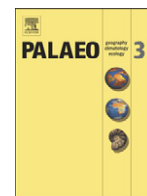




Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

journal homepage: www.elsevier.com/locate/palaeo

Not all sponges will thrive in a high-CO₂ ocean: Review of the mineralogy of calcifying sponges



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ARTICLE INFO

Article history:

Received 11 July 2013

Received in revised form 8 October 2013

Accepted 9 October 2013

Available online 17 October 2013

Keywords:

Sponges

Porifera

Ocean acidification

Calcite

Aragonite

Skeletal biomineralogy

ABSTRACT

Most marine sponges precipitate silicate skeletal elements, and it has been predicted that they would be among the few “winners” among invertebrates in an acidifying, high-CO₂ ocean. But members of Class Calcarea and a small proportion of the Demospongiae have calcified skeletal structures, which puts them among those calcifying organisms which are vulnerable to lowered pH and CO₃²⁻ availability. A review of carbonate mineralogy in marine sponges (75 specimens, 32 species), along with new data from New Zealand (42 specimens in 15 species) allows us to investigate patterns and make predictions. In general sponges show little variability within individuals and within species (± 0.5 wt.% MgCO₃ in calcite). Extant sponges in Class Calcarea generally produce calcitic spicules with relatively high Mg contents, up to 15 wt.% MgCO₃. Whereas most of the calcifying demosponges are aragonitic, the genus *Acanthochaetetes* in the order Hadromerida produces extremely high-Mg calcite (14 to 18 wt.% MgCO₃). There is generally a weak phylogenetic consistency among classes, orders and families. Statistical analyses, including those accounting for these phylogenetic effects, fail to find a substantial or significant effect of water temperature on mineralogical variation. In the context of global ocean acidification, sponges which produce high-Mg calcite and/or aragonite will be most vulnerable to dissolution, meaning that not all sponges will be “winners” in a high-CO₂ ocean.

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1. Introduction

Recent advances clarifying the interactions between atmospheric CO₂, the carbonate system in sea water, and marine calcifying organisms (Raven et al., 2005) have led to a great deal of new research on marine calcification and marine carbonates. While biologists and ecologists have examined the effect of lowered-pH sea water on development and survival of marine organisms (e.g., Clark et al., 2009; Ries, 2011), geochemists have begun to consider dissolution and, in particular, the effects of skeletal carbonate mineralogy on susceptibility to dissolution (e.g., Andersson et al., 2008; Gehlen et al., 2008). In the course of this research, it has become clear that, in many taxa, we know far too little about the patterns of carbonate mineralogy, and that the generalisations commonly made about particular taxa turn out to be less than accurate

when detailed data are examined (e.g., Smith et al., 2006; Smith et al., 2013).

Differences in carbonate mineralogy are reflected in susceptibility to dissolution. Aragonite is more soluble than calcite, and high-Mg calcite (above about 12 wt.% MgCO₃) is even more soluble than aragonite. Some ocean waters are expected to reach undersaturation with respect to aragonite and high-Mg calcite within a few decades (Andersson et al., 2008), putting taxa which rely on those minerals under stress, and possibly moving towards a sea dominated by low-Mg calcite (Andersson et al., 2008), due to changes in both calcification and preservation.

At first glance it seems that sponges might well thrive in low-pH waters (e.g., Wisshak et al., 2012). Most of them are siliceous and would presumably be able to take advantage of ecological niches that were once occupied by, for example, coralline algae and/or bryozoans (as has occurred in the past, see Beauchamp and Grasby, 2012). But not all sponges are siliceous: about 8% of sponge species are calcifying (Uriz, 2006), some 650 of the over 8000 known species (van Soest et al., 2012). Naturally, most biomineralization research on sponges has been focused on silicification, and carbonate mineralogy has been studied little or not at all. Here we review and add to the data on

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carbonate mineralogy of calcifying sponges, investigating patterns of calcification and what they will mean in a high-CO₂ ocean.

2. Mineralization in sponges

Most marine sponges (Phylum Porifera) create a structural framework from a network of spicules in a range of morphologies, made of silica or calcium carbonate. These spicules can be simple or complex, with megascleres normally up to 0.5 mm long (though some unusual glass sponges have spicules 3 m in length) and tiny microscleres up to 100 μm long (Wang et al., 2008). Some groups also fuse spicules together with silica (dictyonine hexactinellids) or CaCO₃ cement (Uriz, 2006), or have complex interlocking terminations to the spicules ('lithistids'). Members of a small subgroup of calcisponges (sensu Wörheide, 2008) precipitate massive calcium carbonate skeletons, sometimes accompanied by silicate or calcareous spicules. These calcifying sponges are characteristic of, though not restricted to, temperate cryptic and deep-water environments.

The phylum Porifera is divided into five classes, of which four are extant (Debrenne et al., 2002; Gazave et al., 2010, 2012) comprising over 8000 species (Van Soest et al., 2012). Of these, only about 675 species are known to be calcifying, found in Classes Calcarea and Demospongiae (Voigt et al., 2012). Calcarea (about 600 described species) are generally small (less than 10 cm in height although some species can grow much larger), found in shallow marine waters, and mostly produce calcareous spicules which act as single crystals of more-or-less impure calcite (Ledger and Jones, 1977). The demosponges (over 6000 species described) are heterogeneous biomineralizers. They may have siliceous spicules and/or a fibrous skeleton or no skeleton at all, or they may have solid calcitic or siliceous skeletons which include the 'sclerosponges', 'sphinctozoans' and 'lithistids'. The polyphyletic coralline sclerosponges produce massive skeletons of aragonite or magnesium calcite (Hartman and Goreau, 1975). These coralline sponges are "living fossils," with convergent architectures similar to Paleozoic and Mesozoic reef-building stromatoporoids, chaetetids, sphinctozoans, and inozoans (Wood, 1990). Systematic relationships among them and their position within the classification of recent sponges are controversial (Mastandrea and Russo, 1995).

