Evaluation of geochemical records as a paleoenvironmental proxy in the hypercalcified demosponge *Astrosclera willeyana*

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Abstract

The geochemistry of the calcium carbonates of marine organisms is an excellent proxy for reconstruction of the paleoceanographic history. However, previous studies of hypercalcified demosponges (sclerosponges) are considerably fewer than those of corals, foraminifers, and bivalves. Here, we investigated stable oxygen (δ^{18}O) and carbon (δ^{13}C) isotopes and minor and trace element (Mg, Sr, Ba, Pb, and U) to Ca ratios of 36 living sclerosponges (*Astrosclera willeyana*) collected from Kume Island in the Ryukyu Islands, southwestern Japan, to evaluate the utility of geochemistry as a paleoenvironmental proxy. The δ^{18}O, δ^{13}C, and Sr/Ca deviations of the coevally precipitated skeleton were extremely small and almost constant at all skeletal portions, strongly suggesting that within-skeletal variations in the chemical components are negligibly small for non-symbiotic sclerosponges. Mean δ^{18}O, δ^{13}C, and Sr/Ca values ($N = 36$), falling within a quite narrow range, showed no significant evidence for intraspecific (inter-specimen) variations in the sclerosponges. The sclerosponges δ^{18}O and δ^{13}C were consistent with those of the aragonites precipitated in isotopic equilibrium with seawater at the growth site. The sclerosponge Sr/Ca was close to that of inorganically precipitated aragonite, and the estimated partition coefficient of 1.1 (almost unity) is identical to previously reported values for different species (*Ceratoporella nicholsoni*). Consequently, these results suggest that *A. willeyana* sclerosponge, having little vital effects on the geochemistry, is a robust indicator of paleocean environments (seawater δ^{18}O, temperature, and dissolved inorganic carbon δ^{13}C). Further, our evaluation study documents that sclerosponges living in deeper ocean environments can support the reconstruction of spatial and vertical paleoceanographic changes in conjunction with coral proxy records. The sclerosponge U/Ca showed little within-skeletal and intraspecific variations, but the heterogeneity and individual difference of the Mg/Ca, Ba/Ca, and Pb/Ca were relatively large, the reasons of which still remain unresolved.

Keywords: Sclerosponge, *Astrosclera willeyana*, Oxygen and carbon isotopic composition, Minor and trace elements, Isotope equilibrium, Paleoenvironmental proxy

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Introduction

The hypercalcified demosponges ("sclerosponge" hereinafter), members of the earliest branching metazoan taxon (Porifera), have been dominant reef-building marine organisms throughout the Phanerozoic (e.g., Vacelet 1985; Reitner and Engeser 1987; Wood 1990; Reitner 1992). The taxon *Astrosclera* is present in the fossil record from the Late Triassic (Vacelet 1979, 1985). In modern coral reefs, the sclerosponges can be found in cryptic niches of low-light environments, unlike zooxanthellate scleractinian corals (e.g., Wörheide 1998). Sclerosponges, commonly mushroom-shaped in form, deposit a $CaCO_3$ skeleton at a very slow growth rate of mostly less than about 2 mm/year and can grow for up to several hundred years (e.g., Benavides and Druffel 1986; Böhm et al. 1996; Reitner and Gautret 1996; Wörheide et al. 1997; Wörheide 1998; Swart et al. 2002; Fallon et al. 2003; Grottoli et al. 2010).

To elucidate the processes underpinning climate change and global warming, environmental proxy archives such as trees, sediments, and corals for documenting air and sea surface temperature variation over the last millennia are needed (PAGES 2 k Consortium 2013; Abram et al. 2016). The stable oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) isotope records of sclerosponges are a useful proxy for reconstructing seawater temperature and salinity (e.g., Wörheide 1998; Böhm et al. 2000; Moore et al. 2000; Rosenheim et al. 2005a) and dissolved inorganic carbon $\delta^{13}C$ of seawater (e.g., Böhm et al. 1996; Swart et al. 2010) for the past. Results of previous studies have shown that, like corals, the $\delta^{18}O$ and $\delta^{13}C$ values of sclerosponges have respectively reflected interannual climate variability (Swart et al. 2002; Grottoli 2006; Grottoli et al. 2010; Wu and Grottoli 2010) and increasing fossil fuel CO_2 in seawater (Böhm et al. 2002; Swart et al. 2010). Moreover, other minor and trace elements and isotopes can be a proxy for monitoring ocean environments and chemistry (e.g., Lazareth et al. 2000; Fallon et al. 2005; Rosenheim et al. 2005b; Ohmori et al. 2014). Some studies showed that sclerosponge strontium/calcium (Sr/Ca) can offer a potential for paleotemperature determination of seawater (e.g., Rosenheim et al. 2004; Waite et al. 2018).

Importantly, sclerosponges can live in environments with less sunlight (ex. reef caves and overhangs) and at greater water depths of up to several hundred meters in the Indo-Pacific tropical regions (e.g., Hartman 1980) and in the Atlantic and Caribbean regions (e.g., Druffel and Benavides 1986; Böhm et al. 1996), unlike zooxanthellate corals and giant clams living in shallow coral reefs. For that reason, their skeletal chemistry can be useful for elucidating vertical variations of physical and chemical parameters of seawater and generating their several-century-long time series that overlap with and extend beyond the instrumental climate data. Nevertheless, sclerosponge-based

reconstruction studies are extremely few (especially in the North Pacific) relative to those of other marine $CaCO_3$ organisms such as corals, foraminifers, and mollusks. Furthermore, evaluation and calibration studies of sclerosponges for fidelity as a paleoenvironmental proxy are few and they were only based on time series analyses along the growth direction (Böhm et al. 2000; Rosenheim et al. 2005b, 2009). Therefore, distribution (homogeneity/heterogeneity) and intraspecific difference of chemical composition in the sclerosponge skeleton should be evaluated for further robust application to paleoenvironmental reconstruction.

We investigated 36 specimens of living sclerosponges collected in Kume Island, southwestern part of Japan in the North Pacific to clarify (1) within-skeletal variations in the $\delta^{18}O$, $\delta^{13}C$, and elements/Ca ratios (magnesium/Ca (Mg/Ca), Sr/Ca, barium/Ca (Ba/Ca), lead/Ca (Pb/Ca), and uranium/Ca (U/Ca)) and (2) their intraspecific variations (individual difference = inter-specimen variations). In addition, to evaluate the fidelity as a paleoenvironmental proxy, we compared the isotopic values of the sclerosponge samples to theoretically calculated values of aragonites precipitated close to isotope equilibrium with seawater at the living site and estimated partition coefficients for elements/Ca between seawater and aragonitic skeleton. Knowledge acquired through the results of our evaluation study can contribute to the expansion of applications of multi-proxy reconstructions for climate and ocean environmental changes and can provide insight into a better understanding of calcium carbonate biomineralization for marine organisms.

Materials and methods

Study site and environment

The study site (26°20′12–17′′ N, 126°43′40–49′′ E) is located off the western coast of Kume Island in the Ryukyu Islands, southwestern Japan (Fig. 1). The climate of this region is subtropical, with atmospheric temperatures of 17–29 °C and an annual mean of 23 °C (Japan Meteorological Agency 2016). The average annual precipitation is ca. 2100 mm/year. The warm Kuroshio current (the western North Pacific current) flows into the East China Sea and passes northeastward along the Ryukyu Islands. It allows the development of coral reefs with a high bio-diversity at Kume Island (e.g., Naruse et al. 2012).

