



The modern record of “concretionary” carbonate: Reassessing a discrepancy between modern sediments and the geologic record

S.J. Loyd ^{a,*}, W.M. Berelson ^b

^a Department of Geological Sciences, California State University of Fullerton, 800 North State College Blvd., Fullerton, CA 92831, United States

^b Department of Earth Sciences, University of Southern California, 3651 Trousdale Pkwy., Los Angeles, CA 90089, United States

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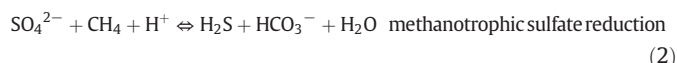
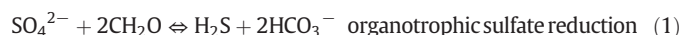
ABSTRACT

Carbonate concretions have long been recognized as common constituents of sedimentary rocks exposed in outcrop. Although formation mechanisms vary, organic matter degradation often plays a role in carbonate concretion authigenesis, providing a source of alkalinity for mineral production. Perhaps surprisingly, modern examples of concretionary carbonates are rarely identified in cores despite ubiquitous organic matter degradation in marine sediments. This has prompted the general notion that the modern record of concretionary carbonate does not mirror that preserved in the geologic record. Here, we present data from continental margin sediments that receive enhanced delivery of organic matter and demonstrate that concretionary carbonates are indeed recovered from many of these sites. In addition, sites where concretionary carbonates have not been recovered exhibit chemical profiles that suggest local authigenesis. The lack of concretion recovery from some locations likely reflects the poor potential for modern coring techniques to adequately capture concretions or provide context for their identification once recovered. Concretionary carbonate recovered from the Peru Margin, Cascadia, the Gulf of California, the Cariaco Basin and the western margin of southern Africa exhibit evidence for modern or very recent formation via methanogenesis or the anaerobic oxidation of methane. Demonstrably modern organotrophic sulfate reduction concretions have not been found.

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1. Introduction

Authigenic carbonates in the form of nodules, concretions and cemented layers comprise a significant lithologic component of some ancient sedimentary rock units (e.g., the Miocene Monterey Formation; [Bramlette \(1946\)](#)). Modern marine concretionary carbonate formation has long been interpreted as non-reflective of the extensive geologic occurrence ([Raiswell and Fisher, 2000](#); [Wetzel, 1991](#)). Apparently, true modern concretions have only been documented from non-marine deposits including marsh ([Allison and Pye, 1994](#); [Pye, 1981](#)), intertidal ([Al-Agha et al., 1995](#)) and fresh water ([Ho and Coleman, 1969](#)) environments. Extensive geochemical analyses of concretionary carbonates (both marine and non-marine) have revealed that the microbial degradation of organic matter plays an important role in mineral precipitation ([Curtis et al., 1972](#); [Irwin et al., 1977](#); [Loyd et al., 2012](#); [Mozley and Burns, 1993](#); [Raiswell and Fisher, 2000](#)). Specifically, anaerobic reactions involving bacterial sulfate reduction (BSR) and methane production are interpreted to have led to carbonate authigenesis largely because these reactions generate alkalinity ([Coleman et al., 1993](#)), as follows:



BSR (Eqs. (1) and (2)) and methanogenesis (Eq. (3)) are common in modern marine sediments, particularly in those under highly productive, upwelling water masses (note, organotrophic sulfate reduction excludes methane here). Therefore, the apparent modern under-representation of marine concretionary carbonate does not match the well-documented extent of concretion-yielding processes.

Here, the modern record of concretionary carbonate is reassessed with specific search criteria applied to Ocean Drilling Program (ODP) and Deep Sea Drilling Program (DSDP) site sediment and pore water data. Sediments along western continental margins experiencing high productivity due to extensive upwelling and sites exhibiting anoxic sediments due to basin restriction are targeted because of the common occurrence of BSR and methanogenesis. It is demonstrated herein that concretionary (and otherwise authigenic) carbonates are not only present in some of these cores, but that they are relatively common. In addition, most cores that do not contain authigenic carbonates exhibit pore water profile characteristics that are consistent with early diagenetic mineral precipitation in sediments, suggesting that coring may have missed the concretionary body and that authigenesis is, nonetheless, ongoing.

* Corresponding author.

E-mail address: sloyd@fullerton.edu (S.J. Loyd).

2. Modern sediment search criteria

Deposits forming under highly productive surface waters where the flux of organic matter to the sediments is high characterize multiple ODP and DSDP sites. As a result of this high export, sediments become anoxic relatively soon after deposition. Such anoxic sediments with high organic carbon contents generally exhibit extensive BSR and methanogenesis as evidenced by decreases and increases in pore water sulfate and methane, respectively. Here, BSR includes the microbially mediated reduction of sulfate by methane. Although this process does not strictly involve bacteria (archaea are thought to play a significant role, (Hinrichs et al., 2000; Orphan et al., 2002)), it would influence pore water profiles similar to BSR (decreased sulfate and increased alkalinity with depth, albeit with a different stoichiometry). Therefore whereas the specific electron donors differ, these two distinct processes would influence pore water chemistry similarly.

Sites off the western margin of North America, South America and Africa and the southern margin of Oman are well known for exhibiting relatively high surface ocean productivity. Here, western margin ODP and DSDP records from the Gulf of California (Leg 64), the Oman margin (Leg 117), the Peru margin (Leg 112), the Cascadia margin (Leg 146), the Santa Barbara Basin (Leg 146), the north African western margin (legs 108 and 157), the central African western margin (Leg 159) and the southern Africa western margin (Leg 175) as well as Blake Ridge (Leg 76) and the Cariaco Basin (legs 15 and 165) (Fig. 1) are targeted to assess 1) the presence of anaerobic organic matter degradation, 2) the presence or absence of authigenic carbonates and 3) indirect evidence for carbonate precipitation. As mentioned above, anaerobic organic matter degradation is identified by pore water profiles of

sulfate and methane (Figs. 2–5). Further evidence for organic matter degradation is provided by ammonia contents of pore waters because organic matter degradation represents a major source of sedimentary ammonia in marine systems (King, 1984; Koike and Hattori, 1978). Organic matter remineralization is also identifiable by carbon isotope compositions ($\delta^{13}\text{C}$) of dissolved inorganic carbon or total CO_2 (TCO_2) that differ from marine values (i.e., $\delta^{13}\text{C}_{\text{TCO}_2} \neq 0\text{‰ VPDB}$) (Claypool and Kaplan, 1974; Irwin et al., 1977). The presence of authigenic carbonate is assessed by core descriptions and includes not only concretionary calcites and dolomites but also disseminated dolomite and calcite crystals, perhaps even as overgrowths precipitated on existing carbonate grains. Indirect evidence for carbonate precipitation is inferred by significant pore water depletions in either calcium or magnesium. Carbonate precipitation potential is indicated by elevated pore water alkalinity and the degree of saturation with respect to calcite and dolomite. The degree of saturation is quantified as the saturation index (SI) defined as $\log \Omega$, where Ω is the saturation state (Berner, 1980), calculated as the respective ion activity product divided by the empirically determined solubility product (e.g., for calcite or dolomite). The SI was calculated via PHREEQC using existing pore water chemical constituents to derive electric charge balances consistently better than 7% and generally to within ~4%. Positive SI values indicate supersaturation. It is important to note that recovered sediment cores, especially those rich in carbonate content, exhibit alkalinity uptake as a result of depressurization and that this decrease likely reflects calcium carbonate precipitation (Murray and Wigley, 1998) as an artifact of core recovery. It is unclear whether or not this core retrieval mineral precipitation would be extensive enough to be recognized during initial core description. For this reason and because pressure influences on mineral saturation are not



Fig. 1. Site map.