In addition to aragonite or magnesium calcite, two demosponges (*Dysidea crawshayi* and *Halichondria moorei*) have been found to precipitate spicules formed from a potassium fluorosilicate mineral called Hieratite (K₂SiF₆; Gregson et al., 1979). Several keratose demosponges produce granules of the iron oxide Lepidocrocite (FeO(OH); Towe and Rützler, 1968). Amorphous calcium carbonate, which is non-crystalline and unstable under ambient conditions and therefore hard to detect, is also found in some sponge spicules (Aizenberg et al., 1996, 2003), but may only be a pre-cursor to calcite formation as in some other taxa.

3. Methods and materials

A comprehensive literature review on carbonate mineralogy in the Porifera (examining over 50 papers and books) has uncovered 75 sponge specimens in 32 extant species for which carbonate mineralogy has been described (see Supplementary data on-line for details) (Fig. 1). Among them, only 42 specimens are accompanied by quantitative data. Most authors have made qualitative comments on sponge mineralogy, usually in passing, without a statement of methodology, precision, or significance. These qualitative statements are difficult to interpret, but here we assume that "Mg calcite" is roughly in the range of 4 to 8 wt.% MgCO₃ (equivalent to intermediate Mg calcite sensu Smith et al., 2006) and "high Mg calcite" is greater than about 8 wt.% MgCO₃.

In too many cases, sponge mineralogy in the literature is reported without reference to specimen location, number of specimens, or methodology employed. The geographical distribution of the 50 or so specimens for which the study location is known is limited: most of the specimens (22) are from the UK and Mediterranean, with 14 from

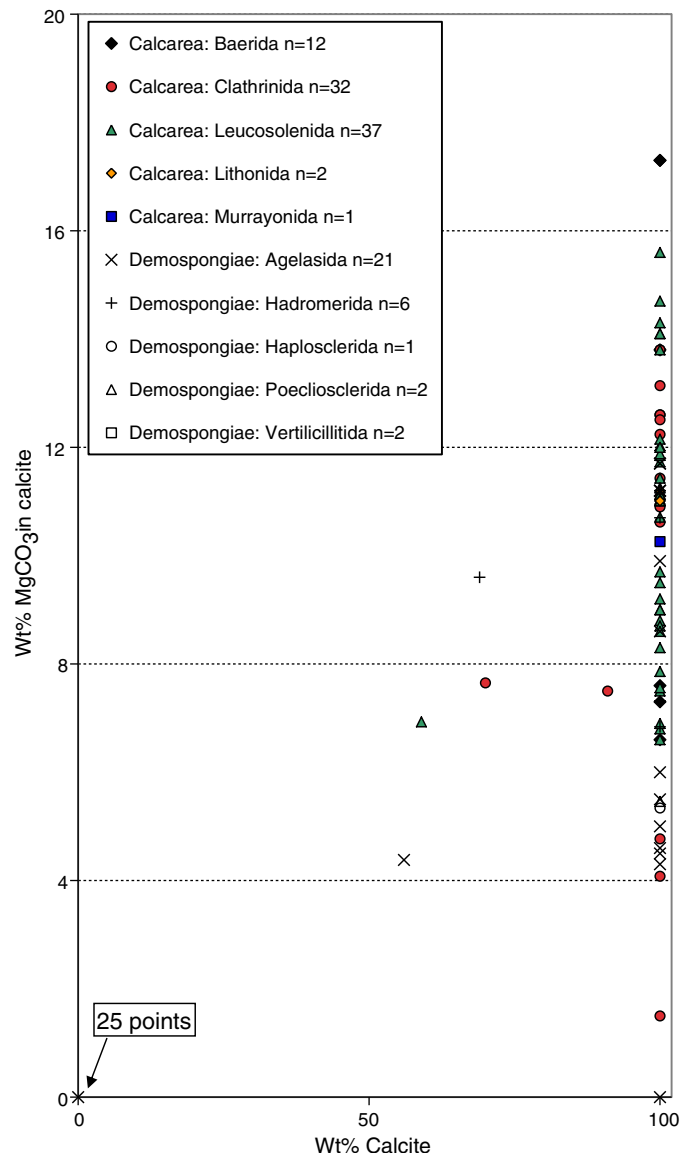


Fig. 1. Skeletal carbonate mineralogy of 74 extant specimens of the phylum Porifera; 28 are from the literature (Lister, 1900; Clarke and Wheeler, 1922; Vinogradov, 1953; Jones and James, 1969; Jones, 1970; Jones and Jenkins, 1970; Schuhmacher and Plevka, 1981; Reitner and Engeser, 1987; Willenz and Hartman, 1989; Cuif and Gautret, 1991; Ledger and Jones, 1991; Reitner, 1991; Vacelet and Uriz, 1991; Wood, 1991; Aizenberg et al., 1995a,b, 1996, 2003; Reitner and Gautret, 1996; Böhm et al., 2000; Fallon et al., 2004; Rosenheim et al., 2005; Wombacher et al., 2005; Rossi et al., 2006; Sethmann et al., 2006; Uriz, 2006; Sethmann and Wörheide 2008), whereas the remaining 42 are new data from New Zealand. See Supplementary data for details.

the Caribbean, 11 specimens are from the tropical Indopacific, and one from the south Atlantic. No mineralogical data are published from the western North Atlantic, from the North Pacific, from any polar region, or south of 23°S. Though all the materials require more replication and a wider spread of species, a mineralogical study of sponge carbonate from southern temperate regions, in particular, needs to be done.

Twenty-nine specimens of five species of calcareous sponges were collected by hand from shallow waters around Wellington, New Zealand, and a further nine specimens from more southern localities were selected from the reference collection at Portobello Marine Laboratory, Dunedin, New Zealand. Sponge individuals were cleaned and inspected and all non-sponge carbonates were removed. They were divided into thirds, and voucher specimens were kept and stored in ethanol at the University of Otago, Dunedin, New Zealand. One subsample of each sponge was dissected for identification (to genus

level). The other third was immersed in 5% bleach for three days to remove organic material. One particularly large specimen was divided into five replicate subsamples, so that a total of 42 specimens were prepared for X-ray diffractometry (XRD).