In situ seawater temperature and salinity at the study site in water depths of 34–40 m were measured every 1 h from the 5th of October 2015 through the 13th of November 2016 using data loggers (Infinity CTW; JFE Advantech Co., Ltd. and HOBO Tidbit v2; Onset Computer Corp.). The observation data were calibrated with actual temperature and salinity measurements of seawater collected at the study site using a calibration thermometer and a conductivity meter (CM-41X: DKK-
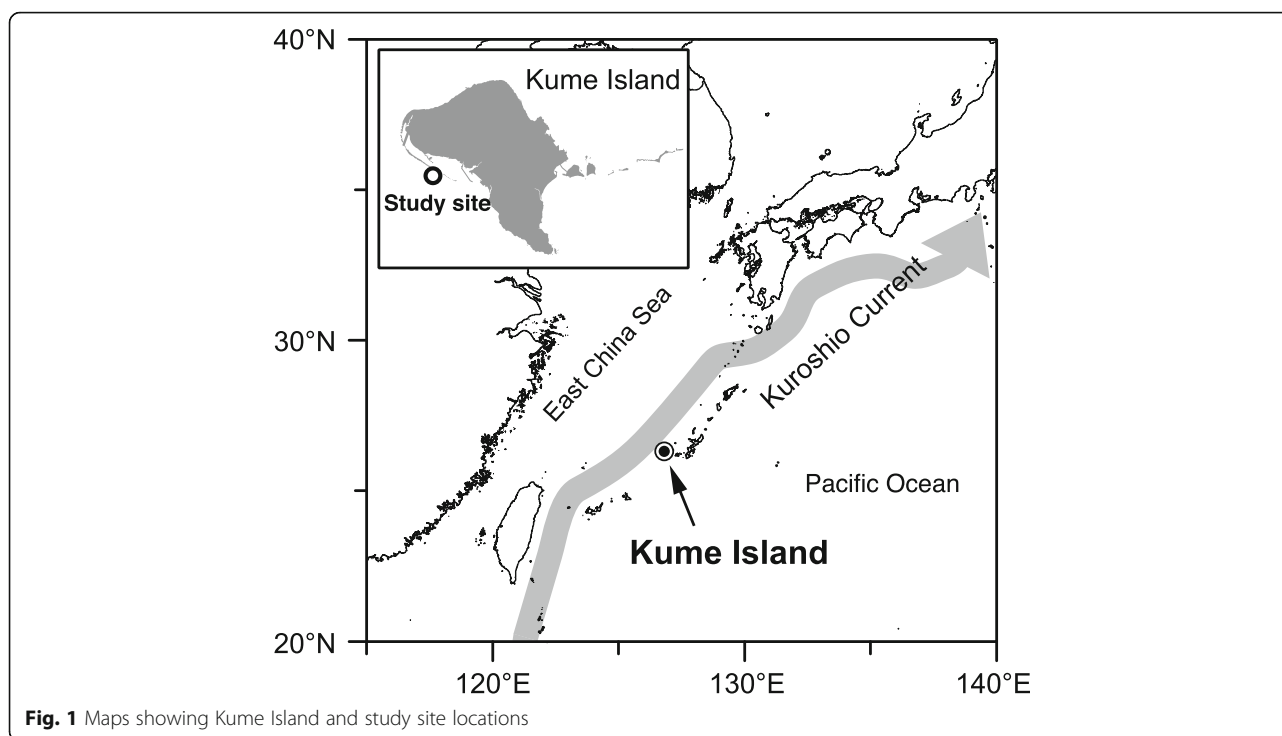
Fig. 1 Maps showing Kume Island and study site locations

TOA Corp.). The in situ data for 2015–2016 are fundamentally consistent with monthly average data at a depth of 30 m, available from the Japan Oceanographic Data Center (JODC) for 1906–2003 (26°–27° N, 126°–127° E; http://www.jodc.go.jp/) (Fig. 2). The seawater temperature and salinity vary respectively, as 20 °C–31 °C and 33.6–35.0 (psu) with annual means of 25.4 °C and 34.6 (psu).

Samples

The hypercalcified demosponges (*Astrosclera willeyana* Lister 1900) examined in this study were growing on the ceiling or wall in dark submarine caves, crevasses, or overhung of reef outer edge. In October 2015 and November 2016, 36 living sclerosponge samples were collected by scuba diving. Specifically, 6 samples (KMJ-40), 4 samples (KMJ-34), and 26 samples (KMJ-38) were collected respectively at water depths of 40 m, 34 m, and 38 m (Table 1 and Fig. 3). The surfaces of samples are mostly light-to-dark brown and/or orange. The samples, which were from 5.4 mm × 5.0 mm × 2.5 mm to 24.9 mm × 18.0 mm × 11.6 mm, were rinsed three times ultrasonically with milli-Q water (resistance = 18.2 mΩ; Millipore Corp.) and were then dried in a desiccator.

To check the mineralogy and preservation state of the skeleton, five selected sclerosponges (KMJ-38-14, KMJ-38-20, KMJ-38-22, KMJ-38-25, and KMJ-38-26) were examined using X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) (Fig. 4). At the University of the Ryukyus, XRD analysis was conducted using a multipurpose XRD device (RINT Ultima/PC; Rigaku Corp.) to test for the presence of calcite. Powdered samples were mounted on well-cleaned glass slides with HCl, ethanol, and milli-Q water and were analyzed using Cu Kα radiation (40 kV, 30 mA) by scanning from 20 to 37° at a 2θ angle at 0.02° steps. SEM imaging of the skeleton was conducted using a microscope (TM3030; Hitachi High-Tech. Corp.).

