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Author(s)	Taylor, Paul D.
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Seawater Chemistry, Biomineralization and the Fossil Record of Calcareous Organisms

Paul D. Taylor*

Department of Palaeontology, Natural History Museum, London SW7 5BD, U.K.

ABSTRACT

Oscillations in seawater chemistry have characterized at least the last 600 million years of earth history. Three phases of aragonite seas have been separated by two of calcite seas, the former due to high molar ratios of Mg/Ca in seawater and the latter to low ratios. During aragonite seas, inorganic marine cements and ooids are aragonitic, whereas during calcite seas they are calcitic. Recent interest has focused on the effects of this cyclical change in seawater chemistry on biomineralization, as well as on taphonomy (including diagenesis) and hence fossil preservation. Although there is a need for rigorous testing of hypotheses, data on the geological distributions of aragonite and calcite skeletons among marine invertebrates lends variable support to links between seawater chemistry and: (1) de-novo evolution of calcite vs aragonite skeletons, (2) switchovers in mineralogy during subsequent clade evolution, (3) the relative success of clades using calcite or aragonite as biominerals, and (4) the development of hardgrounds with associated sclerobiont communities.

Keywords: Aragonite and calcite seas, Biomineralization, Evolution, Taphonomy, Hardgrounds

INTRODUCTION

The impact of long-term secular variations in the environment on the fossil record, and hence our interpretation of the Phanerozoic history of life, has been addressed from several different perspectives in recent years. For example, sea-level has been implicated as a major driver of apparent diversity in the marine fossil record [1], while O₂ levels have been suggested to play a role in evolutionary radiations [2]. Another factor that has received attention is seawater chemistry. Beginning with the work of Sandberg in 1983 on oscillations in the CaCO₃ polymorphs (calcite or aragonite) forming marine ooids and inorganic cements [3], cyclical changes in seawater chemistry have been recognized through the

Phanerozoic. These have entailed switches between so-called aragonite and calcite seas (Fig. 1). Three phases of aragonite seas (Ediacaran-Early Cambrian, Mid Carboniferous-Late Triassic, and Late Paleogene-Recent) have been interposed by two of calcite seas (Early Cambrian-Mid Carboniferous and Early Jurassic-Late Paleogene).

Sandberg [3] believed that changing CO₂ concentrations were probably responsible for oscillations between calcite and aragonite seas, with calcite seas corresponding to times of high CO₂ and aragonite seas to times of low CO₂, and correlating respectively with Fischer's [4] Greenhouse and Icehouse conditions. Various lines of evidence, from the composition of marine evaporites [5] and fluid inclusions in bedded marine halites [6], to the Mg