Each bleached slurry of spicules was rinsed several times in distilled water, ground fine while wet in an agate mortar along with 0.1 g NaCl as an internal XRD standard, spread out on a glass slide and dried. Each slide was run through a Phillips X-ray diffractometer at 50 counts per degree with a count time of 1 s, over the range of 26 to 33°2 θ . Peak heights (in counts) and positions (in °2 θ) were determined, the halite peak position was standardized to 31.72°2 θ , and other peak positions were corrected.

Weight percent Mg in calcite was calculated from the calcite peak position (in °2 θ) using a machine-specific calibration ($y = 30 \times - 882$). Each spectrum was visually inspected as well, and locations of ragged peaks were confirmed by eye. Relative peak height counts (ht) of aragonite (A1 at 26.213°2 θ and A2 at 27.216°2 θ) and calcite (C1 at 29.4 to 29.8°2 θ) were used to calculate the Peak Height Ratio (PR) for each graph: $PR = (ht\ A1 + ht\ A2) / (ht\ A1 + ht\ A2 + ht\ C1)$. Wt.% calcite was calculated using the calibration of Gray and Smith (2004): $Wt.\% \text{ calcite} = 80.4(PR)^2 - 180.9(PR) + 101.2$. This method assumes that only calcite and aragonite are present in the skeletal carbonate.

A combined dataset (comprising the mineralogy reported in the literature alongside our own new results) was used to examine whether variation in water temperature can explain mineralogical variation in these sponges. For each specimen from which the location was known or could be deduced ($n = 89$), the mean sea surface temperature was extracted from the NOAA Optimum Interpolation Sea Surface Temperature data (Reynolds et al., 2002). The relationship between mineralogy and water temperature was then explored using generalised linear mixed models (GLMMs). Specifically, models with wt.% MgCO₃ as a response variable and sea surface temperature as a fixed predictor variable were fitted using the R (R Development Core Team, 2012) package MCMCglmm (Hadfield, 2010). As these data are drawn from an evolutionary diverse range of species, taxonomic and, where possible, phylogenetic effects were included as random effects in the GLMMs using the phylogeny presented by Voigt et al. (2012) and taxonomic information retrieved from the World Register of Marine Species (<http://www.marinespecies.org/>).

4. Results

Our literature review provided mineralogical data for 74 sponge specimens in 32 species, and the New Zealand results added 42 specimens in 15 species, for a total of 116 specimens from 46 species in 24 genera (Table 1). Most specimens are either 100% calcite or 100% aragonite, with only a few specimens from New Zealand showing combinations of the two (56 to 91 wt.% calcite, mean = 69 wt.% calcite, $N = 5$). In the calcitic specimens, Mg content showed much more variation, ranging from 0 to 17.3 wt.% MgCO₃ (mean = 9.7 wt.% MgCO₃, $N = 83$).

Of the 46 species studied, 9 were entirely aragonitic, 33 were entirely calcitic (with the majority producing high-Mg calcite), and only 4 species showed some mixture of the two.

5. Discussion

5.1. Variation within species

The combination of the detailed literature review and the New Zealand specimens gives 116 sponge specimens from 46 species in 24 genera (Table 1). Of the 650 or so sponge species which precipitate calcium carbonate, only 5% have been mineralogically characterised, and in most cases they were measured only once. Work in other phyla (e.g., Smith et al., 2006; 2012) suggests that variability within and among species requires a more rigorous approach. Any study on sponge

mineralogy must address both within-individual and within-species variabilities before any further progress can be made.

Very few sponges have been examined for within-individual variation. In most cases where a single individual was tested several times, it was in order to compare rather than to truly randomly replicate different types of spicules. Calcium carbonate spicules in a specimen of *Sycon* sp. from the Eastern Mediterranean varied from 10.7 to 11.7 wt.% MgCO₃ (Aizenberg et al., 1995b), whereas those of *Amphiute paulini* from Brittany, France ranged from 6.6 to 7.6 wt.% MgCO₃ (Jones and Jenkins, 1970); and *Leuconia nivea* from Menai Strait, UK ranged from 8.6 to 9.7 wt.% MgCO₃ (Jones and Jenkins, 1970). Five replicate subsamples from a single large specimen of *Clathrina* sp. 2 (small, yellow) from Breaker Bay, near Wellington, 5 m water depth, were all 100% calcite, with Mg content ranging from 11.7 to 12.5 wt.% MgCO₃ (mean = 12.1; standard deviation = 0.3 wt.% MgCO₃, $N = 5$). This small degree of variation within an individual suggests that variability within species is on the order of ± 0.5 wt.% MgCO₃.

There are only three species for which we have measurements of more than 10 specimens; they range from quite consistent to remarkably variable. All ten specimens of the Caribbean sponge *Ceratoporella nicholsoni* are aragonitic (Hartman and Goreau, 1970; Schuhmacher and Plewka, 1981; Willenz and Hartman, 1989; Wood, 1991; Böhm et al., 2000; Rosenheim et al., 2005). Our own data show that calcitic *Clathrina* sp. 2 from central New Zealand has a range of 2.5 wt.% MgCO₃ (10.6 to 13.1, mean = 12.0, standard deviation = 0.7 wt.% MgCO₃, $N = 12$). A calcitic species of *Sycon* from the Eastern Mediterranean has one individual that registered no Mg content, but all the other specimens range from 9.9 to 11.7 wt.% MgCO₃ (mean = 11.1, standard deviation = 0.5 wt.% MgCO₃, $N = 9$) (Aizenberg et al., 1995a,b). If we assume that the outlier represents some kind of sampling or measurement anomaly, then within-species variability in Mg ranges from almost none to about ± 1.0 wt.% MgCO₃. This means that single-specimen measurements are probably reasonably accurate estimates of the mineralogy of the whole species.

In each of these cases, specimens are necessarily aggregates of many spicules, and thus the variability among spicules may be greater than that detected using X-ray diffractometry. A higher-resolution technique such as Raman spectroscopy might elucidate details of within- and among-spicule variations.