Stable isotope analyses

For stable isotope analyses, powdered subsamples (1–20 subsamples per sclerosponge) were taken from the skeleton surface along the X-axis (= long axis) and Y-axis (= short axis) directions (see Fig. 4), to evaluate within-skeleton variations in the isotope values. The top of the sample is regarded as the coordinate origin ($X = 0$, $Y = 0$). A subsample (Φ, 1 mm; depth, ca. 1.5 mm) was taken at intervals of 1–4 mm from the coevally precipitated skeleton using a pre-cleaned diamond drill. The common skeletal growth rates of *A. willeyana* scleroponges are estimated to be about 0.2–1.9 mm/year (e.g., Wörheide 1998; Moore et al. 2000; Fallon and Guilderson 2005; Fallon et al. 2005; Grottoli et al. 2010). The tissue layer in *A. will-eyana* can occupy upwards of about 5 mm and the time between initial deposition and secondary infilling of aragonite skeleton appears to be several years (Fallon et al. 2005; Allison et al. 2012). Furthermore, the skeletal density of *A. willeyana* increases gradually with depth. That in the surface living zone is about half that of inner structures, which is indicative of continual thickening of
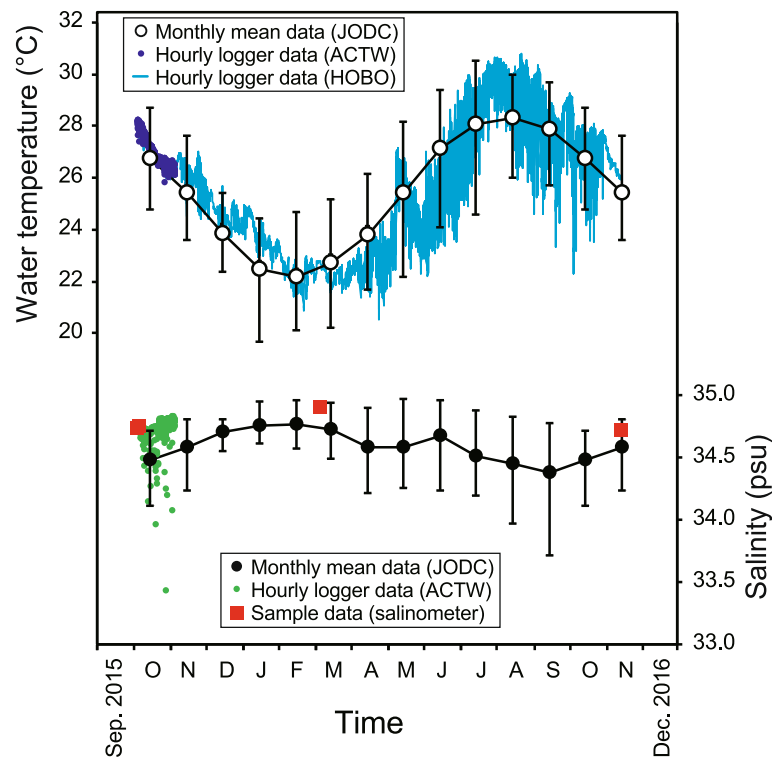
Fig. 2 Monthly mean climatology and logging data of seawater temperature and salinity at the study site. Data are derived from the Japan Oceanographic Data Center (JODC) for 1906–2003 (26°–27° N, 126°–127° E; http://www.jodc.go.jp/) and in situ observations made during October 2015 to November 2016 using loggers in this study. Error bars represent monthly maximum and minimum values in the past. Salinity of seawater samples collected at the site was also measured for cross-validation

aragonite throughout the living tissue layer (Fallon et al. 2005). Considering such characteristics of skeletal growth, the subsampling portion (Φ, ~ 1 mm; depth, ~ 1.5 mm) probably corresponds to an increment during about a few years, assumed to be the years 2013–2016 in this study.

Stable oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) isotope analyses of calcium carbonate (0.14–0.16 mg) were conducted using a continuous flow isotope ratio mass spectrometer attached to a Gasbench II and a GC-PAL auto-sampler (Delta V Advantage; ThermoFisher Scientific Inc.) at the University of the Ryukyus, following the method presented by Asami et al. (2015). The seawater $\delta^{18}O$ was measured using a cavity ring-down spectroscopy (CRDS L2130-i; Picarro Inc.) at the University of the Ryukyus, following the method reported by Uemura et al. (2012). Isotopic ratios were reported in the conventional δ notation relative to Vienna Pee Dee Belemnite (VPDB) for carbonate and Vienna Standard Mean Ocean Water (VSMOW) for seawater. External precision (1σ) throughout the entire analysis was ± 0.07‰ ($\delta^{18}O$) and ± 0.05‰ ($\delta^{13}C$) for carbonate and ± 0.08‰ ($\delta^{18}O$) for seawater. Accuracy of the measurements of sclerosponge samples was evaluated based on replicates of GSJ/AIST JCp-1 (aragonite; Okai et al. 2004), yielding average $\delta^{18}O$ and $\delta^{13}C$ values of – 4.65 ± 0.07‰ and – 1.59 ± 0.06‰

(N = 42), which show excellent agreement with previously reported values of – 4.71‰ and – 1.63‰ (Nakayama et al. 2008), respectively.

Elements/Ca analyses
Elements/Ca ratios (Mg/Ca, Sr/Ca, Ba/Ca, Pb/Ca, U/Ca) were analyzed using an inductively coupled plasma-mass spectrometer (XSeries II, Thermo Fisher Scientific) at the University of the Ryukyus, basically following the method reported by Asami et al. (2009, 2013). Each sclerosponge powder sample (~ 0.15 mg) was dissolved in 4.5 mL of 0.5 mol/L high-purity HNO_3 diluted with ultrapure Milli-Q water. Each seawater sample of 125 μL was diluted 80 times with high-purity HNO_3 and ultrapure Milli-Q water. Internal standard elements (Sc, Y, and Yb) were added to all of the solutions to produce equal concentrations to control matrix effect and to correct for instrumental noise. Solutions were analyzed for ^{24}Mg, ^{43}Ca, ^{44}Ca, ^{45}Sc, ^{87}Sr, ^{88}Sr, ^{89}Y, ^{137}Ba, ^{138}Ba, ^{172}Yb, ^{208}Pb, and ^{238}U. Measurements were conducted in triplicate. Calibrations of the five gravimetric standard solutions yielded high correlation coefficients of r > 0.99998 for Ca, Mg, and Sr and of r > 0.99995 for Ba, Pb, and U. A reference solution, gravimetrically matched to the Ca concentration of the average sclerosponge sample