*pdt@nhm.ac.uk

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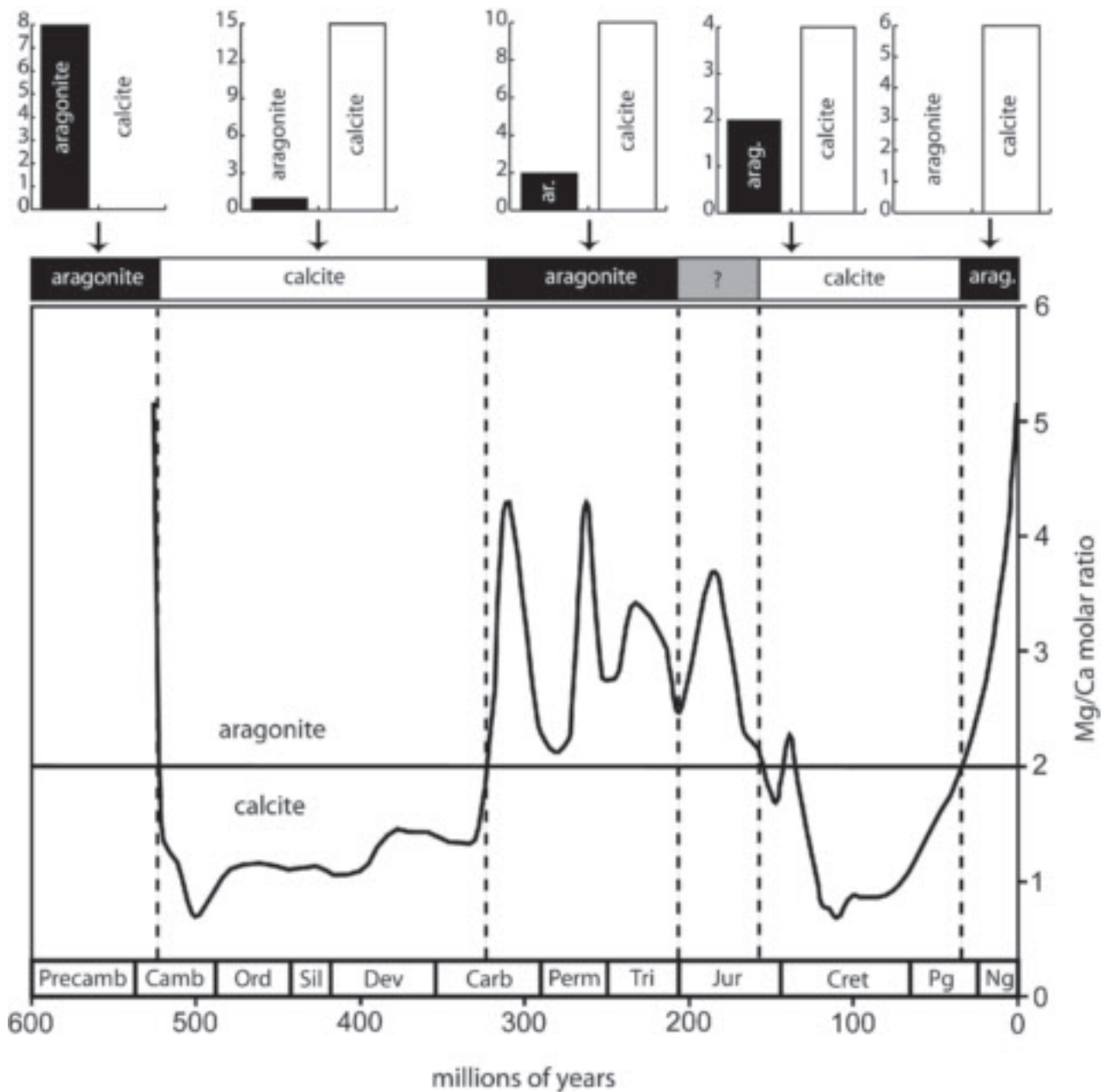


Fig. 1 Fluctuations in the Mg/Ca molar ratio during the last 600 million years [after 6] and oscillations between calcite and aragonite seas. The threshold between calcite and aragonite seas is generally considered to occur at $\text{Mg/Ca} = 2$, but sedimentological evidence suggests that the Mesozoic transition to a calcite sea was around the Triassic/Jurassic boundary rather than in the Late Jurassic. Frequency plots at the top of the figure show the minimum numbers of originations of aragonite and calcite biomineralization in the macroinvertebrates reviewed here during the three phases of aragonite and two of calcite seas. Data on early skeletonization [23] and switches in bivalve mineralogy [39] contribute most to the decreasing match between seawater chemistry and biomineralizational changes through time.

contents of fossil echinoderms [7], have since supported an alternative hypothesis that the molar proportion of Mg/Ca in seawater drives this oscillation. Low molar ratios (< 2) characterized calcite seas and high molar ratios (> 2) aragonite seas (note that

the calcite/aragonite threshold depends on temperature [8], the figures quoted being for 15°C). It is also probable that similar Mg/Ca fluctuations characterized the Precambrian [9]. Magnesium has been shown experimentally to inhibit the growth of cal-

cite while not affecting aragonite growth [10]. Therefore, it is reasoned that high levels of Mg in seawater will favour precipitation of aragonite over calcite. The primary control on Mg/Ca levels in seawater is likely to be variations in brine flux at mid-oceanic ridges [11], although rates of deposition of shallow water carbonates and their dolomitization have also been implicated [12]. When seafloor spreading rates are high, Mg/Ca levels decrease, leading to calcite seas. Conversely, when seafloor spreading rates are low, as at the present-day, Mg/Ca levels increase, leading to aragonite seas. As CO_2 levels are also driven at least in part by seafloor spreading rates, this generates a correlation between aragonite/calcite seas and Icehouse/Greenhouse conditions. There is also a correlation with sea-level as this too is largely dependent on spreading rates and hence the volume of mid-ocean ridges.