5.2. Phylomineralogy and evolution of mineralogy in sponges

There is a phylogenetic overprint to the mineralogy in the Phylum Porifera, with fairly consistent class-to-order level distribution among those species so far studied (Table 2). Calcareous sponges are largely restricted to Class Calcarea. Class Homoscleromorpha as well as the Silicea clade containing Classes Demospongea and Hexactinellida are dominated by silicifying sponges. Only one hexactinellid sponge *Caulophacus* has been found to mineralize calcite (Ehrlich et al., 2011). Calcification is only a little more common in the demosponges.

Only 12 species representing five of the 16 demosponge orders are known to precipitate carbonate in their basal skeletons (Table 2). Although it is not clear how many demosponges are calcifiers, the overall coverage in these “sclerosponges” is barely adequate to allow for generalisations to be made. Most specimens have entirely aragonitic basal skeletons. In the Poecilosclerida order, the basal skeleton of *Merlia lipoclavidisca* is entirely aragonitic (Vacelet and Uriz, 1991), but the basal skeleton of another *Merlia* sp. was found to be low-Mg calcite (Wood, 1991), as are the spherules found in the silica-producing *Hemimycale columella*. It is possible that this particular order has a higher degree of mineralogical flexibility than others in the Phylum Porifera or as discussed below, calcification has polyphyletic origins in the demosponges (Chombard et al., 1997). Unfortunately, with no replication, there is little to constrain the competing hypotheses.

Acanthochaetetes and *Willardia* are the only extant genera within the Acanthochaetetidae family (order Hadromerida). *Acanthochaetetes* spp.

Table 1
Skeletal carbonate mineralogy of 46 extant species of calcifying sponges, recalculated to standard units. Taxonomy follows van Soest et al. (2012). See Supplementary data on-line for details.

Class	Order	Family	Species	Skeletal element	Specimens	Mineralogy	Mean wt.% calcite in carbonate	Mean wt.% MgCO ₃ in calcite	Reference		
Calcarea	Baerida	Baeriidae	<i>Leucandra aspera</i> (Schmidt, 1862)	Spicules	2	MgC	100	7.8	Jones (1970)		
			<i>Leucandra aspera</i> (Schmidt, 1862)								
			<i>Leucandra aspera</i> (Schmidt, 1862)								
			<i>Leucandra pandora</i> (Haeckel, 1872)	Spicules	1		100	10.71	This study		
			<i>Leucandra pandora</i> (Haeckel, 1872)								
			<i>Leucandra pumila</i> (Bowerbank, 1866)	Spicules	1	MgC	100	8.3	Jones and Jenkins (1970)		
			<i>Leucandra pumila</i> (Bowerbank, 1866)								
			<i>Leucandra pumila</i> (Bowerbank, 1866)								
			<i>Leuconia nivea</i> (Grant, 1862)	Various spicules	6	MgC	100	9.2	Jones and Jenkins (1970); Jones and James (1969)		
			<i>Leuconia nivea</i> (Grant, 1862)								
			<i>Leuconia nivea</i> (Grant, 1862)								
			<i>Leuconia</i> sp.	Spicules	1		100	11.01	This study		
	<i>Leuconia</i> sp.										
	<i>Leuconia</i> sp. cf. <i>Leuconia</i>	Spicules	1		100	11.25	This study				
	cf. <i>Leuconia</i>										
	<i>Clathrina contorta</i> (Bowerbank, 1866)	Clathrinida	Clathrinidae	<i>Clathrina contorta</i> (Bowerbank, 1866)	Spicule	1	MgC	100	13.8	Aizenberg et al. (1995b)	
	<i>Clathrina contorta</i> (Bowerbank, 1866)										
	<i>Clathrina coriacea</i> (Montagu, 1818)			Spicules	1	MgC	100	10.9	Jones and Jenkins (1970)		
	<i>Clathrina coriacea</i> (Montagu, 1818)										
	<i>Clathrina coriacea</i> (Montagu, 1818)			Triradiate spicules	2	MgC with ACC layer	100	13.8	Aizenberg et al. (1995a, 1996) (2003);		
	<i>Clathrina</i> sp.										
	<i>Clathrina</i> sp.			Spicules	5	MgC with some aragonite	92.2	5.1	This study		
	<i>Clathrina</i> sp. 1 – white, large										
	<i>Clathrina</i> sp. 1 – white, large			Spicules	12	High Mg C	100	12	This study		
	<i>Clathrina</i> sp. 1 – white, large										
	<i>Clathrina</i> sp. 2 – yellow, small			Spicules	1	High Mg C	100	11.13	This study		
	<i>Clathrina</i> sp. 2 – yellow, small										
	<i>Clathrina</i> sp. 2 – yellow, small	Spicules	1	High Mg C	100	11.13	This study				
	<i>Clathrina</i> sp. 2 – yellow, small										
	<i>Clathrina</i> sp. 3 – yellow, stringy	Spicules	1	MgC	100	9 ^a	Uriz (2006)				
	<i>Clathrina</i> sp. 3 – yellow, stringy										
	<i>Leucetta</i> sp.	Leucettidae		<i>Leucetta</i> sp.	Spicules	1	MgC	100	9 ^a	Uriz (2006)	
<i>Leucetta</i> sp.											
<i>Leucetta</i> sp.	Spicules			1	High Mg C	100	11.88	This study			
<i>Leucetta</i> sp.											
<i>Leucetta</i> sp.	Spicules			4	High Mg C	100	11.2	This study			
<i>Leucetta</i> sp. 1 – large oscules											
<i>Leucetta</i> sp. 1 – large oscules	Spicules			3	High Mg C	100	10.2	This study			
<i>Leucetta</i> sp. 1 – large oscules											
<i>Leucetta</i> sp. 2 – small ostia	Triactine spicules			1	MgC	100	8.6	Sethmann et al. (2006)			
<i>Leucetta</i> sp. 2 – small ostia											
<i>Pericharax heteroraphis</i> Poléjaeff, 1883	Leucosolenida			Amphoriscidae	<i>Pericharax heteroraphis</i> Poléjaeff, 1883	Spicules	1	High Mg C	100	14.1	Vinogradov (1953)
<i>Leucilla "carteri"</i> (not clear what species is meant here)											
<i>Leucilla "carteri"</i> (not clear what species is meant here)											
<i>Amphiute paulini</i> Hanitsch, 1894	Grantiidae		<i>Amphiute paulini</i> Hanitsch, 1894	Spicules, oxea	3	MgC	100	7.2	Jones and Jenkins (1970)		
<i>Amphiute paulini</i> Hanitsch, 1894											