Table 1 Details of sclerosponge samples and analytical results of geochemistry

Sample ID	Collection Date	Water Depth (m)	Size			N	$\delta^{13}C$ (‰)		$\delta^{18}O$ (‰)		Mg/Ca (mmol/mol)		Sr/Ca (mmol/mol)		Ba/Ca (µmol/mol)		Pb/Ca (µmol/mol)		U/Ca (µmol/mol)	
			X (mm)	Y (mm)	H (mm)		Avg.	SD (1σ)	Avg.	SD (1σ)	Avg.	SD (1σ)	Avg.	SD (1σ)	Avg.	SD (1σ)	Avg.	SD (1σ)	Avg.	SD (1σ)
KMJ-40-1	6-Oct-15	40	9.4	8.8	6.0	9	3.49	0.07	-1.08	0.07	1.45	0.36	9.42	0.17	0.59	0.70	0.45	0.28	3.26	0.04
KMJ-40-2			11.4	7.9	4.8	8	3.40	0.05	-1.16	0.10	1.49	0.64	9.36	0.11	1.06	0.64	0.51	0.17	3.23	0.03
KMJ-40-3			12.3	11.8	5.5	9	3.43	0.05	-1.00	0.17	2.11	0.61	9.41	0.11	1.39	0.76	0.71	0.17	3.13	0.06
KMJ-40-4			19.0	15.5	8.9	14	3.42	0.06	-1.00	0.11	1.59	0.25	9.52	0.15	1.90	1.02	0.63	0.15	3.25	0.02
KMJ-40-5			24.9	18.0	11.6	13	3.47	0.08	-1.01	0.13	1.85	0.36	9.42	0.16	2.74	0.77	N/A		3.24	0.06
KMJ-40-6			21.0	18.6	12.6	14	3.51	0.08	-0.75	0.12	1.33	0.38	9.58	0.19	2.97	0.69	N/A		3.21	0.07
KMJ-34-1	7-Oct-15	34	10.3	10.2	5.9	13	3.51	0.05	-0.98	0.07	1.45	0.47	9.63	0.13	1.96	0.44	0.71	0.11	3.17	0.04
KMJ-34-2			12.4	11.3	6.0	12	3.45	0.09	-0.88	0.06	1.26	0.23	9.76	0.09	2.06	0.40	0.81	0.13	3.12	0.04
KMJ-34-3			13.9	10.8	6.8	14	3.42	0.12	-1.02	0.09	1.47	0.39	9.52	0.09	2.04	0.44	0.74	0.12	3.17	0.07
KMJ-34-4			15.2	13.8	11.4	17	3.44	0.07	-1.07	0.12	1.61	0.37	9.43	0.14	1.86	0.43	0.73	0.12	3.27	0.05
ALL (KMJ-34 and -40): 95% CL							**3.454 ± 0.024**		**-0.995 ± 0.072**		**1.560 ± 0.160**		**9.503 ± 0.077**		**1.857 ± 0.451**		**0.663 ± 0.086**		**3.205 ± 0.033**	
KMJ-38-1	13-Nov-16	38	14.7	13.2	8.8	16	3.41	0.05	-0.98	0.06	1.31	0.32	9.15	0.17	1.44	0.94	N/A		3.27	0.14
KMJ-38-2			17.7	12.5	10.5	18	3.40	0.05	-1.01	0.16	1.29	0.34	9.27	0.28	1.47	1.11	N/A		3.24	0.12
KMJ-38-3			5.4	5.0	2.5	1	3.37		-1.17		2.14		9.26		N/A		N/A		3.36	
KMJ-38-4			6.0	5.7	2.0	1	3.48		-0.95		1.40		9.29		N/A		0.08		3.27	
KMJ-38-5			6.0	6.0	3.0	1	3.44		-0.99		1.45		9.55		N/A		0.53		3.42	
KMJ-38-6			7.2	6.9	3.5	5	3.36	0.02	-0.89	0.10	1.78	0.51	9.43	0.28	0.59	1.07	N/A		3.29	0.10
KMJ-38-7			7.8	7.1	3.0	5	3.38	0.03	-0.95	0.08	1.67	0.17	9.45	0.16	0.75	0.99	N/A		3.40	0.15
KMJ-38-8			7.7	7.2	4.0	5	3.34	0.05	-1.02	0.09	1.33	0.20	9.35	0.12	0.31	0.29	N/A		3.54	0.08
KMJ-38-9			9.7	8.7	4.0	5	3.38	0.04	-1.00	0.09	0.95	0.10	9.74	0.08	N/A		2.32	1.64	3.35	0.06
KMJ-38-10			10.0	9.9	6.0	5	3.41	0.05	-0.93	0.03	1.07	0.12	9.80	0.15	0.43	0.97	0.98	0.75	3.34	0.14
KMJ-38-11			11.0	10.3	7.0	15	3.40	0.06	-1.09	0.11	0.90	0.06	9.33	0.09	0.12	0.33	2.53	1.16	3.37	0.10
KMJ-38-12			11.4	8.9	5.1	12	3.42	0.05	-0.99	0.08	0.96	0.28	9.41	0.08	0.09	0.31	3.53	1.37	3.30	0.07
KMJ-38-13			12.8	8.9	7.3	11	3.44	0.05	-0.94	0.06	1.03	0.18	9.51	0.09	0.09	0.20	4.55	2.49	3.48	0.07
KMJ-38-14			12.3	10.8	7.0	14	3.37	0.04	-0.90	0.05	1.08	0.12	9.73	0.40	2.41	0.85	3.20	1.36	3.11	0.07
KMJ-38-			12.7	11.8	6.4	13	3.40	0.03	-1.06	0.09	1.14	0.22	9.44	0.25	1.59	1.14	3.82	2.70	3.18	0.06

Table 1 Details of sclerosponge samples and analytical results of geochemistry *(Continued)*

Sample ID	Collection Date	Water Depth (m)	Size			N	$\delta^{13}C$ (‰)		$\delta^{18}O$ (‰)		Mg/Ca (mmol/mol)		Sr/Ca (mmol/mol)		Ba/Ca (µmol/mol)		Pb/Ca (µmol/mol)		U/Ca (µmol/mol)	
			X (mm)	Y (mm)	H (mm)		Avg.	SD (1σ)	Avg.	SD (1σ)	Avg.	SD (1σ)	Avg.	SD (1σ)	Avg.	SD (1σ)	Avg.	SD (1σ)	Avg.	SD (1σ)
15																				
KMJ-38-16			15.9	15.5	8.8	16	3.39	0.06	-1.17	0.05	1.02	0.21	9.28	0.09	1.20	0.82	3.01	1.55	3.22	0.06
KMJ-38-17			17.1	15.1	8.8	14	3.41	0.05	-1.07	0.11	1.19	0.31	9.56	0.15	0.84	0.95	N/A	3.80	3.21	0.07
KMJ-38-18			15.6	12.8	8.0	12	3.34	0.06	-1.12	0.12	1.09	0.16	9.36	0.25	1.86	1.03	2.24	0.87	3.16	0.05
KMJ-38-19			14.8	13.6	9.0	15	3.37	0.06	-0.94	0.07	1.22	0.49	9.30	0.17	2.24	0.45	1.50	0.44	3.22	0.05
KMJ-38-20			18.2	15.9	9.5	19	3.38	0.04	-1.01	0.09	1.04	0.14	9.38	0.09	1.01	0.71	N/A	3.49	3.24	0.04
KMJ-38-21			20.0	16.8	10.0	20	3.39	0.05	-1.00	0.07	1.10	0.12	9.41	0.25	1.46	0.86	3.19	1.64	3.20	0.05
KMJ-38-22			18.5	18.2	9.0	15	3.41	0.03	-1.02	0.07	1.10	0.27	9.32	0.19	1.31	0.90	2.37	1.37	3.20	0.07
KMJ-38-23			20.5	15.8	9.0	14	3.35	0.06	-0.95	0.09	1.23	0.20	9.74	0.31	1.75	0.92	1.43	0.61	3.20	0.05
KMJ-38-24			21.6	16.2	10.0	17	3.37	0.06	-0.96	0.11	1.15	0.07	9.43	0.18	2.13	0.44	0.79	0.18	3.17	0.04
KMJ-38-25			19.8	19.7	10.2	18	3.39	0.05	-1.02	0.11	0.99	0.14	9.38	0.20	2.15	0.47	0.77	0.39	3.22	0.06
KMJ-38-26			21.6	19.1	11.8	20	3.39	0.06	-1.01	0.08	0.86	0.09	9.24	0.18	1.55	0.79	0.72	0.12	3.25	0.06
ALL (KMJ-38): 95% CL							3.392 ± 0.012		-1.006 ± 0.029		1.211 ± 0.114		9.428 ± 0.067		1.217 ± 0.312		2.086 ± 0.611		3.277 ± 0.041	

solutions, was measured at intervals of three samples to correct for instrumental drift. Based on replicate measurements of the solution of aragonite reference material JCp-1 coral (Okai et al. 2002), external precisions for Mg/Ca, Sr/Ca, Ba/Ca, Pb/Ca, and U/Ca determinations were better than 0.43%, 0.31%, 1.1%, 4.0%, and 0.82% relative standard deviations ($N = 150$) and the measurement values of samples were calibrated using the widely accepted values of Hathorne et al. (2013).