Links between seawater chemistry and biomineralization of marine organisms have been forged in a series of papers reviewed by Stanley [13]. In addition, seawater chemistry has been claimed to impact the fossil record through its effects on taphonomy and carbonate diagenesis. The current paper is a short summary and critique of how changes in the Mg/Ca level of seawater may have impacted the fossil record of macroinvertebrates with calcareous skeletons. The goal is to formulate some explicit hypotheses and explore the degree to which they are supported by available evidence from the fossil record. Areas not already covered by Stanley [3] are given particular emphasis.

BIOMINERALIZATION AND SEAWATER CHEMISTRY

The process of biomineralization is still remarkably poorly understood for marine invertebrates that secrete calcareous skeletons. Even in the best-studied groups, such as molluscs [e.g. 14], major gaps exist in our knowledge of the physiological, biochemical and genetic mechanisms controlling skeletal ultrastructure, trace element chemistry, and the deployment of the CaCO_3 polymorphs calcite and aragonite. Environmental factors undoubtedly play their part in biomineralization. According to Stanley [13, p. 230]: 'A central issue in the study of biomineralization has been whether biologically induced or biologically controlled skeletal formation has played a larger role among marine organisms'. While the environment can have a direct effect on mineralogy and chemistry [e.g. 15], the intricate and consistent skeletal structures characterizing most species of

calcifying invertebrates shows that biomineralization is not simply a passive process but is subject to a high degree of organismal control. Nevertheless, for physiological reasons natural selection can be expected to favour organisms that 'go with the flow' and adjust their biomineralization to match the chemistry of ambient seawater.

CaCO_3 biomineralization has clearly evolved on many occasions in metazoans, Knoll [16] estimating at least 20 times. Co-option of common genes used for other functions may explain this polyphyletic pattern [17]. Of particular relevance to the present paper are those phyla capable of using both calcite and aragonite in their skeletons. Often these two polymorphs occur together, aragonite typically following calcite during skeletal succession, as in many bivalves and some cheilostome bryozoans. Soluble proteins extracted from the shell have been implicated in controlling the switchover from calcite to aragonite secretion in bimineralic molluscs [18].

Wilkinson [19] was the first to suggest a causal link between seawater composition and biomineralization, explaining the dominance of calcitic biomineralizers in the Palaeozoic as a function of the relatively low Mg/Ca ratio of Palaeozoic seawater that favoured calcite biomineralization. It has since been suggested that a driving force in the biomineralization of some taxonomic groups (e. g. cheilostome bryozoans) was secular change in seawater Mg/Ca [20]. Three hypotheses about the relationships between seawater chemistry and CaCO_3 biomineralization have been proposed:

(1) groups first evolving biomineralization use the form of CaCO_3 matching the seawater of the time, i. e. calcite in calcite seas, aragonite in aragonite seas [13, 16, 21];

(2) aragonite biomineralization is disadvantageous during times of calcite seas, leading to a relative increase in calcitic species, and vice-versa [22];

(3) calcite biomineralizers may become 'hypercalcified' during times of calcite seas, and aragonite biomineralizers during times of aragonite seas [13].

Below I review data on the times of appearance of calcite and aragonite in the fossil record of macroinvertebrates to test these hypotheses.

Early metazoan skeletonization

Most phyla with CaCO_3 skeletons make their first appearance in the fossil record in the Early Cambrian, during the 'Cambrian Explosion', slightly before in the Ediacaran period, or else in the earliest Ordovician. A changeover from aragonite to calcite seas occurred sometime during the basal Nemakit-Dal-

dynian Stage of the Early Cambrian. Porter [23] recently compiled data on the skeletal mineralogies of taxa first evolving CaCO_3 skeletons through this critical phase of metazoan evolution. She found that primary skeletal mineralogy was known or could be inferred with reasonable certainty in 18 of 21 clades, 8 being aragonitic and 10 calcitic. Crucially, all of the aragonitic clades had their first occurrences during the aragonite sea, whereas all of calcitic clades first appeared after the switchover to a calcite sea. Thus, there is a remarkably precise match between the mineralogy of newly evolved skeletons and seawater chemistry when metazoan skeletons first appeared.