		<i>Grantia compressa</i> (Fabricius, 1780)	Spicules	1	MgC	100	6.6	Jones and Jenkins (1970)	
		<i>Grantia compressa</i> (Fabricius, 1780)							
		<i>Grantia</i> sp.	Spicules	2	High Mg C	100	11.01	This study	
	Lelapiidae	<i>Kebira uteoides</i> Row, 1909	Monaxon	3	Mg C	100	15.6	Aizenberg et al. (1995b)	
	Leucosoleniidae	<i>Leucosolenia</i> cf. <i>botryoides</i>	Spicule	1	Mg C plus aragonite	59	6.93	This study	
		<i>Leucosolenia</i> cf. <i>botryoides</i>							
		<i>Leucosolenia complicata</i> (Montagu, 1818)	Spicules	1	Mg C	100	6.9	Jones and Jenkins (1970)	
		<i>Leucosolenia complicata</i> (Montagu, 1818)							
		<i>Leucosolenia echinata</i> (?)	Spicules	4	Mg C	100	10	This study	
		<i>Leucosolenia echinata</i> (?)							
		<i>Leucosolenia</i> sp.	Spicules	1		56	4.38	This study	
		<i>Leucosolenia</i> sp.							
	Sycettidae	<i>Sycon ciliatum</i> (Fabricius, 1780)	Spicules	4	Mg C	100	4.5	Jones and Jenkins (1970); Ledger and Jones (1991); Vinogradov (1953)	
		<i>Sycon ciliatum</i> (Fabricius, 1780)						Rossi et al. (2006)	
		<i>Sycon pentactinale</i> Rossi, Farina, Borojevic & Klautau, 2006	5-Rayed spicules	1	C	100			
		<i>Sycon pentactinale</i> Rossi, Farina, Borojevic & Klautau, 2006							
		<i>Sycon</i> sp.	Various spicules	10	Mg C	100	10	Aizenberg et al. (1995a)	
		<i>Sycon</i> sp.							
		<i>Sycon</i> sp. 1 – collared	Spicules	4	Mg C with some aragonite	92	7.3	This study	
		<i>Sycon</i> sp. 1 – collared							
		<i>Sycon</i> sp. 2 – short vase	Spicules	1	Mg C	100	5.46	This study	
		<i>Sycon</i> sp. 2 – short vase							
	Lithonida	Minchinellidae	<i>Minchinella</i> sp.	Primary skeleton	1	Mg C	100	5	Wood (1991)
		Petrobionidae	<i>Petrobiona massilana</i> Vacelet & Lévi, 1958	Primary skeleton	1	Mg C	100	6	Wood (1991)
		Murrayonidae	<i>Murrayona phanolepis</i> Kirkpatrick, 1910	Primary skeleton	1	Mg C	100	5.5	Wood (1991)
	Demospongiae	Agelasida	<i>Astrosclera willeyana</i> Lister, 1900	Primary skeleton (massive)	7	A	0	Böhm et al. (2000)	
								Fallon et al. (2004); Lister (1900); Wood (1991)	
			<i>Ceratoporella nicholsoni</i> (Hickson, 1911)	Primary skeleton	10	A	0	Schuhmacher & Plewka (1981), Böhm et al. (2000), Rosenheim et al. (2005); Willenz and Hartman (1989); Hartman and Goreau (1970); Wood (1991)	
								Hartman and Goreau (1970); Wood (1991)	
			<i>Goreauella auriculata</i> Hartman, 1969	Primary skeleton	1	A	0	Hartman and Goreau (1970); Wood (1991)	
			<i>Hispidopetra miniana</i> Hartman, 1969	Massive skeleton	1	A	0	Hartman and Goreau (1970); Wood (1991)	
			<i>Stromatospongia norae</i> Hartman, 1969	Basal exoskeleton	1	A	0	Hartman and Goreau (1970); Willenz and Hartman (1989)	
			<i>Stromatospongia vermicola</i> Harman, 1969	Irregular skeleton	1	A	0	Hartman and Goreau (1970); Wood (1991)	
	Hadromerida	Acanthochaetidae	<i>Acanthochaetes</i> sp.	Primary skeleton	2	High Mg C	100	Wood (1991), Womacher et al. (2005)	
			<i>Acanthochaetes wellsii</i> Hartman and Goreau, 1975	Primary and secondary skeleton	4	High Mg C	100	Cuif and Gautret (1991); Reitner (1991); Reitner and Engeser (1987); Reitner and Gautret (1996)	
								Wood (1991)	
	Haplosclerida	Calcifibrospongiidae	<i>Calcifibrospongia actinostromarioides</i> Hartman, 1979	Primary skeleton	1	A	0	Wood (1991)	
	Poecilosclerida	Hymedesmidae	<i>Hemimyscale columella</i> (Bowerbank, 1874)	Spherules	1	C spherules and SiO ₂ spicules together	100	0	Vacelet et al. (1987)
		Merliidae	<i>Merlia lipoclavidsca</i> Vacelet and Uriz, 1991	Basal skeleton	1	A	0	Vacelet and Uriz (1991); Uriz (2006)	
			<i>Merlia</i> sp.	Primary skeleton	1	low Mg C	100	Wood (1991)	
	Verticillitida	Verticillititidae	<i>Vaceletia crypta</i> (Vacelet, 1997)	Rigid skeleton	2	A	0	Cuif and Gautret (1991); Wombacher et al. (2005); Wood (1991)	

^a Uriz (2006) published 8–10 wt.% Mg, which would equate to 57 wt.% MgCO₃. We assume this to be a misprint and have corrected to 8–10 wt.% MgCO₃.

Table 2
Carbonate mineralogy of higher taxa of extant calcifying sponges as reported in the literature (see references in Table 1) and determined here for specimens from New Zealand. Taxonomy follows van Soest et al. (2008).