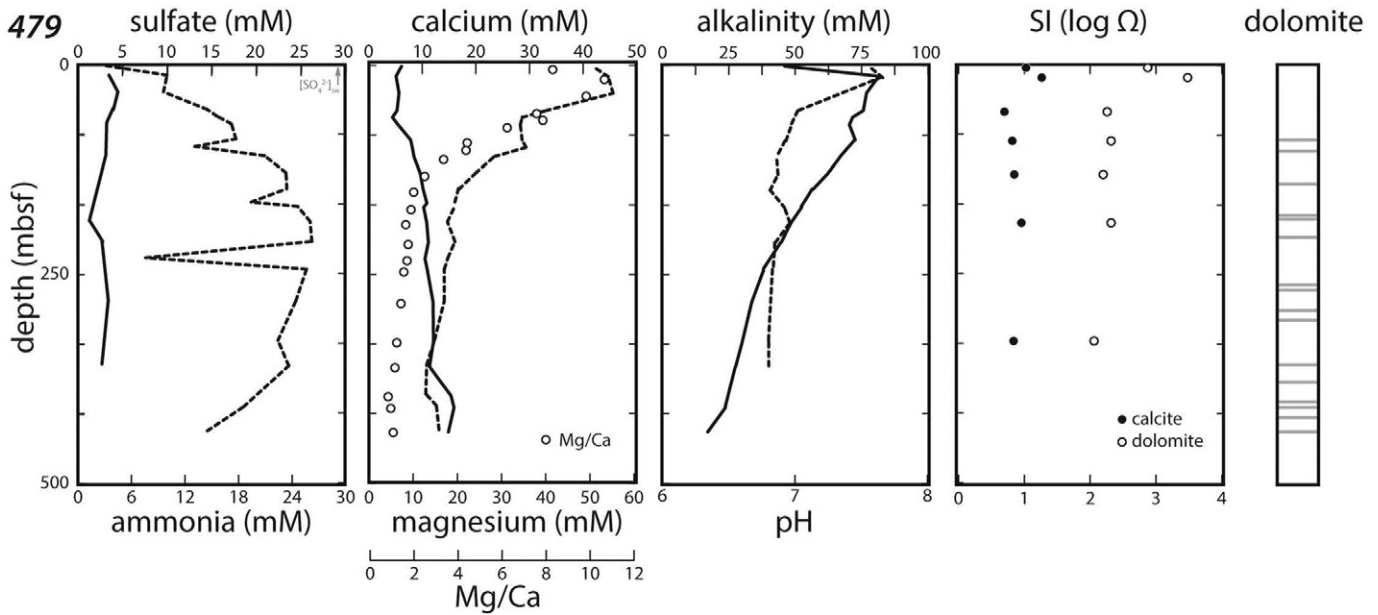


Fig. 2. Pore water data and subsurface concretionary dolomite occurrence of site 479, Gulf of California. Where applicable, top axes correspond to solid lines, bottom axes dashed lines.

accounted for, the saturation values we present should be considered as relative indicators of the preferences of dolomite or calcite saturation (Gieskes, 1974; Raiswell and Fisher, 2004). An explanation of PHREEQC input parameters is provided in the Supplementary Online Material (SOM).

3. Core record results

The sites examined here exhibit fine-grained sediments composed primarily of siliceous micro and nanofossil oozes, silts, muds, mudstones, clays and claystones. Authigenic carbonates are present at many sites and dominated by dolomite (aside from Cascadia and Central Africa) occurring as layers, concretions and disseminated rhombs (Table 1, Figs. 2–5). Calcite and siderite are the dominant authigenic carbonates in sediments from the Cascadia and Central African margins, respectively. In addition to deposition under highly productive surface waters, many of the sites examined here are relatively devoid of primary carbonate. This helps with identification of authigenic carbonate phases that are difficult to identify in carbonate-dominated deposits. In addition, carbonate-rich deposits have a higher potential to be buffered

with respect to calcium, magnesium, alkalinity, TCO_2 and $\delta^{13}\text{C}_{\text{TCO}_2}$ (Banner, 1990). This buffering would limit the ability of pore water records to reflect authigenesis and/or organic matter remineralization. Admittedly, the record of authigenic carbonate reported here is skewed toward the abundance of dolomite. This is because dolomite is almost strictly a diagenetic mineral in open marine systems (Tucker and Wright, 1990), whereas calcium carbonate can have a significant detrital input in the form of primary allochems and sedimentary micrite.

Pore water sulfate concentrations decrease with depth at all sites. Upon sulfate exhaustion, methane contents (where measured) generally increase with depth. Pore water alkalinity is elevated above bottom water concentrations at all sites. Alkalinity correlates well with ammonia, sulfate and methane in nearly all sites (Fig. 6, S14–16). Magnesium concentrations decrease with depth, often correlating with decreasing calcium over shallow sediment depths, generally within 80 m of the seafloor. Site-specific pore water $\delta^{13}\text{C}_{\text{TCO}_2}$ values vary between ~ -20 and $+15\%$ and overlap with authigenic carbonates, where measured, particularly for the shallowest authigenic carbonates. Select profiles are provided in Figs. 2–5. Detailed sediment descriptions, including age constraints, geochemistry, pore water data (including correction for