Corals

Three main groups of anthozoan corals occur in the fossil record. Both Rugosa and Tabulata range from Ordovician-Permian and have calcitic skeletons. Therefore, the CaCO_3 polymorph employed by these corals corresponds to the seawater chemistry at the time they acquired skeletons. The Triassic-Recent Scleractinia, which are usually considered to have evolved biomineralization from a non-calcified ancestor, possibly twice [24], have aragonitic skeletons, matching the seawater chemistry of the Triassic [25]. Experimental studies by Ries et al. [26] on three living scleractinian species have shown that corals grown in seawater with an Mg/Ca ratio simulating that of the calcite sea of the Cretaceous secrete skeletons composed partly of calcite. This finding was used to infer that: (1) corals exert only partial control over their skeletal mineralogy, and (2) the aragonitic skeleton of scleractinians was a factor in their decline during the strongly calcite seas of the Late Cretaceous. It has long been suspected that some of the scleractinian corals found in the Late Cretaceous Chalk of Europe were calcitic. This has been confirmed by a recent study [27] showing conclusively the presence of a primary skeleton of calcite in *Coelosmilia*. The chemistry of Late Cretaceous seawater may have prompted a switch in mineralogy in some, but not all, scleractinians.

Hydrozoans have independently evolved CaCO_3 skeletons on several occasions, for example stylasterids, milleporids and some hydractiniids. The evolution of stylasterid biomineralogy is best known thanks to the work of Cairns and Macintyre [28] who mapped the distribution of CaCO_3 polymorphs onto a cladogram of the phylogenetic relationships between 71 species of Recent stylasterids. Aragonite was found to be both the predominant and primitive biomineral in stylasterids but one switchover to cal-

cite and three reversals back to aragonite occurred during their subsequent evolution. Stylasterids range back to the Danian, possibly Maastrichtian, and therefore probably evolved their primitively aragonitic skeletons in a calcite sea. It is not known when the switchover to calcite occurred.

Brachiopods

Brachiopods with CaCO_3 shells are almost universally calcitic. The sole exception appears to be the Ordovician (Llandeilo) to Silurian (Ludlow) Trimerellida. These craniformeans are widely believed to have secreted aragonitic shells. Evidence for aragonite biomineralization comes from the consistently mouldic preservation of trimerellids in settings where other brachiopods have well preserved shells. In those trimerellids not preserved as moulds the 'shell' is found to consist of a drusy mosaic characteristic of void-filling calcite that resembles the preservation of aragonitic molluscs [29]. Despite having aragonitic shells, trimerellids originated and spent their entire evolutionary history in a calcite sea.

Bryozoans

Bryozoans twice evolved CaCO_3 skeletons from soft-bodied ancestors. Biomineralized bryozoans first appeared in the Early Ordovician (Tremadoc) in the Stenolaemata [30]. All known stenolaemates, living and fossil, have calcitic skeletons, consistent with the calcite sea at the time of skeletonization acquisition. Biomineralization evolved a second time in bryozoans during the Late Jurassic in the Cheilostomata [31]. Modern cheilostomes may be calcitic, aragonitic or bimineralic. Mineralogical data is available for fewer than one-fifth of cheilostome genera. Of those analysed [32, 33], some 60% are calcitic, 10% aragonitic and 13% bimineralic, while in 18% mineralogy is variable within the genus. The fossil record suggests that all early cheilostomes had calcite skeletons. The first indication of aragonite occurs in some Maastrichtian aragonite-leached deposits containing cheilostomes [e.g. 34] with peculiar, partial skeletons probably indicating loss of the aragonite components of bimineralic skeletons. Skeletal aragonite has yet to be detected in Cretaceous or Paleocene bryozoans but its presence has been proved using XRD in some Eocene cheilostomes [33]. The widely scattered taxonomic distribution of aragonite among modern cheilostomes implies multiple origins of this biomineral. For example, whereas the oldest species of *Hippoporidra* (Eocene) was almost certainly calcitic, younger species (Miocene-

Recent) have aragonite skeletons [35]. Likewise, Cretaceous species of free-living (lunulitiform) bryozoans are calcitic, Paleogene species calcitic or bimineralic, and Recent species aragonitic [33]. Thus, cheilostomes acquired a skeleton of calcite in the calcite sea of the Late Jurassic and probably began switching over to aragonite in the calcite sea of the Late Cretaceous, the frequency of aragonite acquisition in different clades likely increasing with the onset of aragonite seas in the Late Paleogene.