Classes	Subclasses	Orders	Families	Genera	Species	Specimens	Mean wt% Calcite	Mean wt% MgCO ₃ in calcite	Mineralogy
2 of 4 in Porifera		10	16	24	46	116	77	9.3	
Calcarea	2 of 2	5 of 5	11 of 24	15	34	84	98.2	9.5	Mg to high Mg calcite
		Calcaronea	Baerida	1 of 3	3	6	12	100	9.4
	Leucosolenida		5 of 9	6	14	37	97	9.0	High Mg calcite
	Lithonida		2 of 2	2	2	2	100	5.5	Mg calcite
	Calcinea	Clathrinida	2 of 7	3	11	32	99	10.5 ^a	High Mg calcite
		Murrayonida	1 of 3	1	1	1	100	5.5	Mg calcite
	Demospongiae	n/a	5 of 16	5	9	12	32	22	6.9
Agelasida			1 of 2	5	6	21	0		Aragonite
Hadromerida			1 of 12	1	2	6	100	16.1	High Mg calcite
Haplosclerida			1 of 3	1	1	1	0		Aragonite
Poecilosclerida			1 of 4	1	2	2	50	0	Aragonite or low Mg calcite
	Verticillitida ^b	1 of 1	1	1	2	0		Aragonite	

^a Excluding the anomalously high reported Mg content in *Leucetta* by [Uriz, 2006](#).

^b But [Wörheide, 2008](#) places *Vaceletia* in the Dictyoceratida in its own new family.

are known to produce extremely high-Mg calcite (14 to 18 wt.% MgCO₃) compared with *Willardia caicosensis* which has an aragonite basal skeleton. Do these distinct mineralogical compositions within the same family reflect a different biomineralizing evolutionary path within this family?

Calcification of secondary and basal skeletons is known from only a few demosponge orders (and phylogenetic arguments continue as to their correct placement), of which we record five. The orders Agelasida, Haplosclerida, Poecilosclerida, and Verticillitida (or perhaps Dictyoceratida after [Wörheide, 2008](#)) comprise 42 families with about 230 genera ([Van Soest et al., 2012](#)). Most of the species for which mineralogy is known in these orders form massive secondary skeletons of aragonite, though they can hardly be considered 'typical', as they represent less than 4% of the known genera in the class. *Hemimycale columella* (Poecilosclerida) is unusual in producing silica spicules and calcareous spherules. These spherules are formed of very low Mg calcite ([Vacelet et al., 1987](#)).

Within the order Hadromerida there is one family, the Acanthochaetidae, known to have calcified basal skeletons; in that family, *W. caicosensis* is anomalous in that it produces a basal aragonite skeleton ([Willenz and Pomponi, 1996](#)) and the genus *Acanthochaetetes* precipitates very high Mg calcite (12 to 19.9 wt.% MgCO₃) in its basal skeleton according to [Reitner and Engeser \(1987\)](#), the highest recorded in the phylum. As the record for *Acanthochaetetes* is based on six specimens any general statement on mineralogy in this group should be considered provisional.

In Class Calcarea, all spicules measured (14 genera, 19 species, 42 specimens) have been found to be formed of calcite, with no aragonite present. The lowest Mg content reported was 4.3 wt.% MgCO₃ in *Sycon ciliatum* ([Jones and Jenkins, 1970](#)), but most of the specimens showed an Mg content greater than 6 wt.% MgCO₃. The highest Mg content found was 15.6 wt.% MgCO₃ in *Kebira uteoides* ([Aizenberg et al., 1995a](#)). The mean Mg content for the class is 9.6 wt.% MgCO₃.

Even though only 34 of the ~500 described extant sponges in Class Calcarea have been tested for carbonate mineralogy, at least one species from each of the five orders is represented here (Table 2). Though a few specimens show a small amount of aragonite, in general these sponges produce calcitic spicules. Mg contents are usually high, up to 15 wt.% MgCO₃. Two orders, the Lithonida and the Murrayonida, appear to incorporate less Mg in their skeletal carbonate than other orders, but both taxa are represented by only one or two analyses; therefore further work in these groups would be fruitful.

Both calcification and silicification are important in sponges. Which came first, a subject of some debate, affects the subsequent distribution of skeletal composition in the various clades with their different synapomorphic mineralogies. There are three competing hypotheses for the phylogenetically primitive biomineralization state of the

sponges. Below we compare palaeontologic and neontologic evidences for the silica-first, calcite-first, and biomineral-first hypotheses.

[Xiao et al. \(2005\)](#) suggested that both fossil and molecular data indicate that silicification evolved first. Molecular clock data based on a paraphyletic Phylum Porifera suggest that the origin of silica biomineralizing sponges occurred by 759 Ma ([Sperling et al., 2010](#)). This is close to the age of the oldest reported siliceous spicules with demosponge affinities from the Late Proterozoic, ~750 Ma ([Reitner and Wörheide, 2002](#)). By 635 Ma, there is biomarker evidence suggestive of sponges in pre-Marinoan rocks ([Love et al., 2009](#)), but there is a disagreement on the interpretation of such biomarkers ([Brocks and Butterfield, 2009](#)). [Li et al. \(1998\)](#) discovered fossil cellular tissue of sponges and demosponge-like monaxonid siliceous spicules from the Ediacaran, ~580 Ma. Siliceous spicules assigned to the hexactinellids are known from the upper Ediacaran (549–543 Ma) ([Brasier et al., 1997](#)).

Alternatively, sponges may have originally been calcareous ([Ehrlich et al., 2011](#)). The evidence for the primitive biomineralization state in sponges being calcareous comes from the fact that no examples of siliceous spicules have been found in Class Calcarea, but calcareous skeletal elements have been discovered in both classes in the Silicea clade ([Ehrlich et al., 2011](#)). [Philippe et al. \(2009\)](#) and [Pick et al. \(2010\)](#) have argued that sponges are monophyletic and the Silicea are not the most primitive clade in the phylum. The fossil record sheds little light on this. The first metazoan calcifiers of possible poriferan affinity (i.e., *Namapoikia*) were from the late Neoproterozoic, ~549 Ma ([Wood et al., 2002](#)). This 200 Myr gap between the first siliceous sponge fossils and the first calcareous ones could simply be an artefact of the preservation potential of silica versus calcite. Putative calcareous have been reported from the Early Cambrian Tommotian Stage, <542 Ma ([Kruse et al., 1995](#)). The oldest calcareous with preserved mineralogy are not until the Silurian, <444 Ma ([Mehl and Reitner, 1996](#)). The oldest preserved aragonitic sponges are the demosponges from the Upper Triassic, 217–204 Ma ([Senowbari-Daryan and Link, 2011](#)).