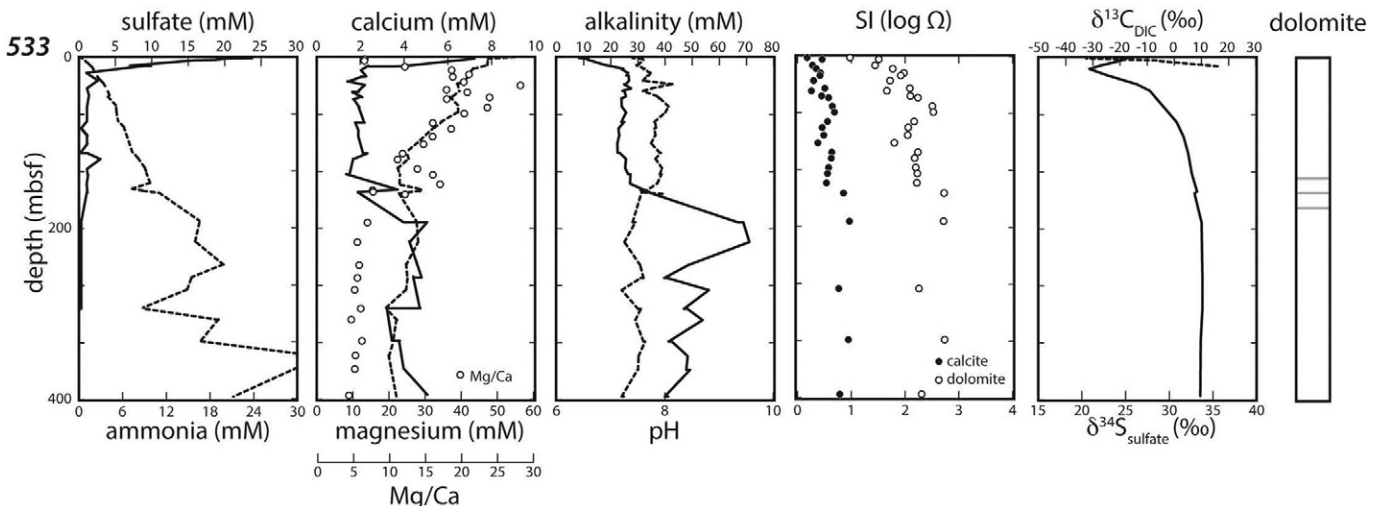


Fig. 3. Pore water data and subsurface concretionary dolomite occurrence of site 533, Blake Ridge. Where applicable, top axes correspond to solid lines, bottom axes dashed lines.

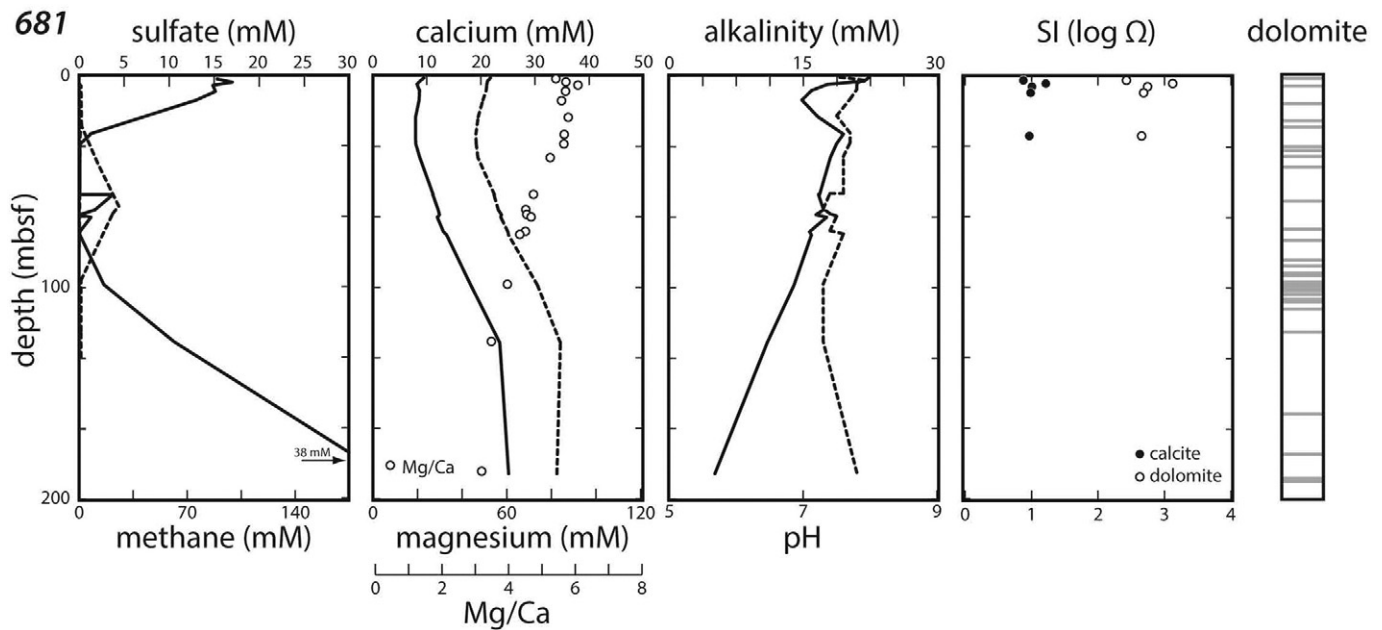


Fig. 4. Pore water data and subsurface concretionary dolomite occurrence of site 681, offshore Peru. Where applicable, top axes correspond to solid lines, bottom axes dashed lines.

potential dilution or mixing) and methods are provided in the SOM or references therein. Specific site data summaries and references are also provided in Table 1.

4. Discussion

Reports of concretionary (and otherwise authigenic) carbonate are relatively common among continental margin ODP and DSDP sites (Table 1). Indeed, when specific sites (those that exhibit evidence for organo-diagenesis) are considered, it is difficult to refute the notion that authigenic carbonate formation does in fact occur in modern sediments. In addition, these concretionary carbonates are well lithified and therefore identifiable and easy to differentiate from normal sediments.

Weak cementation was previously suggested as a potential reason for the apparent lack of modern shallow concretions (Wetzel, 1991). Of the sites examined here, concretionary carbonate has been recovered from 24/64 sites and 8/12 legs. Perhaps deserving more detailed discussions are 1) the relationship between ‘abundant’ outcrop concretionary carbonate and the ‘scarcity’ or ‘lack’ of modern marine concretionary carbonate and 2) what pore water profiles tell us about authigenesis.

4.1. ‘Abundant’ ancient outcrop concretions versus ‘scarce’ modern marine sediment concretions

One possibility is a simple lack of communication between marine geologists and those more focused on outcrop-based research. Although

