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Not All Sponges Will Thrive in a High-CO₂ Ocean: Review of the Mineralogy of Calcifying Sponges

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

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Keywords: sponges; Porifera; ocean acidification; calcite; aragonite; skeletal biomineralogy

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Abstract: Most marine sponges precipitate silicate skeletal elements, and it has been predicted that they would be among the few "winners" 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 CO₃⁼ 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 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.

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

Abigail M. Smith^{a*}, Jade Berman^{b,1}, Marcus M. Key, Jr.^c, David J. Winter^d

Manuscript PALAEO7348

REVISION NOTES

Editor's comments	Authors' Response
This is a nice piece of work, well written and well referenced (although I think there are too many references for the length of the text: the reference list is almost as long as the main text!). Both reviewers enjoyed the ms, and they have only very limited comments.	Thank you. We set out to review this area in depth, which is why there are so many references. There is not, to our knowledge, any other paper that puts this body of literature together. So we think it's justified.
I believe Stephen Grasby's point on adding some lines to explain the relevance of chapter 5.2 is a good one.	We have added some text to the paragraph that begins on line 259 to assist with that.
His suggestion to add some photos is also good. But I let the authors decide on that last issue.	Since we don't have any very good photos, we have not added any.
I guess you can also change the acknowledgements, both reviewers not being anonymous.	Done, see paragraph that begins on line 416.
Reviewer #1	
This is an excellent paper on the biomineralogy of calcareous sponges. This paper is of interest to all biologists, paleobiologists and geochemistry researchers working on ocean acidification problems. I strongly recommend rapid publication of this important paper in its present form.	This comment made our days!
Reviewer #2	
This manuscript addresses elements of the critical issue of ocean acidification. Specifically the MS examines the impact on calcifying sponges, making the point that not all sponges will be survivors in an acid ocean world as commonly stated. It provides some important clarity on how this group will be impacted.	Thank you.
Overall the MS is well written and one of the better edited MS I have reviewed for quite awhile (many thanks to the authors!). It would be worth publication with moderate (but easy) revision.	But we have corrected some small errors on lines: 12, 19, 124, 156, 273, 316, 317, 362.
My only main concern is Section 5.2 that	We have added some text to the

<p>has extensive discussion on the origin of calcifying sponges from the rock record. While interesting it seems out of place and it's not clear how it supports the main focus on modern sponges. I think it could easily be deleted. Either that or it needs to be made clearer how it contributes to the overall goal of the work.</p>	<p>paragraph that begins on line 259 to assist with that.</p>
<p>It might be nice to also add some photos of the specimens they discuss.</p>	<p>See comment above</p>
<p>Otherwise the authors might find interesting our work showing Late Permian sponges occupied and dominated shallow shelf environments as carbonate producers declined due to ocean acidification (Beauchamp and Grasby, 2012, Paleo3). So at least the siliceous ones could end up ruling the seas.</p>	<p>Citation added on line 62, and reference on line 441</p>

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

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17 **Abstract**

18 Most marine sponges precipitate silicate skeletal elements, and it has been predicted that they
19 would be among the few “winners” among invertebrates in an acidifying, high-CO₂ ocean.
20 But members of Class Calcarea and a small proportion of the Demospongiae have calcified
21 skeletal structures, which puts them among those calcifying organisms which are vulnerable
22 to lowered pH and CO₃⁻ availability. A review of carbonate mineralogy in marine sponges
23 (75 specimens, 32 species), along with new data from New Zealand (42 specimens in 15
24 species) allows us to investigate patterns and make predictions. In general sponges show little
25 variability within individuals and within species (+/- 0.5 wt% MgCO₃ in calcite). Extant
26 sponges in Class Calcarea generally produce calcitic spicules with relatively high Mg
27 contents, up to 15 wt% MgCO₃. Whereas most of the calcifying demosponges are aragonitic,
28 the genus *Acanthochaetetes* in the Hadromerida produces extremely high-Mg calcite (14 to 18
29 wt% MgCO₃). There is generally a weak phylogenetic consistency among classes, orders and
30 families. Statistical analyses, including those accounting for these phylogenetic effects, fail to
31 find a substantial or significant effect of water temperature on mineralogical variation. In the
32 context of global ocean acidification, sponges which produce high-Mg calcite and/or
33 aragonite will be most vulnerable to dissolution, meaning that not all sponges will be
34 “winners” in a high-CO₂ ocean.

35 **Keywords:** sponges; Porifera; ocean acidification; calcite; aragonite; skeletal biomineralogy

36 **Highlights**

- 37 Calcifying sponges show a range of mineralogies from high-Mg calcite to aragonite.
- 38 Association between phylogeny and mineralogy undercuts environmental correlations.
- 39 Sponges producing high-Mg calcite/aragonite will not be “winners” in high-CO₂ seas.

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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 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; 2103).

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

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3 64 known species (van Soest et al., 2012). Naturally, most biomineralisation research on sponges
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5 65 has been focused on silicification, and carbonate mineralogy has been studied little or not at
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7 66 all. Here we review and add to the data on carbonate mineralogy of calcifying sponges,
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9 67 investigating patterns of calcification and what they will mean in a high-CO₂ ocean.
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11 68 **2. Mineralisation in Sponges**

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15 69 Most marine sponges (Phylum Porifera) create a structural framework from a network of
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17 70 spicules in a range of morphologies, made of silica or calcium carbonate. These spicules can
18
19 71 be simple or complex, with megascleres normally up to 0.5 mm long (though some unusual
20
21 72 glass sponges have spicules 3 m in length) and tiny microscleres up to 100 µm long (Wang et
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23 73 al., 2008). Some groups also fuse spicules together with silica (dictyonine hexactinellids) or
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25 74 CaCO₃ cement (Uriz, 2006), or have complex interlocking terminations to the spicules
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27 75 ('lithistids'). Members of a small subgroup of calcisponges (*sensu* Wörheide, 2008)
28
29 76 precipitate massive calcium carbonate skeletons, sometimes accompanied by silicate or
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31 77 calcareous spicules. These calcifying sponges are characteristic of, though not restricted to,
32
33 78 temperate cryptic and deep-water environments.
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35
36 79 The phylum Porifera is divided into five classes, of which four are extant (Debrenne et al.,
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38 80 2002; Gazave et al., 2010, 2012) comprising over 8000 species (Van Soest et al., 2012). Of
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40 81 these, only about 675 species are known to be calcifying, found in Classes Calcarea and
41
42 82 Demospongiae (Voigt et al., 2012). Calcarea (about 600 described species) are generally
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44 83 small (less than 10 cm in height although some species can grow much larger), found in
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46 84 shallow marine waters, and most produce calcareous spicules which act as single crystals of
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48 85 more-or-less impure calcite (Ledger and Jones, 1977). The demosponges (over 6000 species
49
50 86 described) are heterogeneous biomineralisers. They may have siliceous spicules and/or a
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52 87 fibrous skeleton or no skeleton at all, or they may have solid calcitic or siliceous skeletons
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3 88 which include the ‘sclerosponges’, ‘sphinctozoans’ and the ‘lithistids’. The polyphyletic
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5 89 coralline sclerosponges produce massive skeletons of aragonite or magnesium calcite
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7 90 (Hartman and Goreau, 1975). These coralline sponges are "living fossils," with convergent
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9 91 architectures similar to Paleozoic and Mesozoic reef-building stromatoporoids, chaetetids,
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11 92 sphinctozoans, and inozoans (Wood, 1990). Systematic relationships among them and their
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13 93 position within the classification of recent sponges are controversial (Mastandrea and Russo,
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15 94 1995).

16
17 95 In addition to aragonite or magnesium calcite, two demosponges (*Dysidea crawshayi* and
18
19 96 *Halichondria moorei*) have been found to precipitate spicules formed from a potassium
20
21 97 fluorosilicate mineral called Hieratite (K_2SiF_6 ; Gregson et al., 1979). Several keratose
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23 98 demosponges produce granules of the iron oxide Lepidocrocite ($FeO(OH)$; Towe and Rützler,
24
25 99 1968). Amorphous calcium carbonate, which is non-crystalline and unstable under ambient
26
27 100 conditions and therefore hard to detect, is also found in some sponge spicules (Aizenberg et
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29 101 al., 1996, 2003), but may only be a pre-cursor to calcite formation as in some other taxa.
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31 32 102 **3. Methods and materials**

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35 103 A comprehensive literature review on carbonate mineralogy in the Porifera (examining over
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37 104 50 papers and books) has uncovered 75 sponge specimens in 32 extant species for which
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39 105 carbonate mineralogy has been described (see supplementary data on-line for details). Among
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41 106 them, only 42 specimens are accompanied by quantitative data. Most authors have made
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43 107 qualitative comments on sponge mineralogy, usually in passing, without a statement of
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45 108 methodology, precision, or significance. These qualitative statements are difficult to interpret,
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47 109 but here we assume that “Mg calcite” is roughly in the range of 4 to 8 wt% $MgCO_3$
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49 110 (equivalent to intermediate Mg calcite *sensu* Smith et al., 2006) and “high Mg calcite” is
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51 111 greater than about 8 wt% $MgCO_3$.