Results and discussion
Skeletal structures and preservation
The results of XRD analysis indicate that the skeleton samples of *Astrosclera willeyana* consist exclusively of aragonite (> 99.9%), with no detection of calcite. The SEM images of skeletal samples also reveal no evidence of the existence of calcite (Fig. 5). Skeletal aspects of our sclerosponge samples closely resemble those found in earlier studies (e.g., Wörheide 1998; Jackson et al. 2010; Gilis et al. 2013), clearly showing a typical macrostructure of reticulate skeletal organization with branches composed of aragonitic spherulitic structural elements (Ayling 1982; Reitner 1992; Allison et al. 2012). Pristine aragonite crystals were observed without evidence of

diagenetic alteration such as overgrowth of inorganically precipitated secondary cements, traces of dissolution, or bioerosion. Consequently, these results indicate that *A. willeyana* samples used for this study can retain pristine skeletons with original values of isotope composition and elemental concentrations.

Within-skeleton variations
Oxygen and carbon isotopes
Biological carbonates are known to precipitate out of ^{13}C and ^{18}O equilibrium with seawater attributable to kinetic and metabolic isotope effects (e.g., McConnaughey 1998, 2003). For a photosynthetic scleractinian aragonitic coral with symbiotic algae, McConnaughey (1989) showed that the $\delta^{13}C$ and $\delta^{18}O$ variations (1σ) of the coeval skeletal increments were significantly different between sunshine side samples (± 0.17‰ and ± 0.04‰, respectively) and shade side samples (± 0.47‰ and ± 0.49‰, respectively). Furthermore, a strong positive correlation ($r = 0.90$) between coral $\delta^{13}C$ and $\delta^{18}O$ was found for the shade side. These results suggest that the isotopic composition is different depending on the skeletal portion of $CaCO_3$ in photosynthetic corals.
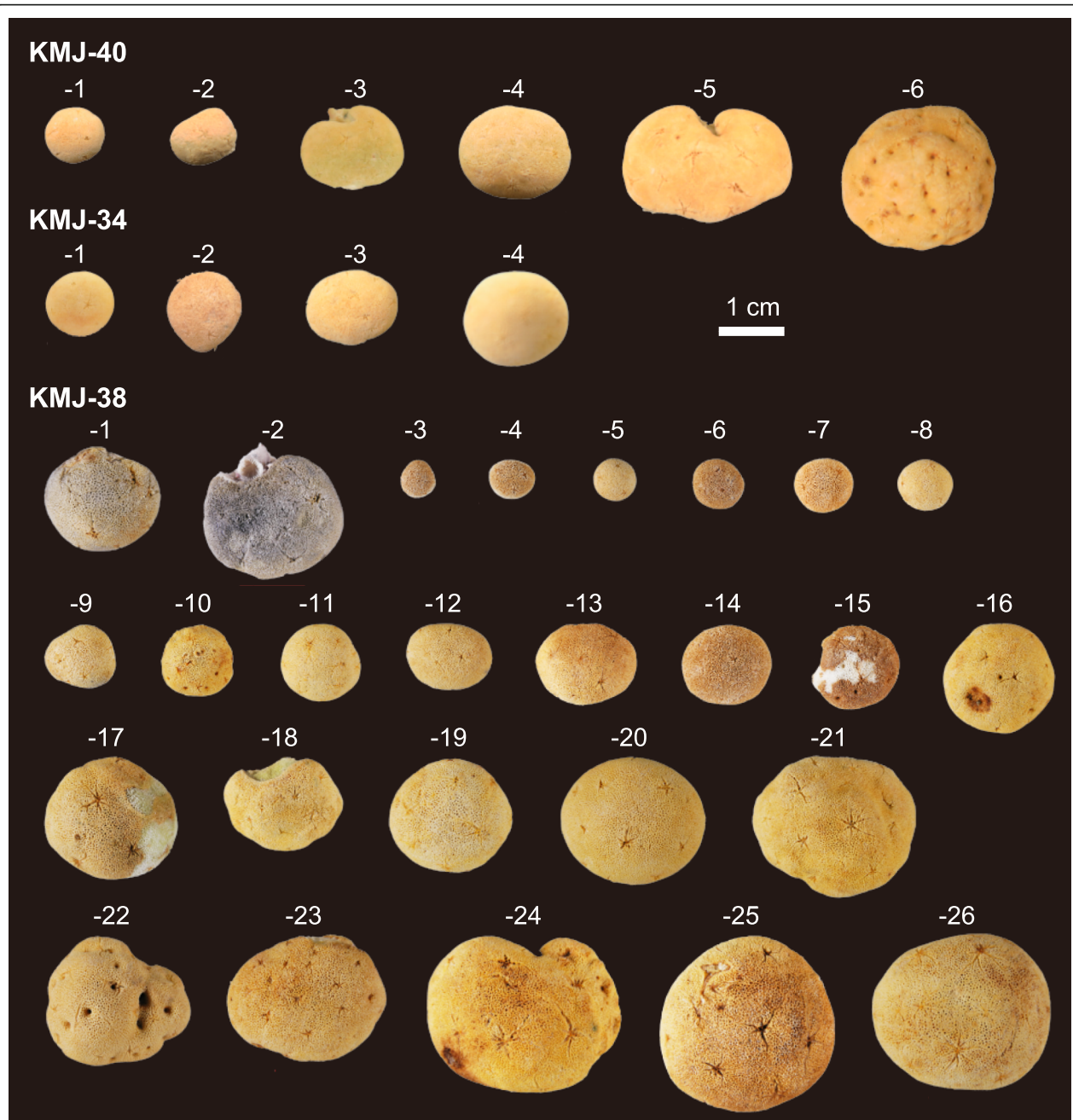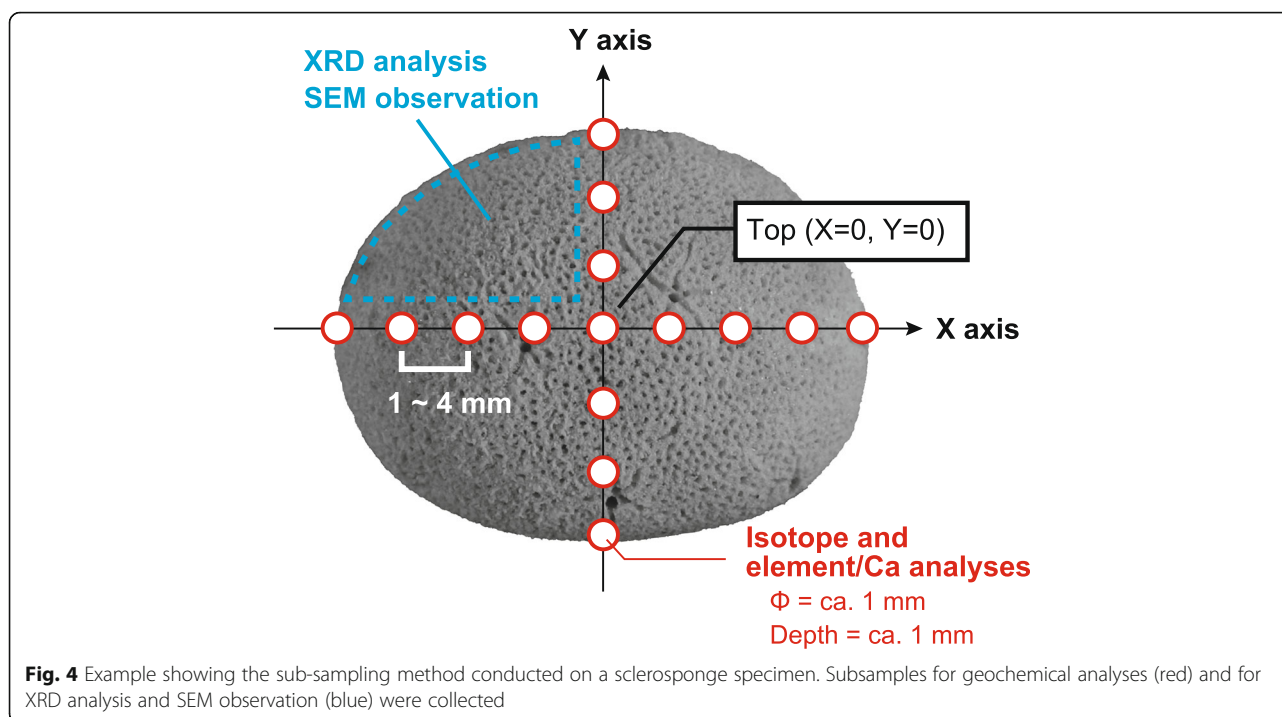
Fig. 3 Photographs of sclerosponge samples