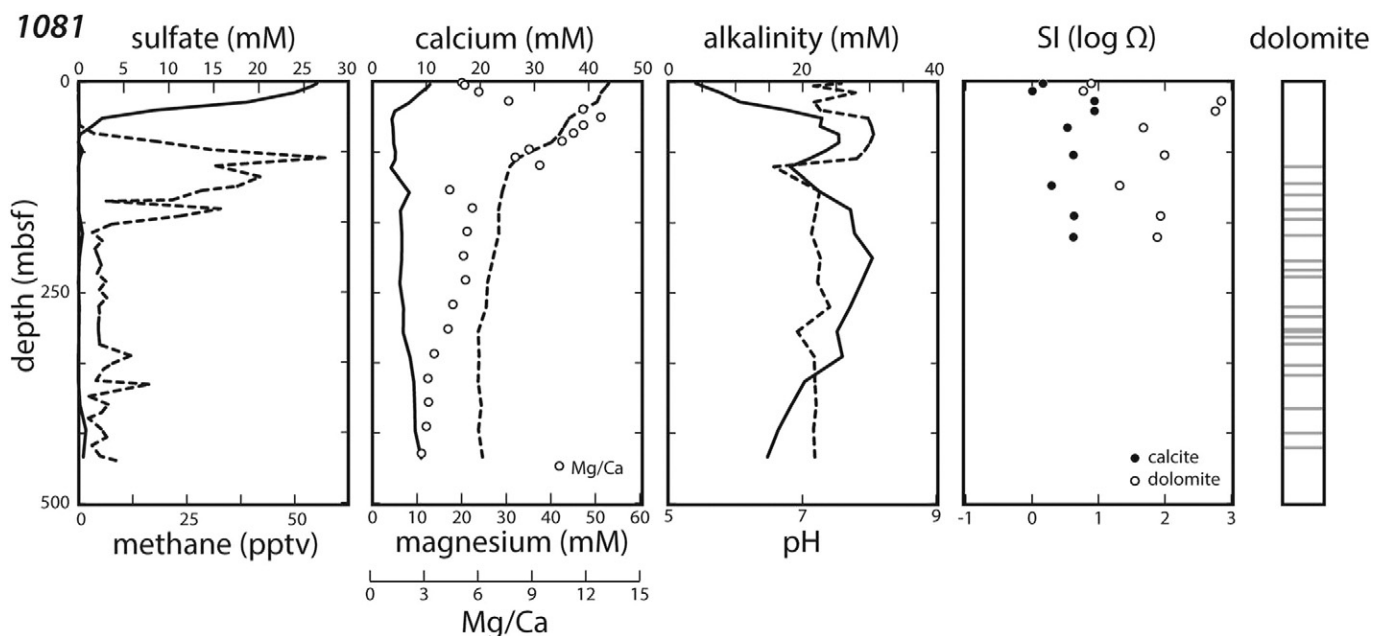


Fig. 5. Pore water data and subsurface concretionary dolomite occurrence of Site 1081, offshore southern Africa. Where applicable, top axes correspond to solid lines, bottom axes dashed lines.

Table 1

Summary of core and pore water data. Direct Evidence for Carbonate Authigenesis includes authigenic carbonate phases recovered from core (Carb. Cement = carbonate cement, Dissem. Carb. Crystals = disseminated carbonate crystals, Undiff. Dolo./Sid. = undifferentiated dolomite and/or siderite). Indirect Evidence for Carbonate Authigenesis includes pore water calcium and magnesium data. Increased pore water alkalinity indicates the potential for carbonate authigenesis. Organo-diagenetic reactions identified by sulfate and methane profiles as discussed in text. Correlations between ammonia, sulfate or methane with alkalinity indicate organic matter remineralization induced alkalinity production (see text). References include ⁶Claypool and Threlkeld (1983); ¹¹Emeis and Morse (1990); ²Gieskes et al. (1982); ³Gradstein and Sheridan (1983); ⁵Jenden and Gieskes (1983); ¹⁵Kastner et al. (1995); ¹Kelts and McKenzie (1982); ¹⁶Kennett and Baldauf (1994); ¹⁴Kopf et al. (1995); ²⁰Masle et al. (1996); ⁴Matsumoto (1983); ¹²Meister et al. (2007); ²³Murray and Wigley (1998); ⁹Pedersen and Shimmield (1991); ⁸Prell et al. (1989); ¹⁸Ruddiman et al. (1988); ¹⁹Schmincke et al. (1995); ⁷Sigurdsson et al. (1997); ¹⁰Suess et al. (1988); ^{21,22}Wefer et al. (1998a, 1998b); ¹³Westbrook et al. (1994).

Direct evidence for carbonate authigenesis															Indirect Evidence for carbonate authigenesis		Organo-diagenesis			Organo-diagenetic alkalinity Increase			References
Location/Leg	Site	Water depth (m)	Concretionary authigenesis		Carb. cement	Dissem. carb. crystals	Carbonate vein fill	Undiff. dolo./Sid.	Downcore ^a Ca ²⁺ decrease	Downcore ^a Mg ²⁺ decrease	Increased pore water alkalinity	Sulfate reduction	Methano-genesis	NH ₄ -Alk correlation	SO ₄ ²⁻ -Alk correlation	CH ₄ -Alk correlation							
			Concretion /nodule	Conc. layer																			
Gulf of California Leg 64	474	3023		x		x			x	x	x	x	x	x	x	N/A	1, 2						
	475	2631		x		x			x	x	x	x	x	x	x	N/A							
	476	2403		x		x			x	x	x	x	x	x	x	N/A							
	478	1889		x		x			x	x	x	x	x	x	x	N/A							
	479	747		x		x			x	x	x	x	x	x	x	N/A							
	481	1998		x		x			x	x	x	x	x			N/A							
Blake Ridge Leg 76	533	>5000		x		x		x	x	x	x	x	x	x	x	N/A	3-6						
Cariaco Basin Leg 165 Leg 15	1002	904	x	x		x			x	x		x	x	N/A		N/A	7						
	147	892										x	x	N/A	N/A	N/A							
Oman Margin Leg 117	721	1945					x	x	x	x	x	x	x	x	x		8, 9						
	722	2028				x	x	x	x	x	x	x	x	x	x	x							
	723	808	x	x		x		x	x	x	x	x	x	x	x								
	724	593						x	x	x	x	x	x	x	x								
	725	312				x		x	x	x	x	x	x	x	x								
	726	331			x			x	x	x	x	x	x	x	x								
	727	915			x			x	x	x	x	x	x	x	x								
	728	1428						x	x	x	x	x	x	x	x								
	730	1066				x			x	x	x	x	x										
	731	2366				x		x	x	x	x			x	x								
Peru Margin Leg 112	679	450	x	x		x				x	x	x	x	x	x	x	10-12						
	680	253	x	x		x		x			x	x	x		x								
	681	151	x	x		x					x	x	x										
	682	3789		x	x			x	x	x	x	x	x	x	x	x							
	683	3072		x	x	x		x	x	x	x	x	x	x	x								
	684	426	x	x		x			x	x	x	x	x		x	x							
	685	5071		x		x			x	x	x	x	x	x	x								
	686	447	x	x		x			x	x	x	x	x	x	x								
	687	307	x	x					x	x	x	x	x		x								
	688	3820				x			x	x	x	x	x	x									
Cascadia Margin Leg 146	888	2516			x	x		x	x	x	x	x	x	x	x		13-15						
	889	1311	x	x	x				x	x	x	x	x			x							
	890	1337	x	x	x				x	x	x	x	x	x	x								
	891	2663	x	x		x			x	x	x	x	x	x	x								
	892	675			x					x	x	x	x		(D only)								
Santa Barbara Basin Leg 146*	893	577				x						x		x	N/A	N/A	16, 17						
North African Western Margin Leg 157	950	5438					x		x	x	x					N/A	18, 19						
	951	5437						x	x	x	x					N/A							
	952	5432						x	x	x	x	x				x							
	953	3578						x	x	x	x					N/A							
	955	2854			x			x	x	x	x	x			x								
	956	3442							x	x	x	x		N/A		N/A							
Leg 108	657	4222							x		x	x		N/A		N/A	20						
	658**	2263							x	x	x	x		N/A	x	N/A							
	659	3070							x	x	x	x		N/A		N/A							
	660	4328								x	x	x		N/A		N/A							
	661	4006								x	x	x		N/A	x	N/A							
	662	3821									x	x		N/A	x	N/A							
Central African Western Margin Leg 159	959	2091			x	x		x	x	x	x	x	x	x	x		21-23						
	960	2048					x		x	x	x	x	x	x	x	N/A							
	961	3292	x			x			x	x	x	x	x	x	x	N/A							
	962	4637			x	x		x		x	x	x	x	x	x	N/A							
South African Western Margin Leg 175	1075	2996							x	x	x	x	x	x	x	x	21-23						
	1076	1402					x		x	x	x	x	x	x	x	x							
	1077	2382							x	x	x	x	x	x	x	x							
	1078	427	x	x					x	x	x	x	x	x	x	N/A							
	1079	738							x	x	x	x	x	x	x	x							
	1080	2766		x					x	x	x	x	x	x	x	x							
	1081	794	x	x		x			x	x	x	x	x	x	x	x							
	1082	1280	x	x		x			x	x	x	x	x	x	x	x							
	1083	2179				x			x	x	x	x	x	x	x	x							
	1084	1992	x	x		x			x	x	x	x	x	x									
	1085	1713							x	x	x	x	x	x	x								
	1086	782	x						x	x	x	x	x	x	x								
1087	1374							x	x	x	x	x	x	x									