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3 112 In too many cases, sponge mineralogy in the literature is reported without reference to
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5 113 specimen location, number of specimens, or methodology employed. The geographical
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7 114 distribution of the 50 or so specimens for which study location is known is limited: most of
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9 115 the specimens (22) are from the UK and Mediterranean, with 14 from the Caribbean, 11
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11 116 specimens are from the tropical Indopacific, and one from the south Atlantic. No
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13 117 mineralogical data are published from the western North Atlantic, from the North Pacific,
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15 118 from any polar region, or south of 23°S. Though all the material requires more replication and
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17 119 a wider spread of species, a mineralogical study of sponge carbonate from southern temperate
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19 120 regions, in particular, needs to be done.
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22 121 Twenty-nine specimens of five species of calcareous sponges were collected by hand from
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24 122 shallow waters around Wellington, New Zealand, and a further nine specimens from more
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26 123 southern localities were selected from the reference collection at Portobello Marine
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28 124 Laboratory, [Dunedin, New Zealand](#). Sponge individuals were cleaned and inspected and all
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30 125 non-sponge carbonate was removed. They were divided into thirds, and voucher specimens
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32 126 were kept and stored in ethanol at the Otago University, Dunedin, New Zealand. One
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34 127 subsample of each sponge was dissected for identification (to genus level). The other third
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36 128 was immersed in 5% bleach for three days to remove organic material. One particularly large
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38 129 specimen was divided into five replicate subsamples, so that a total of 42 specimens were
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40 130 prepared for X-ray diffractometry (XRD).
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43 131 Each bleached slurry of spicules was rinsed several times in distilled water, ground fine while
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45 132 wet in an agate mortar along with 0.1 g NaCl as an internal XRD standard, spread out on a
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47 133 glass slide and dried. Each slide was run through a Phillips X-ray diffractometer at 50 counts
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49 134 per degree with a count time of 1 sec, over the range of 26 to 33 °2θ. Peak heights (in counts)

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3 135 and positions (in °2θ) were determined, the halite peak position was standardized to 31.72
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5 136 °2θ, and other peak positions corrected.
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8 137 Weight percent Mg in calcite was calculated from calcite peak position (in °2θ) using a
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10 138 machine-specific calibration ($y = 30x - 882$). Each spectrum was visually inspected as well,
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12 139 and locations of ragged peaks were confirmed by eye. Relative peak height counts (ht) of
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14 140 aragonite (A1 at 26.213 °2θ and A2 at 27.216 °2θ) and calcite (C1 at 29.4 to 29.8 °2θ) were
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16 141 used to calculate Peak Height Ratio (PR) for each graph: $PR = (ht\ A1 + ht\ A2)/(ht\ A1 + ht\ A2$
17
18 142 $+ ht\ C1)$. Wt% calcite was calculated using the calibration of Gray and Smith (2004): $Wt\%$
19
20 143 $Calcite = 80.4 (PR)^2 - 180.9 (PR) + 101.2$. This method assumes that only calcite and
21
22 144 aragonite are present in the skeletal carbonate.
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24
25 145 A combined dataset (comprising mineralogy reported in the literature alongside our own new
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27 146 results) was used to examine whether variation in water temperature can explain
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29 147 mineralogical variation in these sponges. For each specimen from which the location was
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31 148 known or could be deduced (n=89), mean sea surface temperature was extracted from the
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33 149 NOAA Optimum Interpolation Sea Surface Temperature (Reynolds et al., 2002). The
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35 150 relationship between mineralogy and water temperature was then explored using generalized
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37 151 linear mixed models (GLMMs). Specifically, models with wt% MgCO₃ as a response variable
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39 152 and sea surface temperature as fixed predictor variable were fitted using the R (R
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41 153 Development Core Team, 2012) package MCMCglmm (Hadfield, 2010). As these data are
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43 154 drawn from an evolutionary diverse range of species, taxonomic and, where possible,
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45 155 phylogenetic effects were included as random effects in the GLMMs using the phylogeny
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47 156 presented by Voigt et al. (2012) and taxonomic information retrieved from Worlds Register
48
49 157 of Marine Species (<http://www.marinespecies.org/>)
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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 variability 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 different types of spicules rather than truly random replication. 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

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3 182 7.6 wt% MgCO₃ (Jones and Jenkins, 1970); and *Leuconia nivea* from Menai Strait, UK
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5 183 ranged from 8.6 to 9.7 wt% MgCO₃ (Jones and Jenkins, 1970). Five replicate subsamples
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7 184 from a single large specimen of *Clathrina* sp. 2 (small, yellow) from Breaker Bay, near
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9 185 Wellington, 5 m water depth, were all 100% calcite, with Mg content ranging from 11.7 to
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11 186 12.5 wt% MgCO₃ (mean = 12.1; standard deviation = 0.3 wt% MgCO₃, N = 5). This small
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13 187 degree of variation within an individual suggests that variability within species is on the order
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15 188 of +/- 0.5 wt% MgCO₃.

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18 189 There are only three species for which we have measurements of more than 10 specimens;
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20 190 they range from quite consistent to remarkably variable. All ten specimens of the Caribbean
21
22 191 sponge *Ceratoporella nicholsoni* are aragonitic (Hartman and Goreau, 1970; Schumacher and
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24 192 Plewka, 1981; Willenz and Hartman, 1989; Wood, 1991; Bøhm et al., 2000; Rosenheim et al.,
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26 193 2005). Our own data show that calcitic *Clathrina* sp. 2 from central New Zealand has a range
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28 194 of 2.5 wt% MgCO₃ (10.6 to 13.1, mean = 12.0, standard deviation = 0.7 wt% MgCO₃, N =
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30 195 12). A calcitic species of *Sycon* from the eastern Mediterranean has one individual that
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32 196 registered no Mg content, but all the other specimens range from 9.9 to 11.7 wt% MgCO₃
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34 197 (mean = 11.1, standard deviation = 0.5 wt% MgCO₃, N = 9) (Aizenberg et al., 1995a, b). If
35
36 198 we assume that the outlier represents some kind of sampling or measurement anomaly, then
37
38 199 within-species variability in Mg ranges from almost none to about +/- 1.0 wt% MgCO₃. This
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40 200 means that single-specimen measurements are probably reasonably accurate estimates of the
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42 201 mineralogy of the whole species.

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45 202 In each of these cases, specimens are necessarily aggregates of many spicules, and thus the
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47 203 variability among spicules may be greater than that detected using X-ray diffractometry. A
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49 204 higher-resolution technique such as Raman spectroscopy might elucidate details of within-
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51 205 and among-spicule variation.

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3 206 5.2. *Phylomineralogy and evolution of mineralogy in sponges*
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6 207 There is a phylogenetic overprint to mineralogy in Phylum Porifera, with fairly consistent
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8 208 class-to-order level distribution among those species so far studied (Table 2). Calcareous
9
10 209 sponges are largely restricted to Class Calcarea. Class Homoscleromorpha as well as the
11
12 210 Silicea clade containing Classes Demospongea and Hexactinellida are dominated by
13
14 211 silicifying sponges. Only one hexactinellid sponge *Caulophacus* has been found to mineralize
15
16 212 calcite (Ehrlich et al., 2011). Calcification is only a little more common in the demosponges.
17
18
19 213 Only 12 species representing five of the 16 demosponge orders are known to precipitate
20
21 214 carbonate in their basal skeletons (Table 2). Although it is not clear how many demosponges
22
23 215 are calcifiers, the overall coverage in these “sclerosponges” is barely adequate to allow for
24
25 216 generalisations to be made. Most specimens have entirely aragonitic basal skeletons. In the
26
27 217 Poecilosclerida, the basal skeleton of *Merlia lipoclavidisca* is entirely aragonitic (Vacelet and
28
29 218 Uriz, 1991), but the basal skeleton of another *Merlia* sp. was found to be low-Mg calcite
30
31 219 (Wood, 1991), as are the spherules found in the silica-producing *Hemimycale columella*. It is
32
33 220 possible that this particular order has a higher degree of mineralogical flexibility than others
34
35 221 in the Porifera or as discussed below, calcification has polyphyletic origins in the
36
37 222 demosponges (Chombard et al., 1997). Unfortunately, with no replication, there is little to
38
39 223 constrain the competing hypotheses.

40
41
42 224 *Acanthochaetetes* and *Willardia* are the only extant genera within the Acanthochaetetidae
43
44 225 family (order Hadromerida). *Acanthochaetetes* spp. are known to produce extremely high-Mg
45
46 226 calcite (14 to 18 wt% MgCO₃) compared with *Willardia caicosensis* which has an aragonite
47
48 227 basal skeleton. Do these distinct mineralogical compositions within the same family reflect a
49
50 228 different biomineralizing evolutionary path within this family?