Molluscs

Primitively, molluscs have aragonitic shells and some groups (scaphopods, polyplacophorans) have retained this mineralogy in all species [36]. However, calcite has evolved on numerous occasions in bivalves, gastropods and cephalopods, usually to give bimineralic shells. It is also possible that bimineralic shells had evolved in monoplacophorans by the Middle Cambrian [37].

Bimineralic bivalves often show an abrupt switch from an outer layer of calcite to an inner layer of aragonite during shell growth [e.g. 38]. Even the most calcitic bivalves (e.g. oysters) retain a small amount of aragonite where muscles and ligaments are attached to the shell. The first fossil record of calcite in bivalves is either Middle Cambrian [37] or Early Ordovician [39]. The most conservative estimate is that calcite has evolved twice in pteriomorphs and twice in the heteroconchs [40], but calcite may have appeared up to 19 times during bivalve evolution [39]. An analysis of the diversity of wholly aragonitic bivalve families through time showed that these families underwent significant diversification only during times of aragonite seas [22]. The same study found that three major calcite-secreting clades (pteriomorphs, mytiloids and rudists) all first appeared in calcite seas. These concordant patterns between seawater chemistry and biomineralogy are supported by a recent study of Mesozoic epifaunal bivalves [41]. Whereas bivalve clades (e.g. Gryphaeidae, Pectinidae) that replaced aragonite with calcite in their shells during the calcite sea of the Jurassic-Cretaceous prospered, clades with thick aragonitic shells (e.g. Megalodontoidea) declined. Counterbalancing this evidence for a link between seawater chemistry and bivalve mineralogy is the fact that 12 (63%) of the 19 appearances of calcite identified by Carter et al. [39] were in aragonite seas.

Gastropods are predominantly aragonitic but, like bivalves, evolved calcite biomineralization on numerous occasions, including in the primitive Patello-

gastropoda [42]. Some gastropods have bimineralic shells while others retain aragonitic shells but have calcitic opercula [43]. It is less easy to obtain information on the timings of the acquisition of calcite in gastropods than in bivalves. However, calcitic gastropods date back at least to the Ordovician (e.g. platyceratids). Mapping of mineralogy onto a cladogram of modern littorinids revealed wholly aragonitic species to be primitive, and identified one switchover to bimineralic shells and three subsequent reversals to aragonitic shells through secondary loss of the outer calcite layer of the shell [44].

Cephalopods provide an interesting test for a link between seawater chemistry and biomineralization. Calcitic parts have evolved on at least four occasions in these primitively aragonitic molluscs: (1) in the mandibles of nautiloids, (2) the aptychi of ammonoids, (3) the guards of belemnites, and (4) the egg cases of *Argonauta*. Modern *Nautilus* has a complex mandible composed of not only aragonite and calcite but also three other minerals [45]. Unfortunately, the time of origin of calcitic biomineralization in nautiloid mandibles is uncertain, although a variety of nautiloid and ammonoid jaw structures ('rhyncholites') have been found in the fossil record as far back as the Devonian [46]. Aptychi are double valved structures that probably functioned as opercula in ammonoids. They have organic and calcitic layers, first appear in the fossil record in the aragonite sea of the Permian, and probably evolved on multiple occasions in the calcite sea of the Jurassic and Cretaceous [47]. Belemnites are coleoids with solid, bullet-shaped guards (or rostra) preserved in calcite and usually [cf. 48] regarded as having had an originally calcitic mineralogy, in contrast to the chambered phragmocone that has a conventional aragonitic mineralogy. Cephalopods with belemnite-like guards have been described from both the Palaeozoic and Cenozoic but true belemnites are probably confined to the Mesozoic. Equivocal belemnites are known from the Late Triassic (Carnian), a time of aragonite seas, but the earliest certain record is Early Jurassic (Hettangian) [49] when a calcite sea probably existed. It is unclear therefore whether acquisition of calcite biomineralization in belemnites matched seawater chemistry. Finally, the peculiar calcitic pseudoconch of the octopod *Argonauta* used for brooding embryos has a fossil record extending back to the Late Oligocene [50], a time of aragonite seas. It should, however, be noted that molecular evidence suggests that the Argonautoidae originated in the Jurassic [51].