N/A = specific data not available.

The significance of shaded (gray) cells/columns indicate direct the presence of concretionary carbonate.

^a Downcore refers to any portion of the profile that shows recognizable decreases in concentration.

^b No geochemical data available.

^c Site 892 composed of a shallow core (892A) and a deeper core (892D).

^d Site 658 is a composite core.

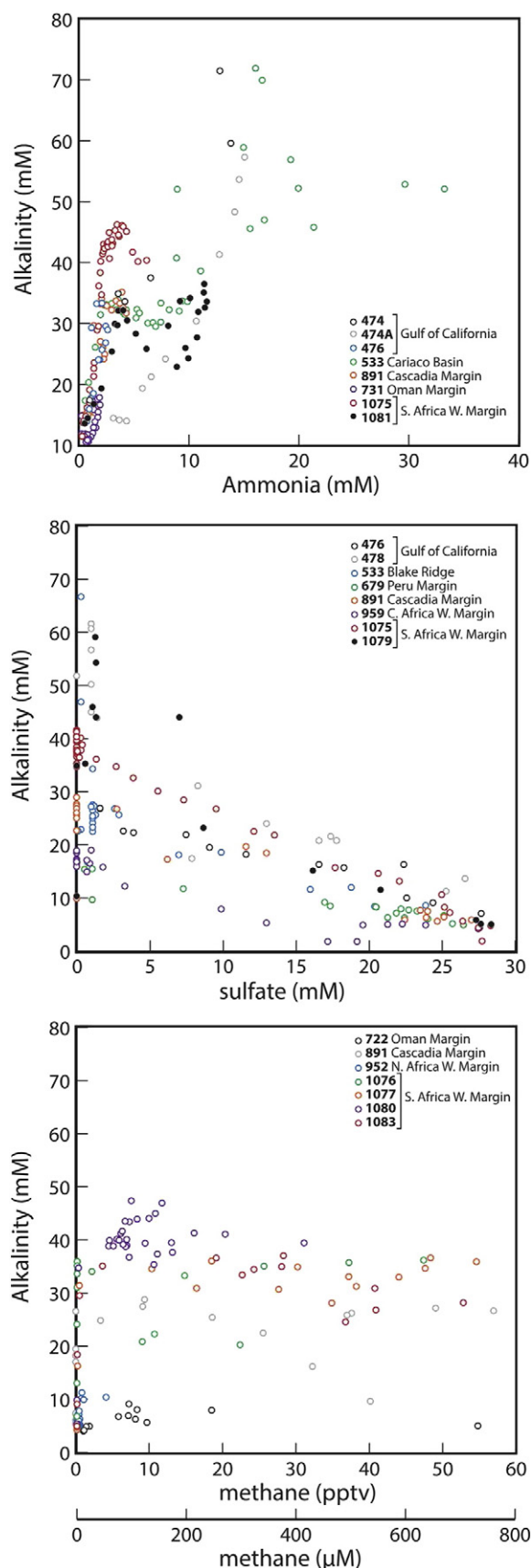


Fig. 6. Select pore water alkalinity versus top) ammonia, middle) sulfate and bottom) methane crossplots. Numbers correspond to ODP/DSDP site. Bottom methane axis corresponds to site 722 only.

there must be at least some overlap among these geologists, it could be argued that the specific workers simply overlooked the 'concretion problem' because of alternate interests. Perhaps a more plausible explanation, however, is that concretionary carbonate does not appear to be concretionary in a sediment core. As Fig. 7 demonstrates, only concretions with diameters smaller than the drill core (normally ~7.5 cm across) can be entirely captured and recovered and therefore identified as concretionary. In addition, the concretion must be in the direct path of the open end of the penetrating core or else it might simply be pushed aside (recall that concretions tend to form in soft sediments as indicated by outcrop textural characteristics) or missed entirely. In addition, cemented sediments are often more difficult to core compared to their uncemented counterparts due to increased rigidity (though this is not an issue for drill core). Perhaps some concretions are missed because of the inability of the core to penetrate these preferentially cemented regions. Ultimately, the likelihood of 'catching' a concretion within a core is probably low, but surprisingly perhaps, entire concretions have been recovered in this fashion.

Oftentimes authigenic carbonates recovered from these sites are described as carbonate 'layers'. These accumulations may be continuous layers, however, they may also be concretions with diameters sufficiently large to preclude identification of the overall morphology of the cemented body (see Fig. 7). The distinction between these two types of concretions (layers versus true concretions) may be an additional reason why modern concretions are rarely described. Of course, it is reasonable to infer that a layered bedform may in fact be primary and not diagenetic (and thus not concretionary). Whereas beds/layers composed of clearly primary constituents such as shells, tests and primary sedimentary structures are easily distinguished from diagenetic structures, layers are sometimes composed of micrite, the origin of which can be primary or diagenetic. Geochemical analyses can be used to distinguish primary versus diagenetic mineral production, however detailed solid-phase geochemistry is not commonly provided in ODP/DSDP records. The bulk mineralogy of layers can be helpful inasmuch as dolomites and siderites do not form as primary marine precipitates; therefore occurrences of these minerals indicate a diagenetic origin.