51
52 229 Calcification of secondary and basal skeletons is known from only a few demosponge orders
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3 230 (and phylogenetic arguments continue as to their correct placement), of which we record five.
4
5 231 The Agelasida, Haplosclerida, Poecilosclerida, and Verticillitida (or perhaps Dictyoceratida
6
7 232 after Wörheide, 2008) comprise 42 families with about 230 genera (Van Soest et al., 2012).
8
9 233 Most of the species for which mineralogy is known in these orders form massive secondary
10
11 234 skeletons of aragonite, though they can hardly be considered 'typical', as they represent less
12
13 235 than 4% of known genera in the class. *Hemimycale columella* (Poecilosclerida) is unusual in
14
15 236 producing silica spicules and calcareous spherules. These spherules are formed of very low
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17 237 Mg calcite (Vacelet et al., 1987).
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20 238 Within the order Hadromerida there is one family, the Acanthochaetetidae, known to have
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22 239 calcified basal skeletons; in that family, *Willardia caicosensis* is anomalous in that it produces
23
24 240 a basal aragonite skeleton (Willenz and Pomponi, 1996) and the genus *Acanthochaetetes*
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26 241 precipitates very high Mg calcite (12 to 19.9 wt% MgCO₃) in its basal skeleton according to
27
28 242 Reitner and Engeser (1987), the highest recorded in the phylum. As the record for
29
30 243 *Acanthochaetetes* is based on six specimens any general statement on mineralogy in this
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32 244 group should be considered provisional.
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35 245 In Class Calcarea, all spicules measured (14 genera, 19 species, 42 specimens) have been
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37 246 found to be formed of calcite, with no aragonite present. The lowest Mg content reported was
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39 247 4.3 wt% MgCO₃ in *Sycon ciliatum* (Jones and Jenkins, 1970), but most of the specimens
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41 248 showed Mg content greater than 6 wt% MgCO₃. The highest Mg content found was 15.6 wt%
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43 249 MgCO₃ in *Kebira uteoides* (Aizenberg et al., 1995a). Mean Mg content for the class is 9.6
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45 250 wt% MgCO₃.
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48 251 Even though only 34 of the ~500 described extant sponges in Class Calcarea have been tested
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50 252 for carbonate mineralogy, at least one species from each of the five orders is represented here
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52 253 (Table 2). Though a few specimens show a small amount of aragonite, in general these

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3 254 sponges produce calcitic spicules. Mg content are usually high, up to 15 wt% MgCO₃. Two
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5 255 orders, the Lithonida and the Murryonida, appear to incorporate less Mg in their skeletal
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7 256 carbonate than other orders, but both taxa are represented by only one or two analyses;
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9 257 therefore further work in these groups would be fruitful.

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12 258 Both calcification and silicification are important in sponges, ~~though which came first is the~~
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14 259 ~~subject of some debate when analyzing the fossil record and molecular data. Which came~~
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16 260 ~~first, a subject of some debate, affects the subsequent distribution of skeletal composition in~~
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18 261 ~~the various clades with their different synapomorphic mineralogies.~~ There are three
19
20 262 competing hypotheses for the phylogenetically primitive biomineralization state of the
21
22 263 sponges. Below we compare paleontologic and neontologic evidence for silica-first, calcite-
23
24 264 first, and biomineral-first hypotheses.

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27 265 Xiao et al. (2005) suggested that both fossil and molecular data indicate silicification evolved
28
29 266 first. Molecular clock data based on a paraphyletic Phylum Porifera suggest that the origin of
30
31 267 silica biomineralizing sponges occurred by 759 Ma (Sperling et al., 2010). This is close to the
32
33 268 age of the oldest reported siliceous spicules with demosponge affinities from the Late
34
35 269 Proterozoic, ~750 Ma (Reitner and Wörheide, 2002). By 635 Ma, there is biomarker
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37 270 evidence suggestive of demosponges in pre-Marinoan rocks (Love et al., 2009), but there is
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39 271 disagreement on the interpretation of such biomarkers (Brocks and Butterfield, 2009). Li et al.
40
41 272 (1998) discovered fossil cellular tissue of sponges and demosponge-like monaxonid siliceous
42
43 273 spicules from the Ediacaran, ~580 Ma. Siliceous spicules assigned to the hexactinellids are
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45 274 known from the upper Ediacaran (549-543 Ma) (Brasier et al., 1997).

46
47 275 Alternatively, sponges may have originally been calcareous (Ehrlich et al., 2011). The
48
49 276 evidence for the primitive biomineralization state in sponges being calcareous comes from the
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51 277 fact that no examples of siliceous spicules have been found in Class Calcarea, but calcareous
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53 278 skeletal elements have been discovered in both classes in the Silicea clade (Ehrlich et al.,

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3 279 2011). Philippe et al. (2009) and Pick et al. (2010) have argued that sponges are monophyletic
4
5 280 and the Silicea are not the most primitive clade in the phylum. The fossil record sheds little
6
7 281 light on this. The first metazoan calcifiers of possible poriferan affinity (i.e., *Namapoikia*)
8
9 282 were from the late Neoproterozoic, ~549 Ma (Wood et al., 2002). This 200 Myr gap between
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11 283 the first siliceous sponge fossils and the first calcareous ones could simply be an artifact of
12
13 284 the preservation potential of silica versus calcite. Putative calcareans have been reported from
14
15 285 the Early Cambrian Tommotian Stage, <542 Ma (Kruse et al., 1995). The oldest calcareans
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17 286 with preserved mineralogy are not until the Silurian, <444 Ma (Mehl and Reitner, 1996). The
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19 287 oldest preserved aragonitic sponges are the demosponges from the Upper Triassic, 217-204
20
21 288 Ma (Senowbari and Link, 2011).
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24 289 From the Cambrian onwards and for much of the Paleozoic and Mesozoic, calcareous sponges
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26 290 such as archaeocyathids and stromatoporoids were dominant reef-builders, and their skeletons
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28 291 form important components of marine sediments from those times (Fagerstrom, 1987).
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30 292 Assuming members of the extinct Class Archaeocyathida were actual sponges and not just
31
32 293 functional equivalents (Debrenne et al., 2002, Debrenne, 2006), then the first large-scale
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34 294 calcitic, reef-forming sponges appear at the start of the Tommotian, ~525 Ma (Maloof et al.,
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36 295 2010a) but possibly as early as the Namakit-Daldynian, 530 Ma (Wood, 1999, Rowland and
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38 296 Shapiro, 2002; Maloof et al., 2010b). Regardless, they were extinct by the Middle Cambrian
39
40 297 (Debrenne et al., 2002). Stromatoporoids were sponge-like animals with hypercalcified
41
42 298 layered skeletons. They have been variously referred to as calcifying demosponges,
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44 299 calcareans, or simply a polyphyletic grade of sponge construction (Wood, 1987; Stearn et al.,
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46 300 1999; Cook, 2002; Cuif et al., 2011; Da Silva et al., 2011). They were important Ordovician
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48 301 to Cretaceous reef-builders, especially in the Silurian and Devonian (Fagerstrom, 1987;
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50 302 Wood, 1987, 1999). The Paleozoic stromatoporoids were likely a different clade from the
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52 303 Mesozoic species which are related to the extant sclerosponges in Class Demospongea
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3 304 (Reitner and Wörheide, 2002).
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6 305 With the molecular debate over the monophyly (Philippe et al., 2009; Pick et al., 2010) or
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8 306 paraphyly (Borchiellini et al., 2001; Sperling et al., 2010) of the sponges not resolved, Botting
9
10 307 et al. (2012) have recently argued that the primitive state of the sponges is neither siliceous or
11
12 308 calcareous, but bimineralic (i.e., containing spicules of both SiO₂ and CaCO₃), ~~because t-~~ because t- ~~This~~
13
14 309 ~~is based on~~ the Early Cambrian sponge *Lenica* (Goryanskiy, 1977) ~~which~~ was inferred,
15
16 310 despite diagenetic problems, to have originally contained bimineralic spicules (Botting et al.,
17
18 311 2012). Botting et al. (2012) hypothesized that sponges were originally bimineralic and silica
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20 312 biomineralization was later lost in Class Calcarea and calcite biomineralization was
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22 313 subsequently lost in Class Homoscleromorpha as well as the Silicea clade containing Classes
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24 314 Demospongea and Hexactinellida. If this is the case, then the rare occurrences of calcification
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26 315 in the dominantly siliceous Classes Demospongea and Hexactinellida had to evolve
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28 316 independently again. This conclusion is required by the well-documented calcitic and
29
30 317 aragonitic sclerosponges in Class Demospongea (Table 1) and the recent discovery of calcite
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32 318 in the hexactinellid sponge *Caulophacus* (Ehrlich et al., 2011), and supported by the
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34 319 ribosomal sequence data of Chombard et al. (1997) that suggests that the calcareous skeleton
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36 320 evolved independently in several lineages of sponges. More data, like this study, on
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38 321 mineralogy across the sponges will allow for improved understanding of the phylomineralogy
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40 322 of this important invertebrate phylum, among the first to biomineralize.
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42 323 Wood (1991) and Cuif et al. (2011) suggested that the history of carbonate mineralogy among
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44 324 sponges reflects secular patterns in sea-water chemistry (e.g., Stanley and Hardie, 1998).
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46 325 Wood (1991) noted that calcifying sponges formed reefs and were more abundant in times of
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48 326 “calcite seas” (Ordovician to Devonian, then again in the Jurassic to Cretaceous). She also
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50 327 suggested that carbonate mineralogy is not a useful character for delineating taxa. There are,
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52 328 however, not enough mineralogic and/or phylogenetic data to rigorously test this hypothesis.

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329 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 & Jenkins, 1970). When Mg content is plotted against water temperature from our data, there is an apparent trend of increasing Mg with warmer water (Figure 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 our data comes from the temperate seas around New Zealand where 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 ~~which that~~ may have limited the statistical power of our analyses.