From the Cambrian onwards and for much of the Paleozoic and Mesozoic, calcareous sponges such as archaeocyathids and stromatoporoids were dominant reef-builders, and their skeletons form important components of marine sediments from those times ([Fagerstrom, 1987](#)). Assuming members of the extinct Class Archaeocyathida were actual sponges and not just functional equivalents ([Debrenne et al., 2002; Debrenne, 2006](#)), then the first large-scale calcitic, reef-forming sponges appear at the start of the Tommotian, ~525 Ma ([Malooof et al., 2010a](#)) but possibly as early as the Namakit-Daldynian, 530 Ma ([Wood, 1999; Rowland and Shapiro, 2002; Malooof et al., 2010b](#)). Regardless, they were extinct by the Middle Cambrian ([Debrenne et al., 2002](#)). Stromatoporoids were sponge-like animals with hypercalcified layered skeletons. They have been variously referred to as calcifying demosponges,

calcareans, or simply a polyphyletic grade of sponge construction (Wood, 1987; Stearn et al., 1999; Cook, 2002; Cuif et al., 2011; Da Silva et al., 2011). They were important Ordovician to Cretaceous reef-builders, especially in the Silurian and Devonian (Fagerstrom, 1987; Wood, 1987, 1999). The Paleozoic stromatoporoids were likely a different clade from the Mesozoic species which are related to the extant sclerosponges in Class Demospongia (Reitner and Wörheide, 2002).

With the molecular debate over the monophyly (Philippe et al., 2009; Pick et al., 2010) or paraphyly (Borchiellini et al., 2001; Sperling et al., 2010) of the sponges not resolved, Botting et al. (2012) have recently argued that the primitive state of the sponges is neither siliceous or calcareous, but bimineralic (i.e., containing spicules of both SiO₂ and CaCO₃), because the Early Cambrian sponge *Lenica* (Goryanskii, 1977) was inferred, despite diagenetic problems, to have originally contained bimineralic spicules (Botting et al., 2012). Botting et al. (2012) hypothesized that sponges were originally bimineralic and silica biomineralization was later lost in Class Calcarea and calcite biomineralization was subsequently lost in Class Homoscleromorpha as well as the Silicea clade containing Classes Demospongia and Hexactinellida. If this is the case, then the rare occurrences of calcification in the dominantly siliceous Classes Demospongia and Hexactinellida had to evolve independently again. This conclusion is required by the well-documented calcitic and aragonitic sclerosponges in Class Demospongia (Table 1) and the recent discovery of calcite in the hexactinellid sponge *Caulophacus* (Ehrlich et al., 2011), and supported by the ribosomal sequence data of Chombard et al. (1997) that suggests that the calcareous skeleton evolved independently in several lineages of sponges. More data, like this study, on mineralogy across the sponges will allow for improved understanding of the phylomineralogy of this important invertebrate phylum, among the first to biomineralize.

Wood (1991) and Cuif et al. (2011) suggested that the history of carbonate mineralogy among sponges reflects secular patterns in sea-water chemistry (e.g., Stanley and Hardie, 1998). Wood (1991) noted that calcifying sponges formed reefs and were more abundant in times of “calcite seas” (Ordovician to Devonian, then again in the Jurassic to Cretaceous). She also suggested that carbonate mineralogy is not a useful character for delineating taxa. There are, however, not enough mineralogical and/or phylogenetic data to rigorously test this hypothesis. Similarly, calcification could be primarily a detoxification mechanism (Kingsley and Watabe, 1982; Saul, 2009), but we have no evidence either way.

5.3. Environmental and ontogenetic influences on mineralogy

Many studies following Chave (1954) have noted a relationship between Mg in calcite and water temperature or a proxy such as latitude. Others have noted increasing Mg content with increasing size of skeletal elements (thus possibly growth rate), including sponge spicules (Jones and Jenkins, 1970). When Mg content is plotted against water temperature from our data, there is an apparent trend of increasing Mg with warmer water (Fig. 2).

We further investigated the relationship between water temperature and Mg content using GLMMs. We ran a phylogenetic comparative analysis on the subset of these data that could be placed in the phylogeny of calcareous sponges presented by Voigt et al. (2012) (n = 50, 56% of samples for which water temperature could be retrieved.). Sea surface temperature was not a significant effect in this model ($p = 0.75$). This model found a phylogenetic signal in these data, with 17% of observed variation in Mg content explained by phylogenetic relatedness among specimens. As the phylogenetic effect cannot be included for data arising from other genera, we ran another model on the complete dataset, containing only effects for water temperature and genus. Again, water temperature was not shown to have a significant effect on Mg content ($p = 0.16$) and the complete model explained only a modest amount of

the variation in this trait ($R^2 = 0.33$). Although we do not find a significant effect of water temperature on Mg content in our analyses, it is possible that such an effect exists but was not detectable in this dataset. In particular, a large proportion of our data comes from the temperate seas around New Zealand where the mean sea surface temperature is around 15 °C (n = 42, or 47% of the observations from which water temperature is discoverable). Warmer and cooler regions are both less well represented in our data, a pattern that may have limited the statistical power of our analyses.

One possible influence on skeletal mineralogy could be the ontogenetic stage of the sponge when collected. No author commented on the “age” of the sponge collected, nor on the growth rate, and we made no attempt to characterise age or growth in our collections. It is sometimes noted in high-Mg biogenic calcites that Mg content is strongly related to growth rate (e.g. Kolesar, 1978). The lack of consistency around the age of specimen and possibly thus growth rate could obscure other signals in mineralogy. Ideally, comparison of laboratory-grown specimens of similar ages would allow for a more precise understanding of the influences on skeletal mineralogy, particularly in regard to temperature and other environmental effects.