4.2. Insights from pore water profiles

It has already been demonstrated that a significant proportion of sample sites show direct evidence for carbonate authigenesis, including truly concretionary forms, some of which have been conclusively tied to microbial organic matter remineralization (Gieskes et al., 1982; Meister et al., 2007; Wefer et al., 1998a, 1998b). Of those sites from which no concretionary carbonate has been directly recovered, all show indirect evidence for the potential for authigenesis through increased pore water alkalinity (Table 1) and generally positive dolomite and calcite SI values (Figs. 2–5). Indeed, most of these sites exhibit signatures consistent with organic matter degradation related alkalinity production. These include correlations between ammonia and alkalinity, a negative correlation between sulfate and alkalinity and a general association of high methane with high alkalinity (Fig. 6). However, diffusive fluxes calculated from pore water gradients of alkalinity, magnesium and calcium are often quite slow, complicating a diffusive transport-supported authigenesis mechanism (this study; Burns and Baker (1987), Raiswell and Fisher (2004)). This suggests that ion transport may not be strictly diffusive, the carbonates are not entirely modern and/or the pore water sampling resolution is not high enough to capture gradients that are much steeper than can be resolved at the sampling interval. These rates, however, do not preclude modern authigenesis, especially if some of the carbonates are quite thin (see SOM for discussion of rate calculations).

Carbonate mineral precipitation results in decreased concentrations of pore water Ca^{2+} , Mg^{2+} or both, depending on the initial pore water components and the specific authigenic phase forming

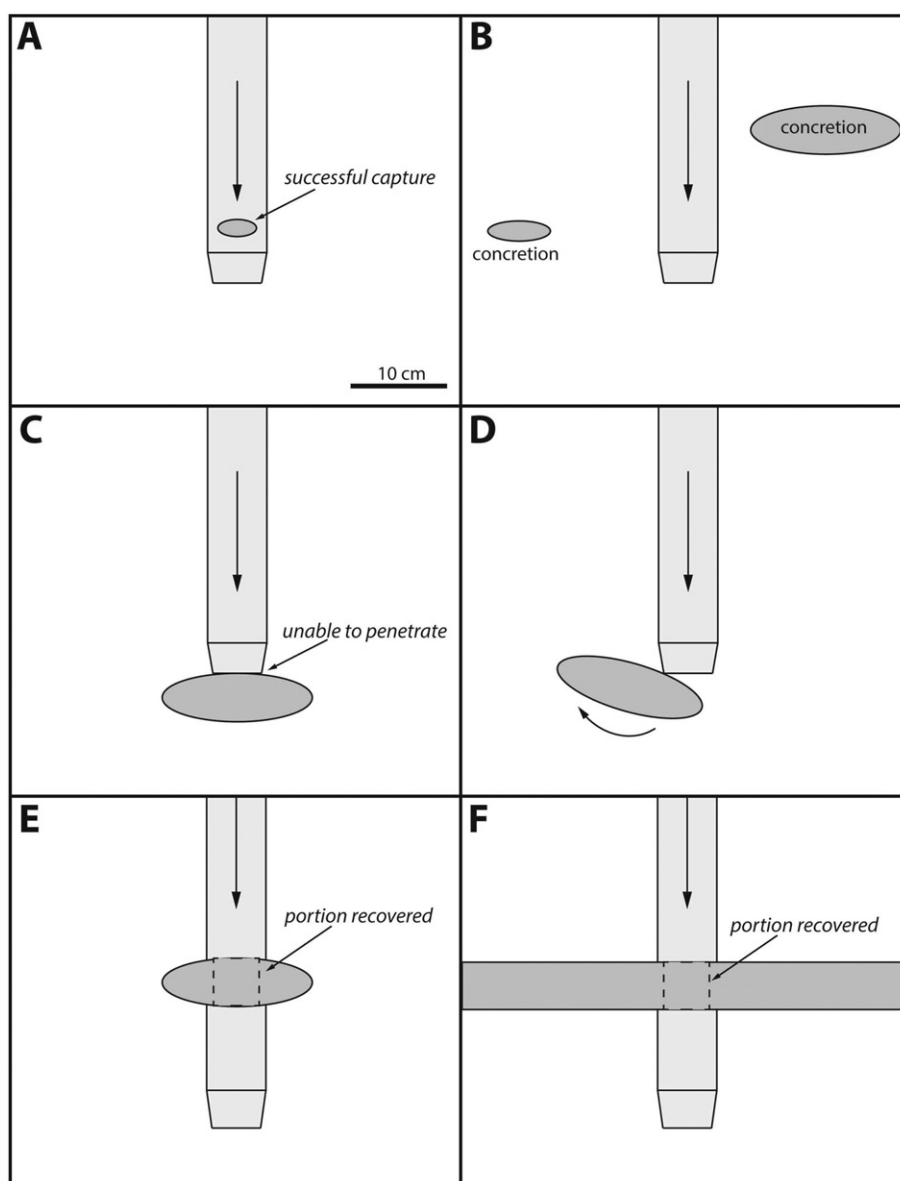
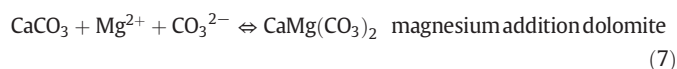
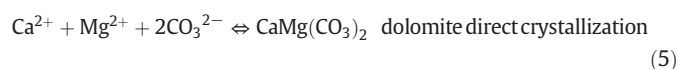


Fig. 7. Potential outcomes of coring sediments containing concretionary carbonate. White corresponds to sediments in all panes. A) Successful recovery and positive identification outcome, notice the relatively small size of the captured concretion. B) Missed concretionary carbonate entirely, pore water chemical profiles may express signatures that identify the presence of local concretions. C) Corer unable to penetrate, and thus recover concretionary carbonate. D) Concretion pushed out of the way of softer sediment-penetrating core. E, F) Successful capture that cannot be used to distinguish a true concretion from a layer/bed.

(calcite or dolomite). Authigenesis may occur through crystallization from fluid or recrystallization of a primary phase. Dolomite replacement of aragonite/calcite may also occur in marine sediments, particularly those influenced by organic matter degradation (Compton, 1988; Murray and Wigley, 1998). These reactions are as follows (Baker and Burns, 1985):



Pore water profiles from all sites exhibit decreasing Ca^{2+} gradients at some depth, most of which occur within the uppermost 80 m of sediment. These decreases may result from precipitation of diagenetic calcite and/or dolomite (Eqs. (4), (5) and (7)) and can help constrain the depths of mineralization, particularly in cores from which carbonate minerals were recovered. In general, the shallow Ca^{2+} decreases are associated with near-equimolar decreases in Mg^{2+} , indicative of dolomite direct mineralization (Eq. (5); Fig. 8). Sediments experiencing direct dolomite precipitation will exhibit pore water concentrations consistent with this 1:1 flux but with profiles somewhat offset due to differences in the diffusivities of Ca^{2+} and Mg^{2+} . Ultimately, when plotted as calcium versus magnesium a slope of ~0.92 (at 10 °C, (Boudreau,

