of meters (Egger et al., 2018; Fig. 8). This is the alkalinity needed to precipitate and preserve the volume of authigenic carbonate deposits, which form an important component of the global carbon sink (Fig. 1). Results from our simulation also reveal a significant release of calcium from silicate minerals (Fig. 2), so that estimates of total carbon sequestered in authigenic carbonates based solely on global calcium fluxes from pore water data may be too low, perhaps as much as by a factor of 2. Authigenic calcium carbonate precipitation may represent an even larger component of the global carbon cycle than previously estimated by Sun and Turchyn (2014).

Wallmann et al. (2008) estimate the carbonate sink driven by silicate weathering in anoxic sediment to be $5\text{--}20 \times 10^{12}$ mol C yr^{-1} . This value is based on published methane generation estimates of 7×10^{12} mol C yr^{-1} (Reeburgh, 1993) to 300×10^{12} mol C yr^{-1} (Hinrichs and Boetius, 2002). Using a new revised methane estimate of $\sim 1.2 \times 10^{12}$ mol C yr^{-1} (Wallmann et al., 2012), the carbonate sink is closer $1\text{--}4 \times 10^{12}$ C mol yr^{-1} , in agreement with the estimate of Sun and Turchyn (2014) based on calcium flux data. The carbon sink driven by silicate weathering in marine sediment is in the same order of magnitude as the carbon trapped as carbonate during alteration of oceanic crust (Alt and Teagle, 1999) which, although in a different setting, also involves coupling of carbon and silica reaction networks.

In contrast to observations along continental margins, Sun and Turchyn (2014) show that large areas of the deep ocean are characterized by a calcium flux out of the sediment, indicating dissolution rather than precipitation of authigenic carbonate, an observation that is linked to the pH drop during oxic respiration typical of abyssal plain settings characterized by very deep SMT zones (Fig. 8). In these regions the buffering effect of reactive silicate minerals is much lower, since reactive silica phases are delivered to the ocean via rivers and volcanoes, and thus are not common in the wide areas of the ocean away from lithogenic input.

MSiW is not only important to constrain global budgets, but it is also significant on carbon recycling in subduction zones, where CO_2 may be released from downgoing rocks by devolatilization or via fluid-induced dissolution of calcium carbonate (Kerrick and Connolly, 2001; Frezzotti et al., 2011; Ague and Nicolescu, 2014; Kelemen and Manning, 2015).

Barry et al. (2019) argue that forearc calcite deposition across the Costa Rica convergent margin can remove ~ 91 % of the carbon released from the subducting slab and mantle, with important implications for mantle volatile inventories. The postulated calcite sink in the Costa Rica forearc accounts for removal of 10^8 to 10^{10} mol C yr^{-1} (Barry et al., 2019). It is important to note that their budgets do not include the carbon associated with deposition and alteration of organic carbon in the submarine forearc. Not only is this a carbon fraction not included in their analysis but, in the context of our review, it is noteworthy that the biogenic methane flux in the northern Costa Rica forearc offshore Nicoya (Site 1040) results in an SMT shallower than 35 mbsf (Kimura et al., 1997); in the southern Costa Rica margin the SMT lies at 12 mbsf at Site U1378 and between 30 and 40 mbsf at Site U1379, responding to changes in biogenic methane fluxes (Vannucchi et al., 2012). Whereas the CO_2 generated is the result of

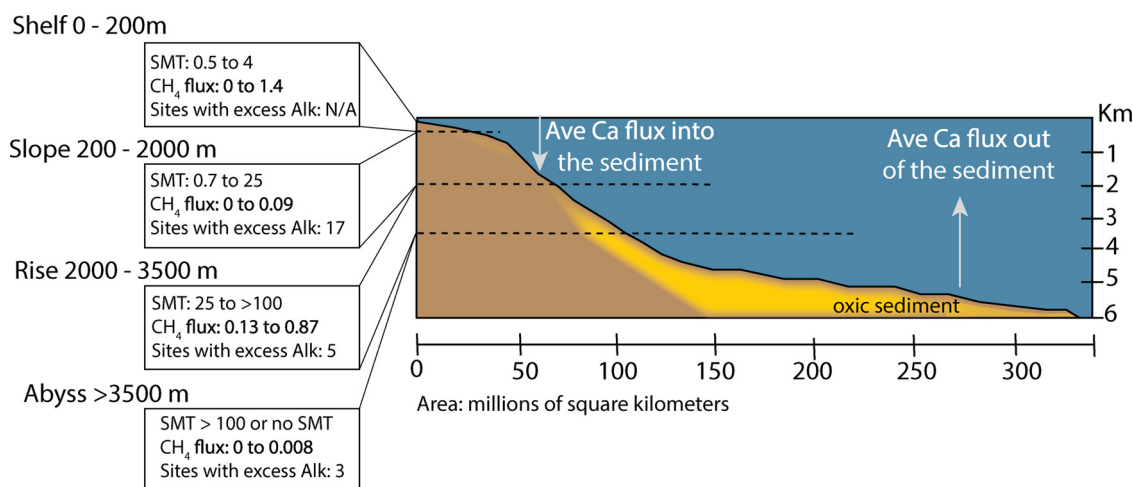


Fig. 8. Schematic diagram that illustrates the role of MSiW in the context of the global ocean. MSiW and associated carbonate formation are more relevant at locations near sources of reactive silicates (input of river discharge and volcanic ash), where the intense organic matter diagenesis results in shallow SMT zones. In these regions there is a calcium flux into the sediment, which, as shown by Sun and Turchin (2014), is indicative of authigenic carbonate formation. Alkalinity in excess of 67 mM, compiled from ocean drilling data bases (Wallmann et al., 2008; Fig. 1), shows that such high values typically occur in the slope and continental rise regions (200 to 3500 m); the shelf is undersampled due to limitations of ocean drilling at shallow depths. MSiW, excess alkalinity and a calcium flux into the sediment occur primarily along continental margins, at water depths < 3500 m (total area $\sim 55 \times 10^6 \text{ km}^2$), which, as shown by Egger et al. (2018), receive significant methane flux to SMT depths that are typically shallower than 25 mbsf. In contrast, in the large areas of the abyssal plain there is a lower rain of organic matter, which results in oxic sediment with SMT depths > 100 mbsf, and $\sim 66\%$ of the abyssal sediment have no SMT (Egger et al., 2018). In these deep settings there is little input of reactive silicates to buffer the decrease in pH associated with oxic respiration, leading to dissolution of calcium carbonate and the observed calcium flux out of the sediment (Sun and Turchin, 2014). Depth to the SMT (given in mbsf) and methane fluxes (given in $\text{mmol m}^{-2} \text{ d}^{-1}$) are from Egger et al. (2018). Numbers of sites with excess alkalinity are from Wallmann et al. (2008).

methanogenesis in forearc sediment or of devolatilization of the subducting crust, the postulated large calcite sink in the forearc basin offshore Costa Rica is only possible if the formation fluids are buffered by silicate weathering.

The above discussion highlights the importance of silica weathering in carbon cycling at global and regional scales. Consideration must always be given to the extent to which the presence of reactive silicate contributes to carbon burial as carbonate minerals, in particular along ocean margins where the bulk of authigenic carbonate is deposited. Exposed dolomite sequences, such as the classic Miocene Monterey Formation in California, provide a visual and impressive reminder of the magnitude of the carbon reservoir that is sequestered in these deposits, which, as we know now, formed in the methanogenesis zone and would not exist today were it not for the buffering effect and cation sources provided by alteration of reactive silica phases.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.earscirev.2019.102960>.

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