Polychaetes

Calcareous tubes have evolved in at least two groups of polychaete annelids, sabellids (*Glomerula*) and serpulimorphs (Filogranidae, Serpulidae and Spirorbidae). Calcifying sabellids are aragonitic at the present day but the mineralogy of the oldest examples, from the Early Jurassic, is unclear. Much more diverse are the serpulimorphs which secrete calcitic, aragonitic or bimineralic tubes [52]. They probably range back to the Middle Triassic (supposed spirorbids from the Palaeozoic are not polychaetes [53]). It seems likely that serpulimorphs are primitively aragonitic (O. Vinn, pers comm.), matching seawater chemistry in the Triassic, although calcitic species had probably appeared before the end of the Triassic [e.g. 54].

TAPHONOMY, DIAGENESIS AND SEAWATER CHEMISTRY

The fossil record depends not only on the organisms living at the time but also taphonomic processes that determine whether or not they will be fossilized. Aragonitic shells are especially prone to destruction through dissolution as, relative to calcite, aragonite has a significantly greater solubility [55]. Preservation of skeletal aragonite in fossils declines rapidly with geological time - there are relatively few occurrences of aragonite fossils in the Palaeozoic [36], and a great many fossil invertebrates from the Palaeozoic and Mesozoic that once had aragonitic shells are preserved as moulds or casts. The extent of destruction of aragonitic fossils becomes clear on occasions when silicification preserves the aragonitic species that are normally lost [56, 57].

Taphonomy, including diagenesis, may be expected to differ between calcite and aragonite seas, with aragonitic skeletons being at particular risk of dissolution in calcite seas [e.g. 58]. Aragonite in calcite seas was often dissolved on the seafloor prior to burial [59–61]. This is evident from the encrustation of moulds of aragonitic fossils and of the inner calcitic surfaces of bimineralic molluscs exposed once the aragonitic layers were lost.

Dissolution of aragonite on the seafloor during times of calcite seas has two important consequences for the fossil record: (1) organisms with aragonitic skeletons can be lost at a very early stage, and (2) the dissolved aragonite may precipitate as calcite cement, creating hardened patches on the seafloor [62]. Seafloor cementation culminated in the formation of hardgrounds capable of supporting diverse sclerobiont communities very different from those coloniz-

ing soft sediments [63]. Hardgrounds do indeed seem to have been commoner during calcite than aragonite seas (Fig. 2), although this pattern may be due as much to the large areas of epicontinental seas that flooded cratons when sea-levels were high at times of calcite seas as it is to seawater chemistry.

Massive loss of aragonite also occurs in the aragonite sea of the present day, particularly in cooler waters [64]. Much of this dissolution occurs when carbonate skeletons pass through a taphonomically active zone where oxidation of organic matter in the sediment causes CaCO_3 undersaturation. Surprisingly, dissolution may be greater in carbonate than siliciclastic sediments [65]. Sanders [66] contended that total syndepositional dissolution of carbonate does not differ in calcite and aragonite seas, local factors playing a dominant role instead.

DISCUSSION

The most striking correlation between seawater chemistry and biomineralization occurred during the latest Precambrian-Early Ordovician when metazoans evolving calcareous skeletons for the first time had mineralogies corresponding precisely with seawater chemistry at a time of transition from an aragonite to a calcite sea [23]. Some later *de novo* origins of calcareous skeletons also match the seawater chemistry of the time whereas others do not. Polymorph switches within clades that had already acquired CaCO_3 skeletons may either match or contrast with seawater chemistry. There is some indication that the correlation between biomineralization and seawater chemistry declined progressively through the Phanerozoic (Fig. 1). Whether taxonomic groups having mineralogies corresponding to seawater chemistry became hypercalcified is difficult to test without quantitative data on comparative calcification rates, skeletal thickness and/or skeleton/soft tissue volume. There are grounds for believing that taphonomic/diagenetic differences between calcite and aragonite seas further affected the fossil record of calcareous marine invertebrates. Loss of aragonitic skeletons may have been greater, and certainly often occurred earlier, in calcite than aragonite seas. Seafloor cementation was also probably enhanced in calcite seas (Fig. 2), creating hardgrounds attractive to sclerobiont communities.