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3 354 One possible influence on skeletal mineralogy could be the ontogenetic stage of the sponge
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5 355 when collected. No author commented on “age” of the sponge collected, nor on the growth
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7 356 rate, and we made no attempt to characterise age or growth in our collections. It is sometimes
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9 357 noted in high-Mg biogenic calcites that Mg content is strongly related to growth rate (e.g.
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11 358 Kolesar, 1978). The lack of consistency around age of specimen and possibly thus growth
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13 359 rate could obscure other signals in mineralogy. Ideally, comparison of laboratory-grown
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15 360 specimens of similar ages would allow for a more precise understanding of influences on
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17 361 skeletal mineralogy, particularly in regard to temperature and other environmental effects.
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20 362 *5.4 Calcareous sponges in a high-CO₂ world*

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23 363 Increasingly, studies of organisms’ responses to ocean acidification have described “winners
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25 364 and losers” in a high-CO₂ ocean. Such studies have relied, at least in part, on skeletal
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27 365 mineralogy to help predict outcomes. Thus silica producers such as diatoms and sponges have
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29 366 been listed among the “winners”, who stand ready to inhabit the vacant niches left by their
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31 367 more soluble carbonate neighbours. It has been common to use sweeping generalisations
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33 368 about mineralogy within taxa, including among the sponges. But a substantial subset of the
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35 369 Porifera are calcareous, and many of them will be vulnerable to projected lowered pH and
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37 370 carbonate availability.
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40 371 This paper demonstrates that there is both within-specimen and within-species variability of
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42 372 wt% MgCO₃ in calcite (and to a lesser extent, variability with respect to aragonite:calcite
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44 373 ratio). Even more variation occurs within higher taxa. This degree of variability calls into
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46 374 question the practice of classifying taxa, maybe even species, in particular mineralogical
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48 375 types. If our generalisations about taxa are over-simplified, it may be that broad-scale
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50 376 inferences about calcite and aragonite seas and the successes of high-Mg vs. low-Mg taxa (see
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52 377 e.g. Stanley and Hardie, 1998, 1999; Zhuravlev and Wood, 2009) are not entirely justified.
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3 378 Among the most vulnerable to ocean acidification will be aragonite and high-Mg calcite
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5 379 skeletons (Smith, 2009), such as those formed by many calcifying sponges. And it is in
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7 380 southern temperate-to-polar waters that ocean acidification will be felt first (Andersson et al.,
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9 381 2008). Species reported on here that are most at risk are the shallow-water species found in
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11 382 cool-to-cold waters, especially in the Southern Hemisphere.

14 383 **6. Conclusions**

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17 384 We report here on 116 measurements of skeletal carbonate mineralogy in the sponges,
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19 385 encompassing 46 species in 24 genera, a small percentage of the 650 species known to
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21 386 calcify. Calcifying sponges are usually formed from aragonite or calcite with Mg substitution
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23 387 of about 4 to 16 wt% MgCO₃. We report here on the first measurements to show that some
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25 388 dominantly calcitic skeletons may contain appreciable amounts of aragonite.

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28 389 Variability within-specimens and within-species of wt% MgCO₃ in calcite is on the order of
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30 390 +/- 0.5 wt% MgCO₃. There is, in general, less variability with respect to aragonite: calcite
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32 391 ratio. There are broad mineralogical patterns in the higher taxa, and it is often possible to
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34 392 classify taxa into particular mineralogical types. There are exceptions: the archaeocyath
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36 393 sponges, for example, are usually described as having high-Mg calcite skeletons, but our
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38 394 results suggest that the group might be more variable.

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40 395 The strong degree of phylogenetic consistency at higher taxonomic levels calls into question
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42 396 the common assumptions regarding phenotypic expression of mineralogy. When the
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44 397 phylogenetic component is removed, we are unable to find a correlation between, for
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46 398 example, mineralogy and latitude.

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49 399 In a high-CO₂ world, many sponges may be “winners”, but the calcareous sponges may not be
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51 400 among them. High-Mg calcite and aragonite are the most soluble forms of CaCO₃, and most

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of the sponges reported here live in the shallow temperate regions where saturation levels are predicted to fall the most rapidly. Deeper-water sponges may be isolated from lowering pH effects for some time.

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46 47 48 683 **9. Figure and Table Captions**

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51 684 Figure 1: Skeletal carbonate mineralogy of 74 extant specimens of the phylum Porifera; 28
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3 685 are from the literature (Lister, 1900; Clarke and Wheeler, 1922; Vinogradov, 1953;
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5 686 Jones and James, 1969; Jones, 1970; Jones and Jenkins, 1970; Schuhmacher and
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7 687 Plewka, 1981; Reitner and Engeser, 1987; Willenz and Hartman, 1989; Cuif and
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9 688 Gautret, 1991; Ledger and Jones, 1991; Reitner, 1991; Vacelet and Uriz, 1991;
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11 689 Wood, 1991; Reitner and Gautret, 1996; Aizenberg et al., 1995a, b, 1996, 2003;
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13 690 Bøhm et al., 2000; Fallon et al., 2004; Rosenheim et al., 2005; Wombacher et al.,
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15 691 2005; Rossi et al., 2006; Sethmann et al., 2006; Uriz, 2006), whereas the remaining
16
17 692 42 are new data from New Zealand. See Supplementary Data for details.
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20 693 Figure 2: There is little relationship between water temperature (approximated by mean sea
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22 694 surface temperature) and Mg content in calcite (top) or overall calcite percentage
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24 695 (bottom) in skeletal carbonate of calcifying sponges. Trend lines are following
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26 696 linear regression, with shaded areas representing 95% confidence intervals. For the
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28 697 calcite data, the regression was performed on logit-transformed data to account for
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30 698 the fact this variable is bounded at 0 and 100%.

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32
33 699 Table 1: Skeletal carbonate mineralogy of 46 extant species of calcifying sponges,
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35 700 recalculated to standard units. Taxonomy follows van Soest et al. (2012). See
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37 701 Supplementary Data on-line for details.
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40 702 Table 2: Carbonate mineralogy of extant higher taxa of calcifying sponges as reported in the
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42 703 literature (see references in Table 1) and determined here for specimens from New
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44 704 Zealand. Taxonomy follows van Soest et al. (2012).
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49 706 Supplementary Data: Skeletal carbonate mineralogy of the extant Porifera: data from the
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51 707 literature and new analyses from New Zealand.
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1 Not all sponges will thrive in a high-CO₂ ocean: Review of the
2 mineralogy of calcifying sponges

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16

17 **Abstract**

18 Most marine sponges precipitate silicate skeletal elements, and it has been predicted that they
19 would be among the few “winners” among invertebrates in an acidifying, high-CO₂ ocean.
20 But members of Class Calcarea and a small proportion of the Demospongiae have calcified
21 skeletal structures, which puts them among those calcifying organisms which are vulnerable
22 to lowered pH and CO₃⁼ availability. A review of carbonate mineralogy in marine sponges
23 (75 specimens, 32 species), along with new data from New Zealand (42 specimens in 15
24 species) allows us to investigate patterns and make predictions. In general sponges show little
25 variability within individuals and within species (+/- 0.5 wt% MgCO₃ in calcite). Extant
26 sponges in Class Calcarea generally produce calcitic spicules with relatively high Mg
27 contents, up to 15 wt% MgCO₃. Whereas most of the calcifying demosponges are aragonitic,
28 the genus *Acanthochaetetes* in the Hadromerida produces extremely high-Mg calcite (14 to 18
29 wt% MgCO₃). There is generally a weak phylogenetic consistency among classes, orders and
30 families. Statistical analyses, including those accounting for these phylogenetic effects, fail to
31 find a substantial or significant effect of water temperature on mineralogical variation. In the
32 context of global ocean acidification, sponges which produce high-Mg calcite and/or
33 aragonite will be most vulnerable to dissolution, meaning that not all sponges will be
34 “winners” in a high-CO₂ ocean.

35 **Keywords:** sponges; Porifera; ocean acidification; calcite; aragonite; skeletal biomineralogy

36 **Highlights**

37 Calcifying sponges show a range of mineralogies from high-Mg calcite to aragonite.

38 Association between phylogeny and mineralogy undercuts environmental correlations.

39 Sponges producing high-Mg calcite/aragonite will not be “winners” in high-CO₂ seas.

40

41 **1. Introduction**

42 Recent advances clarifying the interactions between atmospheric CO₂, the carbonate system
43 in sea water, and marine calcifying organisms (Raven et al., 2005) have led to a great deal of
44 new research on marine calcification and marine carbonates. While biologists and ecologists
45 have examined the effect of lowered-pH sea water on development and survival of marine
46 organisms (e.g., Clark et al., 2009; Ries, 2011), geochemists have begun to consider
47 dissolution and, in particular, the effects of skeletal carbonate mineralogy on susceptibility to
48 dissolution (e.g., Andersson et al., 2008; Gehlen et al., 2008). In the course of this research, it
49 has become clear that, in many taxa, we know far too little about patterns of carbonate
50 mineralogy, and that the generalisations commonly made about particular taxa turn out to be
51 less than accurate when detailed data are examined (e.g., Smith et al., 2006; 2103).

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

59 At first glance it seems that sponges might well thrive in low-pH waters (e.g., Wisshak et al.,
60 2012). Most of them are siliceous and would presumably be able to take advantage of
61 ecological niches that were once occupied by, for example, coralline algae and/or bryozoans
62 (as has occurred in the past, see Beauchamp and Grasby, 2012). But not all sponges are
63 siliceous: about 8% of sponge species are calcifying (Uriz, 2006), some 650 of the over 8000

64 known species (van Soest et al., 2012). Naturally, most biomineralisation research on sponges
65 has been focused on silicification, and carbonate mineralogy has been studied little or not at
66 all. Here we review and add to the data on carbonate mineralogy of calcifying sponges,
67 investigating patterns of calcification and what they will mean in a high-CO₂ ocean.