The average and standard deviation (1σ) of δ¹³C and δ¹⁸O in an *A. willeyana* specimen were estimated from values of sub-samples ($N < 20$) collected at the coevally precipitated skeleton (Table 1; Fig. 4). The δ¹³C and δ¹⁸O records are almost similar among KMJ-40, KMJ-34, and KMJ-38. The δ¹³C and δ¹⁸O variations (standard deviations, 1σ) of the coeval skeleton were quite small: from ± 0.02 to ± 0.12‰ and from ± 0.03 to ± 0.17‰, respectively. To identify within-skeletal variations of all samples, the respective deviations relative to the average

(differences between isotopic values and the average) in an individual specimen are depicted in Fig. 6. The whole standard deviation (2σ) of the isotopic differences was small (± 0.11‰ for δ¹³C and ± 0.19‰ for δ¹⁸O) and almost constant at all skeletal portions, with no significant variations and trends (Fig. 6). These results show that the within-skeletal variations in the isotopic composition are negligibly slight for the species *A. willeyana*.

The distribution of correlation coefficients among respective samples in within-skeleton showed little

Fig. 4 Example showing the sub-sampling method conducted on a sclerosponge specimen. Subsamples for geochemical analyses (red) and for XRD analysis and SEM observation (blue) were collected

systematic relationships and trends (Fig. 7). Only 5 sclerosponge samples showed positive relations between the $\delta^{13}C$ and $\delta^{18}O$ with high r values of 0.6–0.8, but these are expected to be arbitrary in consideration of the very slight within-skeletal variation of ± 0.03–0.06‰ for $\delta^{13}C$ and ± 0.08–0.11‰ for $\delta^{18}O$ and considering analytical errors (Table 1). It is considered that the homogeneity of the isotopic composition in the coevally skeleton for *A. willeyana* is due to little kinetic fractionation effect because the species has no symbiont and a very slow growth rate of the $CaCO_3$ precipitation.

Elements/Ca ratios

Despite $\delta^{13}C$ and $\delta^{18}O$ records, only a few studies have reported minor and trace elements/Ca ratios of sclerosponges (e.g., Fallon et al. 2005; Rosenheim et al. 2005b; Allison et al. 2012). The Sr/Ca and U/Ca records in the coevally precipitated skeletons of *A. willeyana* samples are almost similar among KMJ-40, KMJ-34, and KMJ-38 (Table 1). Overall, the Mg/Ca, Sr/Ca, and U/Ca variations (1σ) of the coeval skeleton were small, ranging respectively from ± 0.06 to ± 0.64 mmol/mol, ± 0.08 to ± 0.40 mmol/mol, and from ± 0.02 to ± 0.15 µmol/mol. The sclerosponge Ba/Ca and Pb/Ca had large fluctuations with respective standard deviations of ± 0.20–1.14 µmol/mol and ± 0.11–3.80 µmol/mol. The deviations (2σ) relative to the average for an individual were almost constant at all skeletal portions (± 0.55 mmol/mol for Mg/Ca, ± 0.37 mmol/mol for Sr/Ca, ± 1.45 µmol/mol for Ba/Ca, ± 2.45 µmol/mol for

Pb/Ca, and ± 0.13 µmol/mol for U/Ca), with no significant variations and trends (Fig. 6). These results show that the elements are homogeneously distributed in coeval skeleton of *A. willeyana* sclerosponge, whereas the relative standard deviations of Sr/Ca (3.9%) and U/Ca (4.2%) were quite smaller than those of Mg/Ca (45%), Ba/Ca (97%), and Pb/Ca (138%), which can be partially caused by the difference in elemental concentrations and respective analytical errors. Therefore, our results suggest that the within-skeletal variations of Sr/Ca and U/Ca in *A. willeyana* sclerosponge are so slight as to be ignored.

The distribution of correlation coefficients among respective samples in within-skeleton showed little systematic relationships and trends, showing that most of the r values fell within a range from – 0.4 to 0.4 (Fig. 7). The relationships mostly explain only < 20% of the covariance among respective geochemical composition, thereby indicating that the within-skeletal geochemistry for *A. willeyana* can be less influenced by kinetic fractionation effect. It is known that sclerosponges are composed of two key crystal structures in the skeleton at a micro-scale resolution: fused aragonitic spherulites (formed intracellularly and fused together at the surface) and epitaxial backfill (deposited extracellularly at the base of the sponge tissue). High-resolution spatial analyses showed that elements/Ca ratios were highly variable in and among these structures (Allison et al. 2012), probably indicating a heterogeneity of chemical composition in the sclerosponge skeleton.
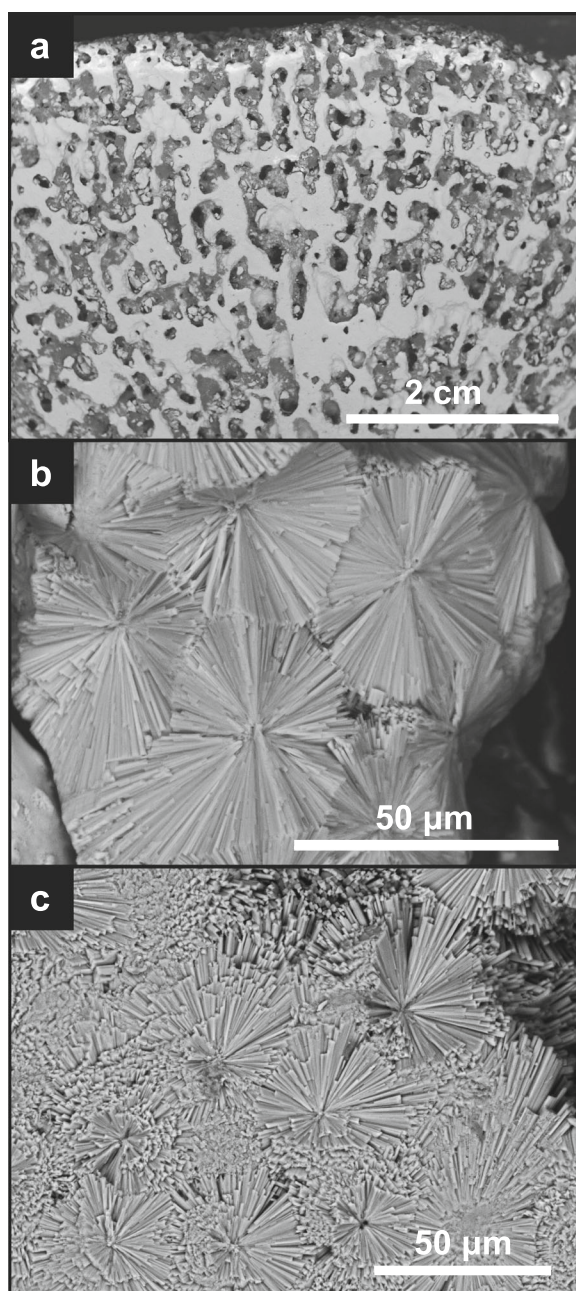
Fig. 5 Scanning electron micrograph images of sclerosponges. A well-preserved pristine aragonite skeleton is visible (**a**, **b** KMJ-38-14; **c** KMJ-38-25)