The combined evolutionary and taphonomic effect of seawater chemistry on the fossil record of macro-invertebrates with calcareous skeletons requires further study. An analysis of bivalve diversity patterns failed to recover the expected correlation between

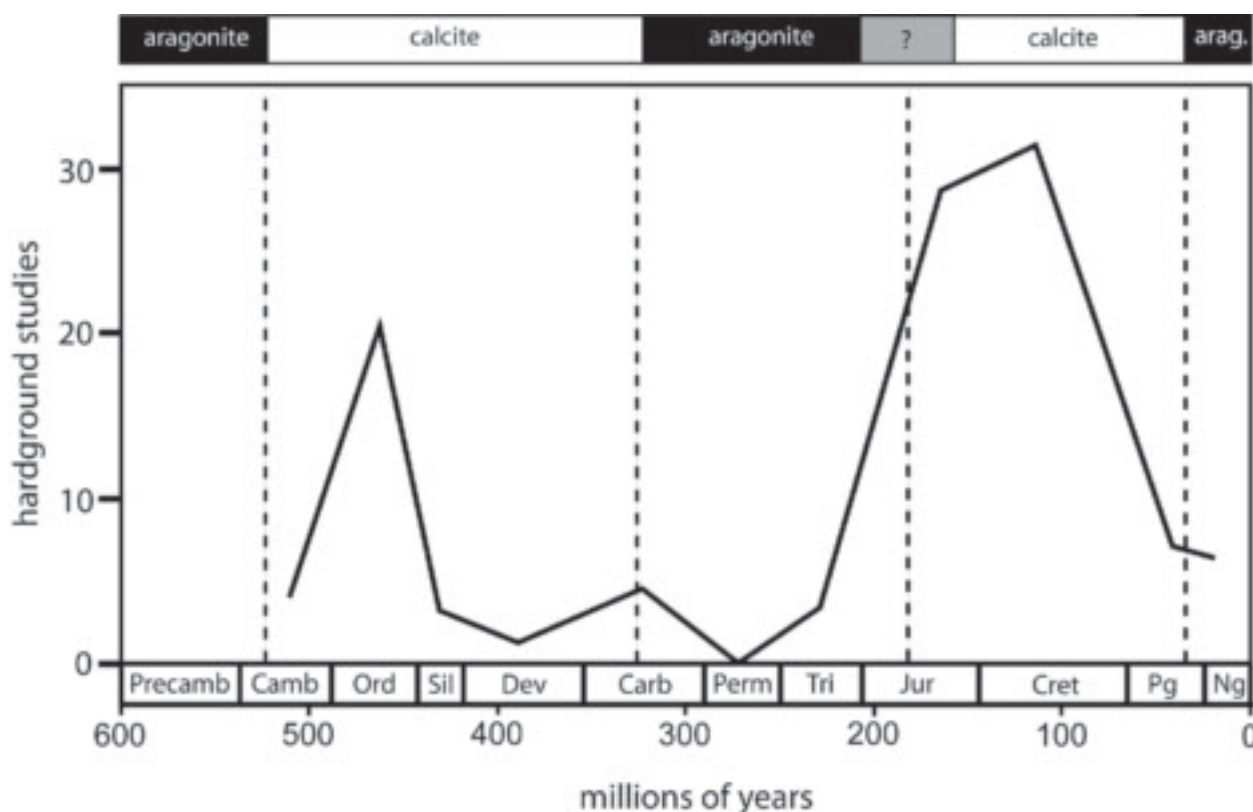


Fig. 2 Variation in hardground studies by geological period as a rough proxy for the abundance of hardgrounds through time. Note the increase at times of calcite seas, particularly in the Ordovician, Jurassic and Cretaceous. Data taken from Mark Wilson's bibliography of inorganic marine hard substrates <<http://www.wooster.edu/geology/WilsonBiblio.pdf>>.

preservation of calcitic and aragonitic families and calcite vs aragonite seas [67]. On the other hand, a study [68] of the volumetric contributions of calcite and aragonite skeletons in Late Triassic-Recent shallow water carbonates did find a slight increase of calcitic components in the calcite sea of the Jurassic-Paleogene compared with the aragonite seas before and after. A challenge for the future will be to disentangle latitudinal and local effects from global secular trends in the biomineralization and taphonomy of marine organisms with calcareous skeletons.

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