68 **2. Mineralisation in Sponges**

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

79 The phylum Porifera is divided into five classes, of which four are extant (Debrenne et al.,
80 2002; Gazave et al., 2010, 2012) comprising over 8000 species (Van Soest et al., 2012). Of
81 these, only about 675 species are known to be calcifying, found in Classes Calcarea and
82 Demospongiae (Voigt et al., 2012). Calcarea (about 600 described species) are generally
83 small (less than 10 cm in height although some species can grow much larger), found in
84 shallow marine waters, and most produce calcareous spicules which act as single crystals of
85 more-or-less impure calcite (Ledger and Jones, 1977). The demosponges (over 6000 species
86 described) are heterogeneous biomineralisers. They may have siliceous spicules and/or a
87 fibrous skeleton or no skeleton at all, or they may have solid calcitic or siliceous skeletons

88 which include the ‘sclerosponges’, ‘sphinctozoans’ and the ‘lithistids’. The polyphyletic
89 coralline sclerosponges produce massive skeletons of aragonite or magnesium calcite
90 (Hartman and Goreau, 1975). These coralline sponges are "living fossils," with convergent
91 architectures similar to Paleozoic and Mesozoic reef-building stromatoporoids, chaetetids,
92 sphinctozoans, and inozoans (Wood, 1990). Systematic relationships among them and their
93 position within the classification of recent sponges are controversial (Mastandrea and Russo,
94 1995).

95 In addition to aragonite or magnesium calcite, two demosponges (*Dysidea crawshayi* and
96 *Halichondria moorei*) have been found to precipitate spicules formed from a potassium
97 fluorosilicate mineral called Hieratite (K_2SiF_6 ; Gregson et al., 1979). Several keratose
98 demosponges produce granules of the iron oxide Lepidocrocite ($FeO(OH)$; Towe and Rützler,
99 1968). Amorphous calcium carbonate, which is non-crystalline and unstable under ambient
100 conditions and therefore hard to detect, is also found in some sponge spicules (Aizenberg et
101 al., 1996, 2003), but may only be a pre-cursor to calcite formation as in some other taxa.

102 **3. Methods and materials**

103 A comprehensive literature review on carbonate mineralogy in the Porifera (examining over
104 50 papers and books) has uncovered 75 sponge specimens in 32 extant species for which
105 carbonate mineralogy has been described (see supplementary data on-line for details). Among
106 them, only 42 specimens are accompanied by quantitative data. Most authors have made
107 qualitative comments on sponge mineralogy, usually in passing, without a statement of
108 methodology, precision, or significance. These qualitative statements are difficult to interpret,
109 but here we assume that “Mg calcite” is roughly in the range of 4 to 8 wt% $MgCO_3$
110 (equivalent to intermediate Mg calcite *sensu* Smith et al., 2006) and “high Mg calcite” is
111 greater than about 8 wt% $MgCO_3$.

112 In too many cases, sponge mineralogy in the literature is reported without reference to
113 specimen location, number of specimens, or methodology employed. The geographical
114 distribution of the 50 or so specimens for which study location is known is limited: most of
115 the specimens (22) are from the UK and Mediterranean, with 14 from the Caribbean, 11
116 specimens are from the tropical Indopacific, and one from the south Atlantic. No
117 mineralogical data are published from the western North Atlantic, from the North Pacific,
118 from any polar region, or south of 23°S. Though all the material requires more replication and
119 a wider spread of species, a mineralogical study of sponge carbonate from southern temperate
120 regions, in particular, needs to be done.

121 Twenty-nine specimens of five species of calcareous sponges were collected by hand from
122 shallow waters around Wellington, New Zealand, and a further nine specimens from more
123 southern localities were selected from the reference collection at Portobello Marine
124 Laboratory, Dunedin, New Zealand. Sponge individuals were cleaned and inspected and all
125 non-sponge carbonate was removed. They were divided into thirds, and voucher specimens
126 were kept and stored in ethanol at the Otago University, Dunedin, New Zealand. One
127 subsample of each sponge was dissected for identification (to genus level). The other third
128 was immersed in 5% bleach for three days to remove organic material. One particularly large
129 specimen was divided into five replicate subsamples, so that a total of 42 specimens were
130 prepared for X-ray diffractometry (XRD).

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

135 and positions (in °2θ) were determined, the halite peak position was standardized to 31.72
136 °2θ, and other peak positions corrected.

137 Weight percent Mg in calcite was calculated from calcite peak position (in °2θ) using a
138 machine-specific calibration ($y = 30x - 882$). Each spectrum was visually inspected as well,
139 and locations of ragged peaks were confirmed by eye. Relative peak height counts (ht) of
140 aragonite (A1 at 26.213 °2θ and A2 at 27.216 °2θ) and calcite (C1 at 29.4 to 29.8 °2θ) were
141 used to calculate Peak Height Ratio (PR) for each graph: $PR = (ht\ A1 + ht\ A2) / (ht\ A1 + ht\ A2$
142 $+ ht\ C1)$. Wt% calcite was calculated using the calibration of Gray and Smith (2004): $Wt\%$
143 $Calcite = 80.4 (PR)^2 - 180.9 (PR) + 101.2$. This method assumes that only calcite and
144 aragonite are present in the skeletal carbonate.

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

158

159 **4. Results**

160 Our literature review provided mineralogical data for 74 sponge specimens in 32 species, and
161 the New Zealand results added 42 specimens in 15 species, for a total of 116 specimens from
162 46 species in 24 genera (Table 1). Most specimens are either 100% calcite or 100% aragonite,
163 with only a few specimens from New Zealand showing combinations of the two (56 to 91
164 wt% calcite, mean = 69 wt% calcite, N = 5). In the calcitic specimens, Mg content showed
165 much more variation, ranging from 0 to 17.3 wt% MgCO₃ (mean = 9.7 wt% MgCO₃, N = 83).

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

168 **5. Discussion**

169 *5.1. Variation within species*

170 The combination of the detailed literature review and the New Zealand specimens gives 116
171 sponge specimens from 46 species in 24 genera (Table 1). Of the 650 or so sponge species
172 which precipitate calcium carbonate, only 5% have been mineralogically characterised, and in
173 most cases they were measured only once. Work in other phyla (e.g., Smith et al., 2006;
174 2012) suggests that variability within and among species requires a more rigorous approach.
175 Any study on sponge mineralogy must address both within-individual and within-species
176 variability before any further progress can be made.

177 Very few sponges have been examined for within-individual variation. In most cases where a
178 single individual was tested several times, it was in order to compare different types of
179 spicules rather than truly random replication. Calcium carbonate spicules in a specimen of
180 *Sycon* sp. from the Eastern Mediterranean varied from 10.7 to 11.7 wt% MgCO₃ (Aizenberg
181 et al., 1995b), whereas those of *Amphiute paulini* from Brittany, France ranged from 6.6 to

182 7.6 wt% MgCO₃ (Jones and Jenkins, 1970); and *Leuconia nivea* from Menai Strait, UK
183 ranged from 8.6 to 9.7 wt% MgCO₃ (Jones and Jenkins, 1970). Five replicate subsamples
184 from a single large specimen of *Clathrina* sp. 2 (small, yellow) from Breaker Bay, near
185 Wellington, 5 m water depth, were all 100% calcite, with Mg content ranging from 11.7 to
186 12.5 wt% MgCO₃ (mean = 12.1; standard deviation = 0.3 wt% MgCO₃, N = 5). This small
187 degree of variation within an individual suggests that variability within species is on the order
188 of +/- 0.5 wt% MgCO₃.

189 There are only three species for which we have measurements of more than 10 specimens;
190 they range from quite consistent to remarkably variable. All ten specimens of the Caribbean
191 sponge *Ceratoporella nicholsoni* are aragonitic (Hartman and Goreau, 1970; Schumacher and
192 Plewka, 1981; Willenz and Hartman, 1989; Wood, 1991; Bøhm et al., 2000; Rosenheim et al.,
193 2005). Our own data show that calcitic *Clathrina* sp. 2 from central New Zealand has a range
194 of 2.5 wt% MgCO₃ (10.6 to 13.1, mean = 12.0, standard deviation = 0.7 wt% MgCO₃, N =
195 12). A calcitic species of *Sycon* from the eastern Mediterranean has one individual that
196 registered no Mg content, but all the other specimens range from 9.9 to 11.7 wt% MgCO₃
197 (mean = 11.1, standard deviation = 0.5 wt% MgCO₃, N = 9) (Aizenberg et al., 1995a, b). If
198 we assume that the outlier represents some kind of sampling or measurement anomaly, then
199 within-species variability in Mg ranges from almost none to about +/- 1.0 wt% MgCO₃. This
200 means that single-specimen measurements are probably reasonably accurate estimates of the
201 mineralogy of the whole species.

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

206 5.2. *Phylomineralogy and evolution of mineralogy in sponges*

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

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

224 *Acanthochaetetes* and *Willardia* are the only extant genera within the Acanthochaetetidae
225 family (order Hadromerida). *Acanthochaetetes* spp. are known to produce extremely high-Mg
226 calcite (14 to 18 wt% MgCO₃) compared with *Willardia caicosensis* which has an aragonite
227 basal skeleton. Do these distinct mineralogical compositions within the same family reflect a
228 different biomineralizing evolutionary path within this family?