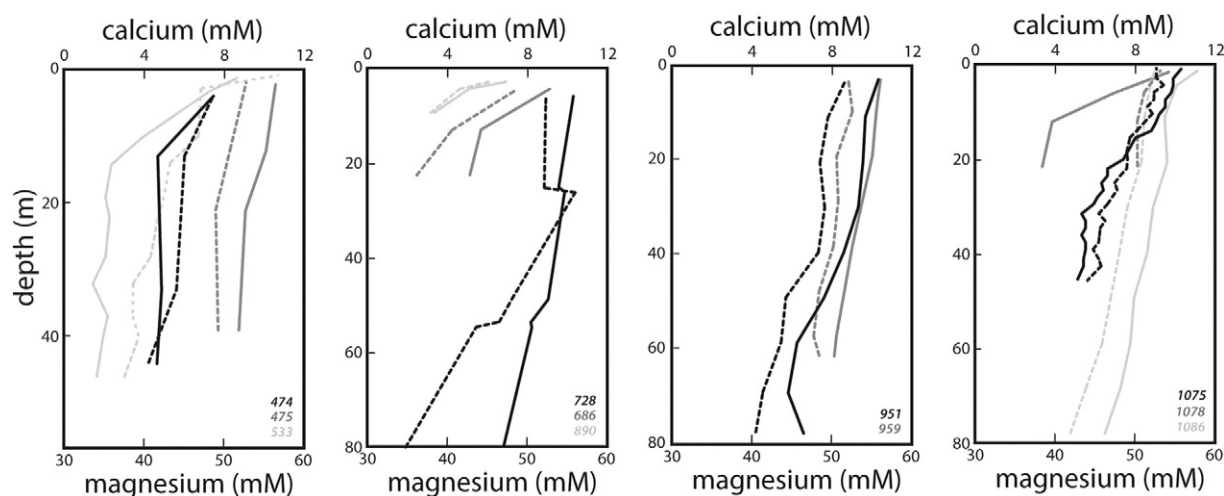


Fig. 8. Calcium and magnesium pore water profiles over depths shallower than 80 m. Notice decreases in both with depth. Numbers correspond to ODP/DSDP site.

1997) will result if only direct dolomitization is responsible for the gradients observed. Fig. 9 demonstrates that shallow sediments from many sites exhibit slopes consistent with at least some influence by direct dolomitization, however they also show an excess removal of magnesium, consistent with Eqs. (6) and (7). Pore water geochemistry and petrographic data from offshore Peru have been argued to reflect initial precipitation rather than replacement dolomitization (Meister et al., 2007). This recurrence along with dramatic alkalinity increases suggests that diagenetic mineralization occurs primarily within the uppermost ~80 m of sediment. Indeed such shallow sediments often contain the most reactive organic carbon species (Berner, 1980) and therefore provide potential for rapid alkalinity production via remineralization.

Profiles also often express progressive decreases in Mg^{2+} content at deeper sediment depths. This may indicate the common occurrence of dolomite replacement (Eqs. (6) and (7)) or cation replacement reactions occurring between pore waters and sediment underlying basalts (Gieskes et al., 1982; Lyons et al., 2000). Modern marine environments are heavily supersaturated with respect to dolomite (Lippmann, 1973), particularly in comparison to calcium carbonate minerals (Tucker and Wright, 1990). It has been proposed that inhibitors prevent marine fluids from mineralizing dolomite. In particular, high sulfate contents are thought to limit dolomite formation (although other processes also influence dolomite precipitation, e.g., Burns et al. (2000); Roberts et al. (2004)), perhaps through extensive complexation with Mg^{2+} to form $MgSO_4^0$ (Baker and Kastner, 1981). Of course, BSR consumes sulfate thereby limiting complexation, freeing Mg^{2+} and relieving a barrier to dolomite precipitation. Sediments experiencing BSR, such as those examined here, have an increased potential for dolomite formation, either as direct crystallization or replacement. Indeed, SI values for dolomite commonly significantly exceed those for calcite (largely due to relatively high Mg/Ca), reflecting a preference toward dolomite formation. Direct evidence for replacement including description of its impacts on earlier mineral phases has yet to be demonstrated, but likely has implications for diagenetic dolomite preserved in the rock record.

It is important to note that along with carbonate authigenesis and basalt alteration, cation exchange in clays represents another potential mechanism producing down core variability in Ca^{2+} and Mg^{2+} concentration (Leslie et al., 1990). This process is more likely to significantly influence profiles where clays are a dominant sedimentary component.

4.3. Modern authigenesis

In addition to the relatively shallow near equimolar removal of Ca^{2+} and Mg^{2+} , other lines of evidence indicate modern or very recent

precipitation of concretionary dolomite. Ultimately, the simple presence of concretionary carbonate within sediments does not require modern authigenesis. Indeed, sediments range in age from the Eocene to the Holocene, providing an upper age limit for authigenesis within specific sediments. Carbon isotope values of concretionary carbonates agree quite well with modern pore water $\delta^{13}C_{TCO2}$ values from sites of the Peru Margin, Cascadia, and the Gulf of California (Kelts and McKenzie, 1982; Kopf et al., 1995; Meister et al., 2007) suggesting modern or very recent authigenesis. The shallowest dolomite concretionary bodies of Blake Ridge, the Cariaco Basin and the western margin of southern Africa occur in pore waters with little residual sulfate (Blake Ridge) or in close association with subsurface peaks in pore water methane (Cariaco Basin and S. Africa). Given the common occurrence of methanogenesis-derived carbonate from various sites, this association is consistent with modern authigenesis as well. The dominance of methanogenesis-derived authigenic dolomite observed here is similar to DSDP sites explored by Baker and Burns (1985).

Interestingly, the sites examined do not exhibit strong evidence for modern organotrophic sulfate reduction-derived (Eq. (1)) concretions. This absence may be related to the limited amount of time a concretion would spend in the sulfate reduction zone, given the relatively shallow exhaustion of sulfate at many sites. Modeling by Raiswell and Fisher (2004) has demonstrated that the ODP/DSDP sites exhibit profiles consistent with only brief authigenesis in sulfate reduction zones. The model results suggest only minor cementation resulting in a mere 1.5 and 3.0 wt.% total calcite and dolomite accumulations, respectively. Such an insignificant amount would be difficult to identify in core records and certainly would not be identified as concretionary in nature (Raiswell and Fisher, 2004). This minor authigenesis, however, may provide a nucleation site for subsequent mineral precipitation, perhaps within the methanogenesis zone (Raiswell and Fisher, 2004). Strictly organotrophic sulfate reduction concretions may form due to extended residence in the sulfate reduction zone, perhaps as a consequence of depositional hiatuses (Raiswell and Fisher, 2004) or relatively slow deposition rate (Baker and Burns, 1985). Regardless of the mechanism, the apparent lack of modern organotrophic sulfate reduction-derived concretions is curious.