5.4. Calcareous sponges in a high-CO₂ world

Increasingly, studies of organisms' responses to ocean acidification have described “winners and losers” in a high-CO₂ ocean. Such studies have relied, at least in part, on skeletal mineralogy to help predict outcomes. Thus silica producers such as diatoms and sponges have been listed among the “winners”, who stand ready to inhabit the vacant niches left by their more soluble carbonate neighbours. It has been common to use sweeping generalisations about mineralogy within taxa, including among the sponges. But substantial subsets of the Porifera are calcareous, and many of them will be vulnerable to projected lowered pH and carbonate availability.

This paper demonstrates that there is both within-specimen and within-species variability of wt.% MgCO₃ in calcite (and to a lesser extent, variability with respect to aragonite:calcite ratio). Even more variation occurs within higher taxa. This degree of variability calls into question the practice of classifying taxa, maybe even species, in particular mineralogical types. If our generalisations about taxa are over-simplified, it may be that broad-scale inferences about calcite and aragonite seas and the successes of high-Mg vs. low-Mg taxa (see e.g. Stanley and Hardie, 1998, 1999; Zhuravlev and Wood, 2009) are not entirely justified.

Among the most vulnerable to ocean acidification will be aragonite and high-Mg calcite skeletons (Smith, 2009), such as those formed by many calcifying sponges. And it is in southern temperate-to-polar waters that ocean acidification will be felt first (Andersson et al., 2008). Species reported on here that are most at risk are the shallow-water species found in cool-to-cold waters, especially in the Southern Hemisphere.

6. Conclusions

We report here on 116 measurements of skeletal carbonate mineralogy in the sponges, encompassing 46 species in 24 genera, a small percentage of the 650 species known to calcify. Calcifying sponges are usually formed from aragonite or calcite with Mg substitution of about 4 to 16 wt.% MgCO₃. We report here on the first measurements to show that some dominantly calcitic skeletons may contain appreciable amounts of aragonite.

Variability within-specimens and within-species of wt.% MgCO₃ in calcite is on the order of ± 0.5 wt.% MgCO₃. There is, in general, less variability with respect to aragonite:calcite ratio. There are broad mineralogical patterns in the higher taxa, and it is often possible to classify taxa into particular mineralogical types. There are exceptions: the archaeocyath sponges, for example, are usually described as having

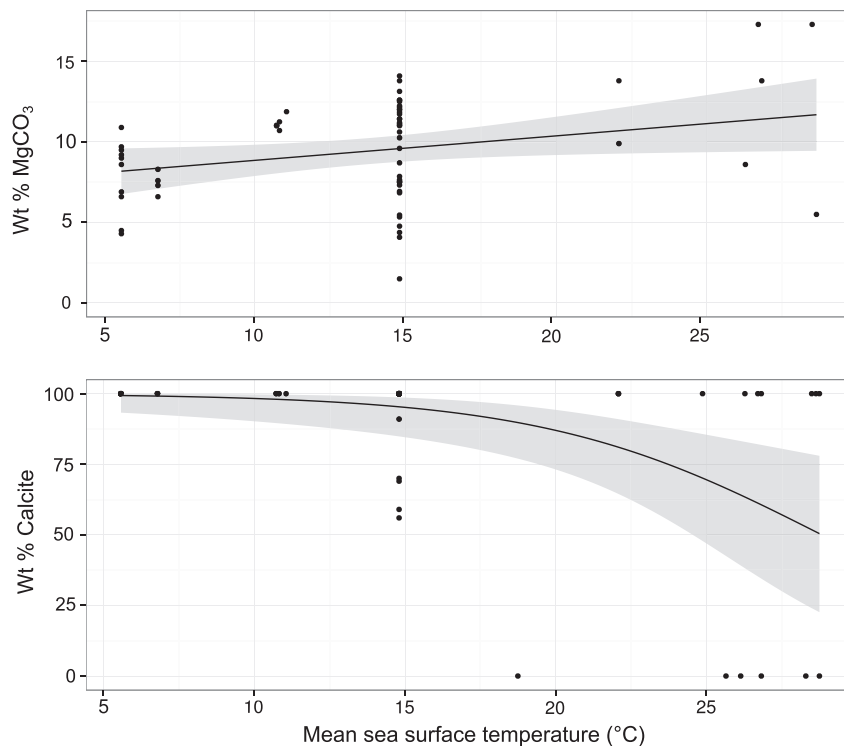


Fig. 2. There is little relationship between water temperature (approximated by mean sea surface temperature) and Mg content in calcite (top) or overall calcite percentage (bottom) in skeletal carbonate of calcifying sponges. Trend lines are following linear regression, with shaded areas representing 95% confidence intervals. For the calcite data, the regression was performed on logit-transformed data to account for the fact this variable is bounded at 0 and 100%.

high-Mg calcite skeletons, but our results suggest that the group might be more variable.

The strong degree of phylogenetic consistency at higher taxonomic levels calls into question the common assumptions regarding phenotypic expression of mineralogy. When the phylogenetic component is removed, we are unable to find a correlation between, for example, mineralogy and latitude.

In a high- CO_2 world, many sponges may be “winners”, but the calcareous sponges may not be among them. High-Mg calcite and aragonite are the most soluble forms of CaCO_3 , and most of the sponges reported here live in the shallow temperate regions where saturation levels are predicted to fall most rapidly. Deeper-water sponges may be isolated from lowering pH effects for some time.

Acknowledgements

Many thanks are due to Judy Fisher and her team at Remote Services, University of Otago Library, for performing above and beyond the call of duty during the literature review. We also thank Oliver Voigt and Gert Wörheide for providing the phylogenetic trees from their own work in a form that could be used in our statistical analyses. Louise Kregting collected some specimens, and performed some of the XRD work. Thanks also to Michelle Liddy who ran many XRD samples. As always Damian Walls, Geology Department, University of Otago, was of great help. We thank Stephen Grasby and other anonymous reviewers for their helpful comments.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.palaeo.2013.10.004>.

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