229 Calcification of secondary and basal skeletons is known from only a few demosponge orders

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

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

245 In Class Calcarea, all spicules measured (14 genera, 19 species, 42 specimens) have been
246 found to be formed of calcite, with no aragonite present. The lowest Mg content reported was
247 4.3 wt% MgCO₃ in *Sycon ciliatum* (Jones and Jenkins, 1970), but most of the specimens
248 showed Mg content greater than 6 wt% MgCO₃. The highest Mg content found was 15.6 wt%
249 MgCO₃ in *Kebira uteoides* (Aizenberg et al., 1995a). Mean Mg content for the class is 9.6
250 wt% MgCO₃.

251 Even though only 34 of the ~500 described extant sponges in Class Calcarea have been tested
252 for carbonate mineralogy, at least one species from each of the five orders is represented here
253 (Table 2). Though a few specimens show a small amount of aragonite, in general these

254 sponges produce calcitic spicules. Mg content are usually high, up to 15 wt% MgCO₃. Two
255 orders, the Lithonida and the Murryonida, appear to incorporate less Mg in their skeletal
256 carbonate than other orders, but both taxa are represented by only one or two analyses;
257 therefore further work in these groups would be fruitful.

258 Both calcification and silicification are important in sponges,. Which came first, a subject of
259 some debate, affects the subsequent distribution of skeletal composition in the various clades
260 with their different synapomorphic mineralogies. There are three competing hypotheses for
261 the phylogenetically primitive biomineralization state of the sponges. Below we compare
262 paleontologic and neontologic evidence for silica-first, calcite-first, and biomineral-first
263 hypotheses.

264 Xiao et al. (2005) suggested that both fossil and molecular data indicate silicification evolved
265 first. Molecular clock data based on a paraphyletic Phylum Porifera suggest that the origin of
266 silica biomineralizing sponges occurred by 759 Ma (Sperling et al., 2010). This is close to the
267 age of the oldest reported siliceous spicules with demosponge affinities from the Late
268 Proterozoic, ~750 Ma (Reitner and Wörheide, 2002). By 635 Ma, there is biomarker
269 evidence suggestive of demosponges in pre-Marinoan rocks (Love et al., 2009), but there is
270 disagreement on the interpretation of such biomarkers (Brocks and Butterfield, 2009). Li et al.
271 (1998) discovered fossil cellular tissue of sponges and demosponge-like monaxonid siliceous
272 spicules from the Ediacaran, ~580 Ma. Siliceous spicules assigned to the hexactinellids are
273 known from the upper Ediacaran (549-543 Ma) (Brasier et al., 1997).

274 Alternatively, sponges may have originally been calcareous (Ehrlich et al., 2011). The
275 evidence for the primitive biomineralization state in sponges being calcareous comes from the
276 fact that no examples of siliceous spicules have been found in Class Calcarea, but calcareous
277 skeletal elements have been discovered in both classes in the Silicea clade (Ehrlich et al.,
278 2011). Philippe et al. (2009) and Pick et al. (2010) have argued that sponges are monophyletic

279 and the Silicea are not the most primitive clade in the phylum. The fossil record sheds little
280 light on this. The first metazoan calcifiers of possible poriferan affinity (i.e., *Namapoikia*)
281 were from the late Neoproterozoic, ~549 Ma (Wood et al., 2002). This 200 Myr gap between
282 the first siliceous sponge fossils and the first calcareous ones could simply be an artifact of
283 the preservation potential of silica versus calcite. Putative calcareans have been reported from
284 the Early Cambrian Tommotian Stage, <542 Ma (Kruse et al., 1995). The oldest calcareans
285 with preserved mineralogy are not until the Silurian, <444 Ma (Mehl and Reitner, 1996). The
286 oldest preserved aragonitic sponges are the demosponges from the Upper Triassic, 217-204
287 Ma (Senowbari and Link, 2011).

288 From the Cambrian onwards and for much of the Paleozoic and Mesozoic, calcareous sponges
289 such as archaeocyathids and stromatoporoids were dominant reef-builders, and their skeletons
290 form important components of marine sediments from those times (Fagerstrom, 1987).

291 Assuming members of the extinct Class Archaeocyathida were actual sponges and not just
292 functional equivalents (Debrenne et al., 2002, Debrenne, 2006), then the first large-scale
293 calcitic, reef-forming sponges appear at the start of the Tommotian, ~525 Ma (Maloof et al.,
294 2010a) but possibly as early as the Namakit-Daldynian, 530 Ma (Wood, 1999, Rowland and
295 Shapiro, 2002; Maloof et al., 2010b). Regardless, they were extinct by the Middle Cambrian
296 (Debrenne et al., 2002). Stromatoporoids were sponge-like animals with hypercalcified
297 layered skeletons. They have been variously referred to as calcifying demosponges,
298 calcareans, or simply a polyphyletic grade of sponge construction (Wood, 1987; Stearn et al.,
299 1999; Cook, 2002; Cuif et al., 2011; Da Silva et al., 2011). They were important Ordovician
300 to Cretaceous reef-builders, especially in the Silurian and Devonian (Fagerstrom, 1987;
301 Wood, 1987, 1999). The Paleozoic stromatoporoids were likely a different clade from the
302 Mesozoic species which are related to the extant sclerosponges in Class Demospongia
303 (Reitner and Wörheide, 2002).

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

322 Wood (1991) and Cuif et al. (2011) suggested that the history of carbonate mineralogy among
323 sponges reflects secular patterns in sea-water chemistry (e.g., Stanley and Hardie, 1998).
324 Wood (1991) noted that calcifying sponges formed reefs and were more abundant in times of
325 “calcite seas” (Ordovician to Devonian, then again in the Jurassic to Cretaceous). She also
326 suggested that carbonate mineralogy is not a useful character for delineating taxa. There are,
327 however, not enough mineralogic and/or phylogenetic data to rigorously test this hypothesis.

328 Similarly, calcification could be primarily a detoxification mechanism (Kingsley and Watabe,
329 1982; Saul, 2009), but we have no evidence either way.

330 *5.3. Environmental and ontogenetic influences on mineralogy*

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

336 We further investigated the relationship between water temperature and Mg content using
337 GLMMs. We ran a phylogenetic comparative analysis on the subset of these data that could
338 be placed in the phylogeny of calcareous sponges presented by Voigt et al. (2012) (n=50, 56%
339 of samples for which water temperature could be retrieved.). Sea surface temperature was not
340 a significant effect in this model ($p=0.75$). This model found a phylogenetic signal in these
341 data, with 17% of observed variation in Mg content explained by phylogenetic relatedness
342 among specimens. As the phylogenetic effect cannot be included for data arising from other
343 genera, we ran another model on the complete dataset, containing only effects for water
344 temperature and genus. Again, water temperature was not shown to have a significant effect
345 on Mg content ($p=0.16$) and the complete model explained only a modest amount of the
346 variation in this trait ($R^2 = 0.33$). Although we do not find a significant effect of water
347 temperature on Mg content in our analyses, it is possible that such an effect exists but was not
348 detectable in this dataset. In particular, a large proportion our data comes from the temperate
349 seas around New Zealand where mean sea surface temperature is around 15°C (n=42, or 47%
350 of the observations from which water temperature is discoverable). Warmer and cooler
351 regions are both less well represented in our data, a pattern that may have limited the
352 statistical power of our analyses.

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

361 *5.4 Calcareous sponges in a high-CO₂ world*

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

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

377 Among the most vulnerable to ocean acidification will be aragonite and high-Mg calcite
378 skeletons (Smith, 2009), such as those formed by many calcifying sponges. And it is in
379 southern temperate-to-polar waters that ocean acidification will be felt first (Andersson et al.,
380 2008). Species reported on here that are most at risk are the shallow-water species found in
381 cool-to-cold waters, especially in the Southern Hemisphere.

382 **6. Conclusions**

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

388 Variability within-specimens and within-species of wt% MgCO₃ in calcite is on the order of
389 +/- 0.5 wt% MgCO₃. There is, in general, less variability with respect to aragonite: calcite
390 ratio. There are broad mineralogical patterns in the higher taxa, and it is often possible to
391 classify taxa into particular mineralogical types. There are exceptions: the archaeocyath
392 sponges, for example, are usually described as having high-Mg calcite skeletons, but our
393 results suggest that the group might be more variable.

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

398 In a high-CO₂ world, many sponges may be “winners”, but the calcareous sponges may not be
399 among them. High-Mg calcite and aragonite are the most soluble forms of CaCO₃, and most

400 of the sponges reported here live in the shallow temperate regions where saturation levels are
401 predicted to fall the most rapidly. Deeper-water sponges may be isolated from lowering pH
402 effects for some time.

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412

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681

682 **9. Figure and Table Captions**

683 Figure 1: Skeletal carbonate mineralogy of 74 extant specimens of the phylum Porifera; 28

684 are from the literature (Lister, 1900; Clarke and Wheeler, 1922; Vinogradov, 1953;
685 Jones and James, 1969; Jones, 1970; Jones and Jenkins, 1970; Schuhmacher and
686 Plewka, 1981; Reitner and Engeser, 1987; Willenz and Hartman, 1989; Cuif and
687 Gautret, 1991; Ledger and Jones, 1991; Reitner, 1991; Vacelet and Uriz, 1991;
688 Wood, 1991; Reitner and Gautret, 1996; Aizenberg et al., 1995a, b, 1996, 2003;
689 Bøhm et al., 2000; Fallon et al., 2004; Rosenheim et al., 2005; Wombacher et al.,
690 2005; Rossi et al., 2006; Sethmann et al., 2006; Uriz, 2006), whereas the remaining
691 42 are new data from New Zealand. See Supplementary Data for details.