As a whole, dolomite represents the dominant concretionary phase in the sediments explored here. In fact, concretionary calcite is only identified in Peru margin and Cascadia sediments. In the Peru margin sediments, calcite is far less abundant than dolomite and bears resemblance to the Miocene Monterey Formation (Meister et al., 2007), which is dominated by concretionary dolomite (Loyd et al., 2012). In contrast to the other sites, Cascadia sediments exhibit active methane venting and, like other cold seep sites, contain significant buildups of

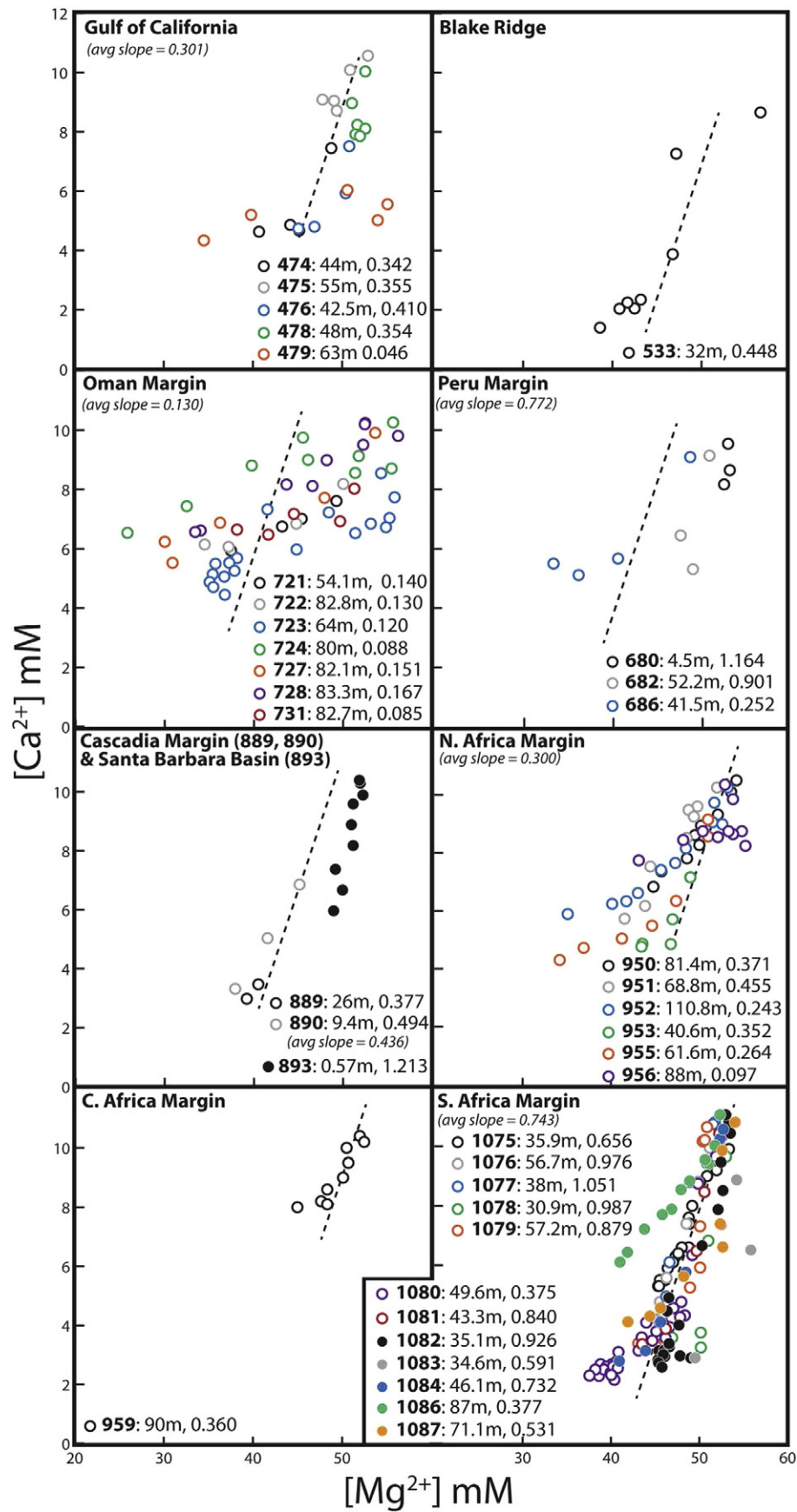


Fig. 9. Crossplot of pore water magnesium and calcium concentrations from sites exhibiting shallow subequimolar reduction in both ions. Icon labels indicate site number (in bold) followed by maximum depth of correlation (all extend from seafloor to this depth) and individual linear regression slope. Average slopes are also provided for each site where applicable. A slope of ~ 0.92 (represented by the dashed lines) would be expected if gradients represented fluxes driven by direct dolomite precipitation (see text).

calcite, aragonite and dolomite (Bohrmann et al., 2002; Gieskes et al., 2005; Orphan et al., 2004). Authigenesis at these sites is dominated by methanotrophic sulfate reduction (Eq. (2)), perhaps indicative of a link between calcium carbonate precipitation and this reaction pathway. Identification of methanotrophic sulfate reduction as a precipitation mechanism can be difficult in ancient concretions, particularly due to the ambiguity in deciphering carbon isotope compositions (Raiswell, 1987). Only isotope values lower than the organic matter value ($\sim -25\%$) indicate a conclusively methane carbon source. Intermediate values (between -25 and 0%), however, can be generated from mixtures of different carbon sources, including methane. Indeed, many concretionary structures fall within this intermediate range (Mozley and Burns, 1993) promoting widespread ambiguity in precipitation mechanism interpretations. Ultimately, methane seepage may have produced many ancient calcium carbonate (and dolomite) concretions. Integrated geochemical analyses beyond carbon and oxygen isotope analyses may aid in the specific identification of methanotrophic sulfate reduction in ancient carbonate concretions.

5. Conclusions

Multiple ODP and DSDP sites that occur under productive water columns and express pore water chemical profiles consistent with extensive sedimentary organic matter degradation exhibit direct and/or indirect evidence for diagenetic carbonate precipitation. True concretionary carbonates have been recovered from nearly half of the sites revisited here. In nearly all other instances, pore water profiles show decreased dissolved calcium and/or magnesium concentrations consistent with dolomite precipitation. The apparent lack of agreement between “concretion-poor” modern marine sediments and “concretion-rich” outcrops may exist due to 1) a lack of communication between geoscientists that generally work in modern versus ancient systems, 2) the inability of modern coring techniques to adequately sample concretionary carbonates, and/or 3) difficulties associated with primary or diagenetic classification of carbonate layers/beds. Ultimately, we suggest that modern concretions do occur and that the apparent discrepancy between modern and ancient systems is largely inaccurate and results from the confounding issues presented above.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.chemgeo.2015.11.009>.

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