On the other hand, our data showed that within-skeletal Sr/Ca and U/Ca of *A. willeyana* sclerosponges were quite small and constant (Table 1 and Fig. 6). These suggest that the chemical components in the sclerosponge skeleton are commonly homogeneous at millimeter-scale resolution and annually resolved reconstruction of ocean environmental changes can be applied.

Intraspecific variations

Oxygen and carbon isotopes

The average $\delta^{13}C$ ($\delta^{18}O$) values of *A. willeyana* samples collected in October 2015 and November 2016 fell within quite narrow ranges from 3.40 to 3.51‰ (from − 0.75 to − 1.16‰) and from 3.35 to 3.48‰ (from − 0.89 to − 1.17‰), respectively (Table 1 and Fig. 8). The respective averages of the $\delta^{13}C$ and $\delta^{18}O$ with 95% confidence levels were 3.45 ± 0.02‰ and − 0.99 ± 0.07‰ for KMJ-40 and KMJ-34 samples (N = 10) and 3.39 ± 0.01‰ and − 1.01 ± 0.03‰ for KMJ-38 samples (N = 26) (Table 1). No significant difference was found between the two population averages for $\delta^{18}O$ (0.01 ± 0.08‰). The $\delta^{13}C$ average for KMJ-38 samples (presumably 2014–2016) was slightly lower than that for KMJ-40 and KMJ-34 samples (presumably 2013–2015) with a significant difference of 0.06 ± 0.03‰, which may reflect the Suess Effect widely accepted as a result of the burning of ^{12}C-enriched fossil fuels (Keeling et al. 1979; Quay et al. 1992). The effect has decreased $\delta^{13}C$ of dissolved inorganic carbon (DIC) in seawater since the mid-20th century because of the accelerated increase of anthropogenically derived CO_2 with isotopically low $\delta^{13}C$ values into the ocean from the atmosphere, results of which are recorded in corals and sclerosponges (e.g., Böhm et al. 2002; Asami et al. 2005; Swart et al. 2010). The difference is roughly consistent with decreasing $\delta^{13}C$ rates of − 0.03‰/year for 2000–2016 (atmospheric CO_2 at Hawaii: derived from Scripps CO_2 Program initiated in 1956 by Keeling CD) and − 0.07‰/year for 2000–2010 (coral data in the Ryukyu Islands; Asami et al. unpublished data).

Cross plots of $\delta^{13}C$ and $\delta^{18}O$ records of our 36 sclerosponge samples converged respectively to the averages of 3.41‰ and − 1.00‰ with very slight standard deviations of ± 0.04‰ and ± 0.08‰ (Fig. 8). The relationship between average $\delta^{13}C$ and $\delta^{18}O$ values of all samples yielded a very weak correlation coefficient of 0.27 (p > 0.01, Table 2), which is unlike those found in photosynthetic marine organisms. Therefore, one can reasonably infer that the intraspecific $\delta^{13}C$ and $\delta^{18}O$ variations (individual difference) for the species *A. willeyana* are quite small and hardly influenced by vital effects because the sclerosponges grow without the need for light and symbiotic algae.

Elements/Ca ratios

The average Sr/Ca (U/Ca) ratios of *A. willeyana* samples collected in October 2015 and November 2016 fell within quite narrow ranges from 9.36 to 9.76 mmol/mol (from 3.12 to 3.27 μmol/mol) and from 9.15 to 9.80 mmol/mol (from 3.11 to 3.54 μmol/mol), respectively (Table 1 and Fig. 8). The respective Sr/Ca and U/Ca averages with 95% confidence levels were 9.50 ± 0.08