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

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

701 Table 2: Carbonate mineralogy of extant higher taxa of calcifying sponges as reported in the
702 literature (see references in Table 1) and determined here for specimens from New
703 Zealand. Taxonomy follows van Soest et al. (2012).

704

705 Supplementary Data: Skeletal carbonate mineralogy of the extant Porifera: data from the
706 literature and new analyses from New Zealand.

Calcifying sponges show a range of mineralogies from high-Mg calcite to aragonite.

Association between phylogeny and mineralogy undercuts environmental correlations.

Sponges producing high-Mg calcite/aragonite will not be “winners” in high-CO₂ seas.

Figure 1

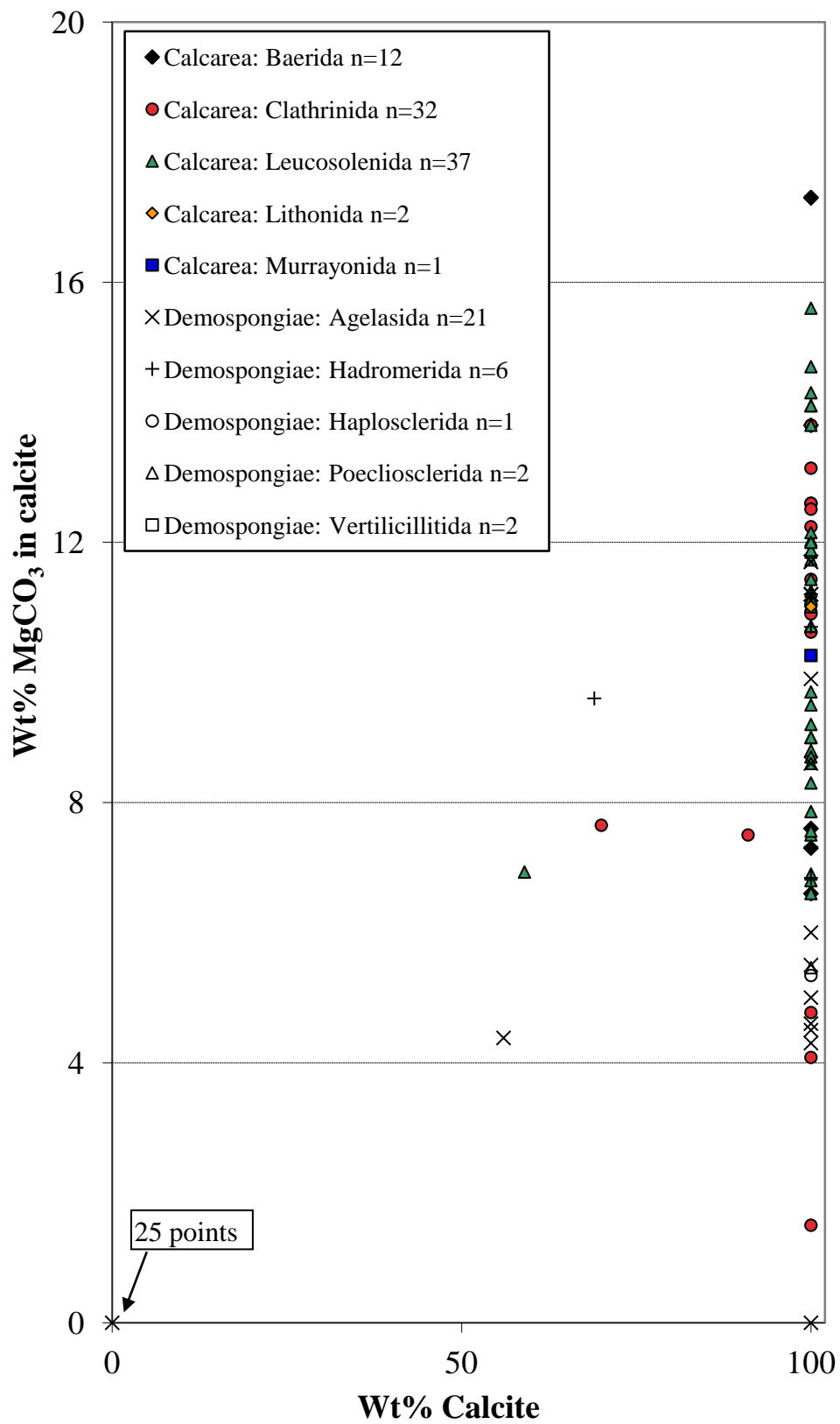
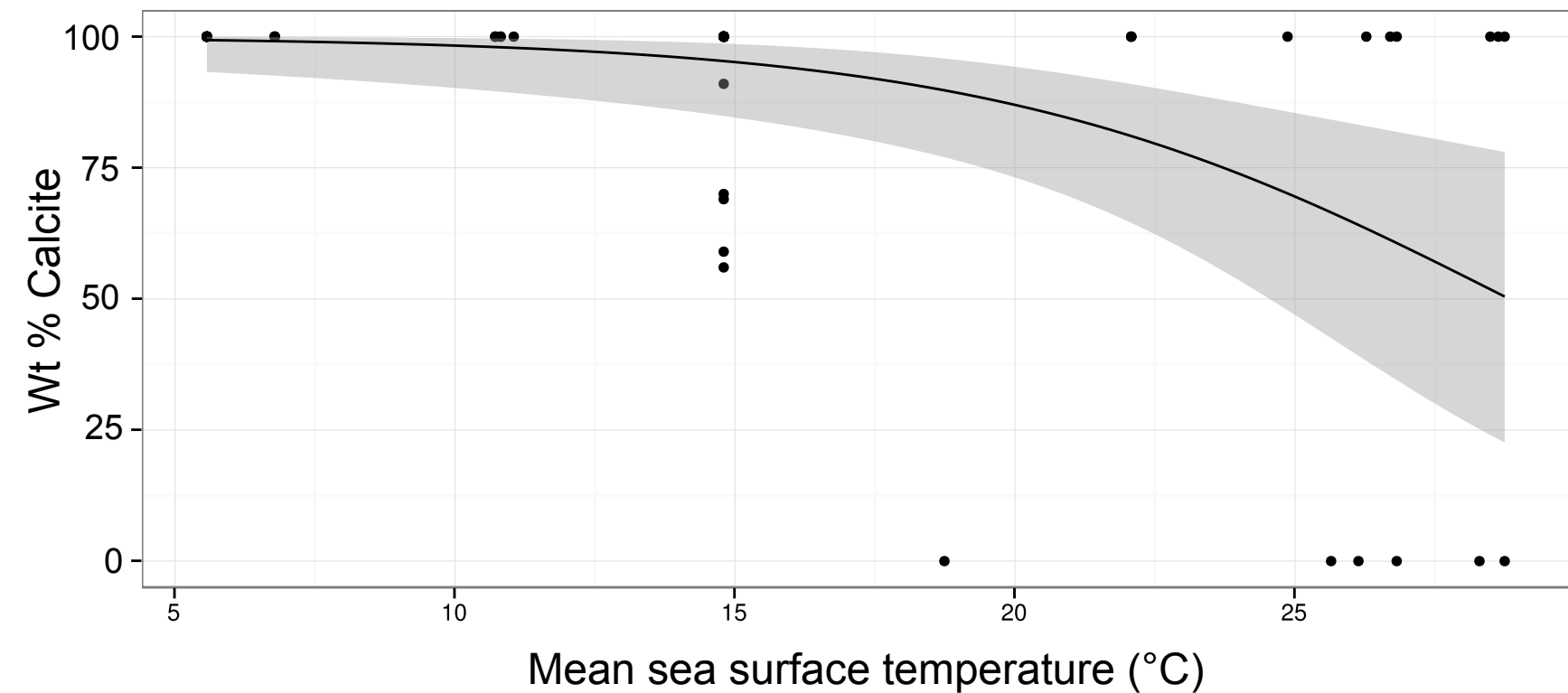
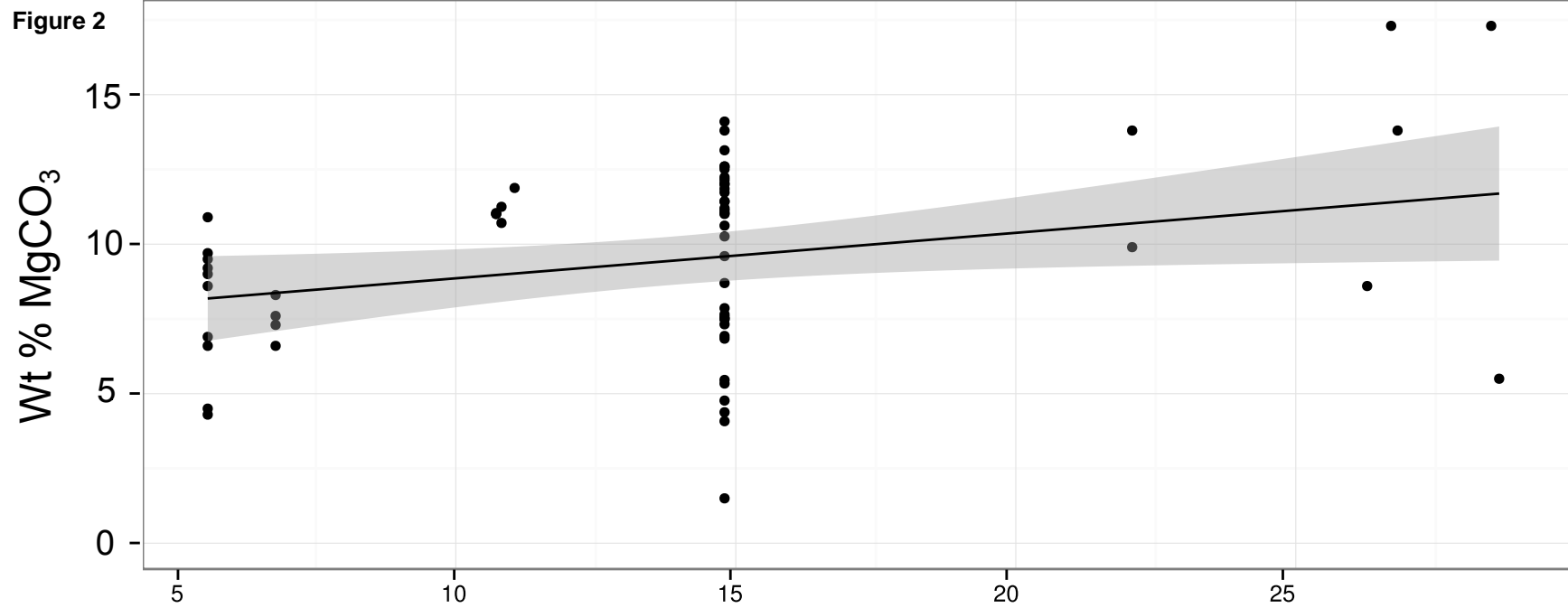


Figure 2



Class	Order	Family	Species	Skeletal element	Specimens	Mineralogy	Mean wt% calcite in carbonate	Mean wt% MgCO3 in calcite	Reference		
Calcareia	Baerida	Baeritidae	<i>Leucandra aspera</i> (Schmidt, 1862)	spicules	2	MgC	100	7.8	Jones 1970		
			<i>Leucandra pandora</i> (Haeckel, 1872)	spicules	1		100	10.71	this study		
			<i>Leucandra pumila</i> (Bowerbank, 1866)	spicules	1	MgC	100	8.3	Jones & Jenkins 1970		
				various					Jones & Jenkins 1970, Jones & James 1969		
			<i>Leuconia nivea</i> (Grant, 1862)	spicules	6	MgC	100	9.2	this study		
			<i>Leuconia</i> sp.	spicules	1		100	11.01	this study		
		Clathrinida	Clathrinidae	cf. <i>Leuconia</i>	spicules	1		100	11.25	this study	
				<i>Clathrina contorta</i> (Bowerbank, 1866)	spicule	1	Mg C	100	13.8	Aizenberg et al 1995b	
				<i>Clathrina coriacea</i> (Montagu, 1818)	spicules	1	MgC	100	10.9	Jones & Jenkins 1970	
					triradiate						
				<i>Clathrina</i> sp.	spicules	2	MgC with ACC layer MgC with some	100	13.8	Aizenberg et al 1995a, 1996a, 2003	
					spicules	5	aragonite	92.2	5.1	this study	
	Leucosolenida	Leucetidae	<i>Clathrina</i> sp. 1 - white, large	spicules	12	High Mg C	100	12	this study		
			<i>Clathrina</i> sp. 2 - yellow, small	spicules	1	High Mg C	100	11.13	this study		
			<i>Clathrina</i> sp. 3 -- yellow, stringy	spicules	1	MgC	100	9*	Uriz 2006		
			<i>Leucetta</i> sp.	spicules	1	High Mg C	100	11.88	this study		
			<i>Leucetta</i> sp. 1 -- large oscules	spicules	4	High Mg C	100	11.2	this study		
		Leucosoleniidae	<i>Leucetta</i> sp. 2 -- small ostia	spicules	3	High Mg C	100	10.2	this study		
			<i>Pericharax heteroraphis</i> Poléjaeff, 1883	spicules	1	MgC	100	8.6	Sethmann et al 2006		
			Grantiida	Amphoriscida	<i>Leucilla "carteri"</i> (not clear what species is meant here)	spicules	1	High Mg C	100	14.1	Vinogradov 1953
					<i>Amphiute paulini</i> Hanitsch, 1894	oxea	3	MgC	100	7.2	Jones & Jenkins 1970
					<i>Grantia compressa</i> (Fabricius, 1780)	spicules	1	MgC	100	6.6	Jones & Jenkins 1970
	Leucosolenida	Sycectidae	<i>Grantia</i> sp.	spicules	2	High Mg C	100	11.01	this study		
			Leucosoleniidae	<i>Kebira uteoides</i> Row, 1909	monaxon	3	Mg C Mg plus aragonite	100	15.6	Aizenberg et al 1995b	
				<i>Leucosolenia</i> cf. <i>botryoides</i>	spicule	1		59	6.93	this study	
			<i>Leucosolenia complicata</i> (Montagu, 1818)	spicules	1	MgC	100	6.9	Jones & Jenkins 1970		
			<i>Leucosolenia echinata</i> (?)	spicules	4	MgC	100	10	this study		
		Sycectidae	<i>Leucosolenia</i> sp.	spicules	1		56	4.38	this study		
			<i>Sycon ciliatum</i> (Fabricius, 1780)	spicules	4	MgC	100	4.5	Jones & Jenkins 1970, Ledger & Jones 1991, Vinogradov 1953		
			<i>Sycon pentactinale</i> Rossi, Farina, Borojevic & Klautau, 2006	5-rayed spicules	1	C	100		Rossi et al 2006		
			<i>Sycon</i> sp.	various spicules	10	MgC MgC with some	100	10	Aizenberg et al 1995a		
			<i>Sycon</i> sp. 1 -- collared	spicules	4	aragonite	92	7.3	this study		
<i>Sycon</i> sp. 2 - short vase	spicules	1	MgC	100	5.46	this study					
Murrayonida	Lithonida	Minchinellida	<i>Minchinella</i> sp.	primary skeleton	1	MgC	100	5	Wood 1991		
			Petrobiontida	<i>Petrobiona massiliana</i> Vacelet & Lévi, 1958	primary skeleton	1	Mg C	100	6	Wood 1991	
				Murrayonidae	<i>Murrayona phanolepis</i> Kirkpatrick, 1910	primary skeleton	1	MgC	100	5.5	Wood 1991
		<i>Astrosclera willeyana</i> Lister, 1900			primary skeleton (massive)	7	A	0		Bohm et al. 2000, Fallon et al 2004, Lister 1900, Wood 1991 Schuhmacher & Pleuka 1981, Bohm et al 200, Rosenheim et al 2005, Willenz & Hartman 1989, Harman & Goreau, 1970, Wood 1991	
		Agelasida	Astroscleridae	<i>Ceratoporella nicholsoni</i> (Hickson, 1911)	primary skeleton	10	A	0			
				<i>Goreauella auriculata</i> Hartman, 1969	primary skeleton	1	A	0		Hartman & Goreau 1970, Wood 1991	
	<i>Hispidopetra miniana</i> Hartman, 1969			massive skeleton	1	A	0		Hartman & Goreau 1970, Wood 1991		
	Acanthochaetidae		<i>Stromatospongia norae</i> Hartman, 1969	basal exoskeleton	1	A	0		Hartman & Goreau 1970, Willenz & Hartman 1989		
			<i>Stromatospongia vermicola</i> Harman, 1969	irregular skeleton	1	A	0		Hartman & Goreau 1970, Wood 1991		
			<i>Acanthochaetetes</i> sp.	primary skeleton	2	High Mg C	100		Wood 1991, Womacher et al 2005		
	Demospongiae	Haplousclerida	Calcifibrospongiida	<i>Acanthochaetetes wellsii</i> Hartman & Goreau, 1975	primary and secondary skeleton	4	High Mg C	100	16.1	Cuif & Gautret 1991, Reitner 1991, Reitner & Engeser 1987, Reitner & Gautret 1996	
				Verticillitida	<i>Calcifibrospongia actinostromarioides</i> Hartman, 1979	primary skeleton	1	A	0		Wood 1991
Hymedesmida					<i>Hemimycala columella</i> (Bowerbank, 1874)	spherules	1	C spherules and SiO2 spicules together	100	0	Vacelet et al 1987
			<i>Merlia lipoclavidisca</i> Vacelet & Uriz, 1991		basal skeleton	1	A	0		Vacelet & Uriz 1991, Uriz 2006	
Verticillitida			Merliida	<i>Merlia</i> sp.	primary skeleton	1	lowMgC	100		Wood 1991	
				Verticillitidae	<i>Vaceletia crypta</i> (Vacelet, 1997)	rigid skeleton	2	A	0		Cuif & Gautret 1991, Wombacher et al 2005, Wood 1991

Table 2

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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	high Mg Calcite
		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*	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	Aragonite or Calcite (low to high Mg)
		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**	1 of 1	1	1	2	0		Aragonite

*Excluding the anomalously high reported Mg content in *Leucetta* by Uriz 2006.

** But Wörheide 2008 places *Vaceletia* in the Dictyoceratida in its own new family

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