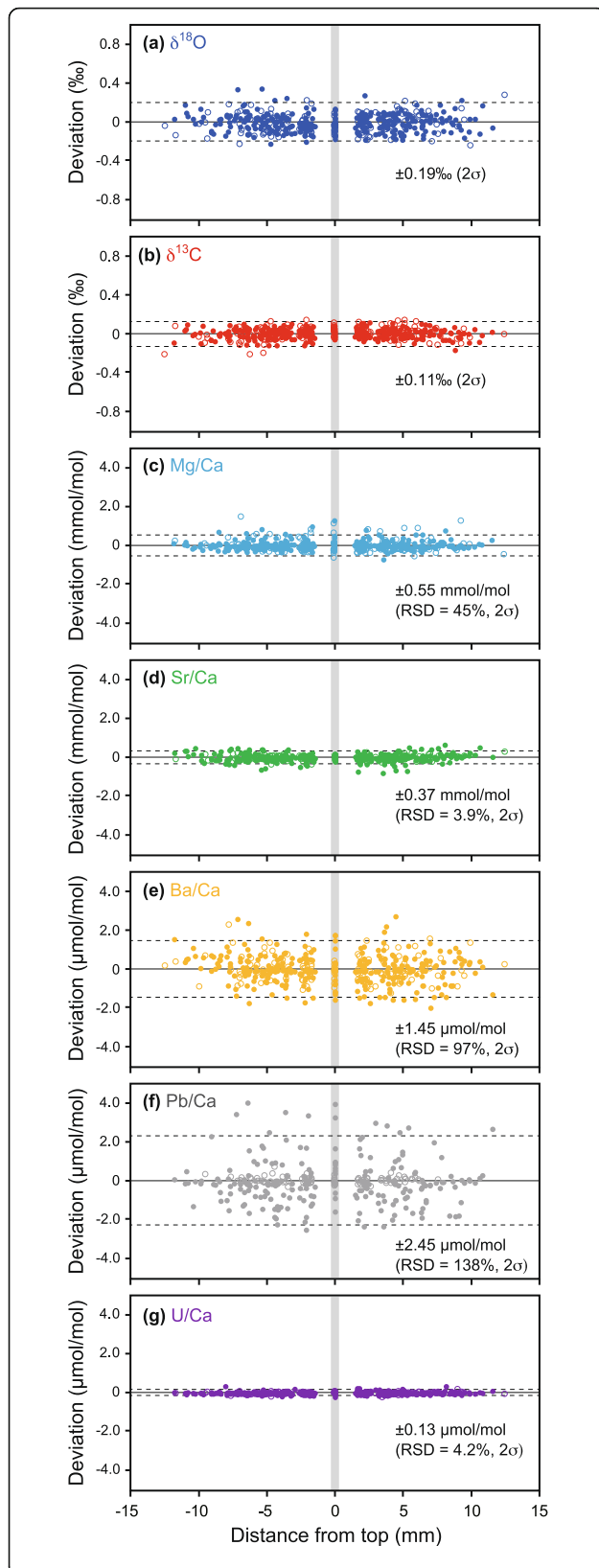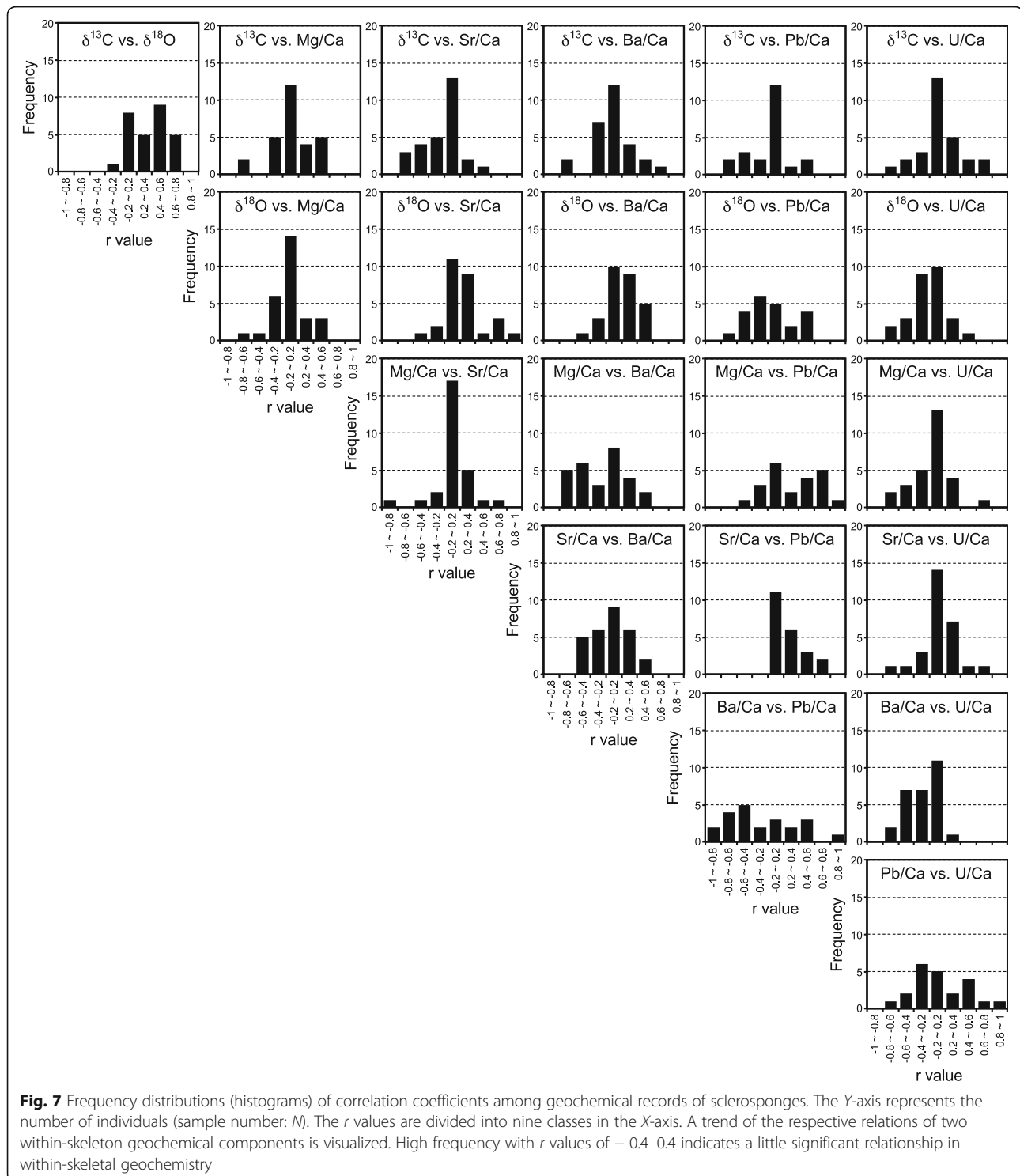**Fig. 6** Within-skeleton variations in **a** $\delta^{18}O$ and **b** $\delta^{13}C$ values and **c–g** elements/Ca ratios of sclerosponges. Deviations to the average in an individual sample are shown. Horizontal lines and dotted lines respectively represent zero and standard deviation (2σ)

mmol/mol and 3.21 ± 0.03 µmol/mol for KMJ-40 and KMJ-34 samples ($N = 10$) and 9.43 ± 0.07 mmol/mol and 3.28 ± 0.04 µmol/mol for KMJ-38 samples ($N = 26$) (Table 1). No significant difference was found between the two population averages for Sr/Ca (0.08 ± 0.10 mmol/mol) and U/Ca (0.07 ± 0.05 µmol/mol). Furthermore, the Sr/Ca and U/Ca records are in agreement with those of the same species from other regions in the Pacific Ocean (Table 3). Consequently, these results strongly suggest that intraspecific variations are negligibly small for Sr/Ca and U/Ca of *A. willeyana*.

The mean values of within-skeletal Mg/Ca, Ba/Ca, and Pb/Ca ratios fall within 1.33–2.11 mmol/mol, 0.59–2.97 µmol/mol, and 0.45–0.81 µmol/mol for KMJ-40 and KMJ-34 samples (collected in 2015) and 0.86–2.14 mmol/mol, 0.09–2.41 µmol/mol, and 0.08–4.55 µmol/mol for KMJ-38 samples (collected in 2016), respectively (Table 1 and Fig. 8). The respective Mg/Ca and Ba/Ca averages with 95% confidence levels were 1.56 ± 0.16 mmol/mol and 1.86 ± 0.45 µmol/mol for KMJ-40 and KMJ-34 and 1.21 ± 0.11 mmol/mol and 1.22 ± 0.31 µmol/mol for KMJ-38 (Table 1). The differences between the two population averages for Mg/Ca (0.35 ± 0.20 mmol/mol) and for Ba/Ca (0.64 ± 0.55 µmol/mol) were statistically significant but not so large (Fig. 8). The respective Pb/Ca averages with 95% confidence levels were 0.66 ± 0.09 µmol/mol for KMJ-40 and KMJ-34 and 2.09 ± 0.61 µmol/mol for KMJ-38, the difference of which is significant (1.42 ± 0.62 µmol/mol). The intraspecific variations for Mg/Ca, Ba/Ca, and Pb/Ca may be due to an individual difference in biological controls on skeletal partitioning of the trace elements.
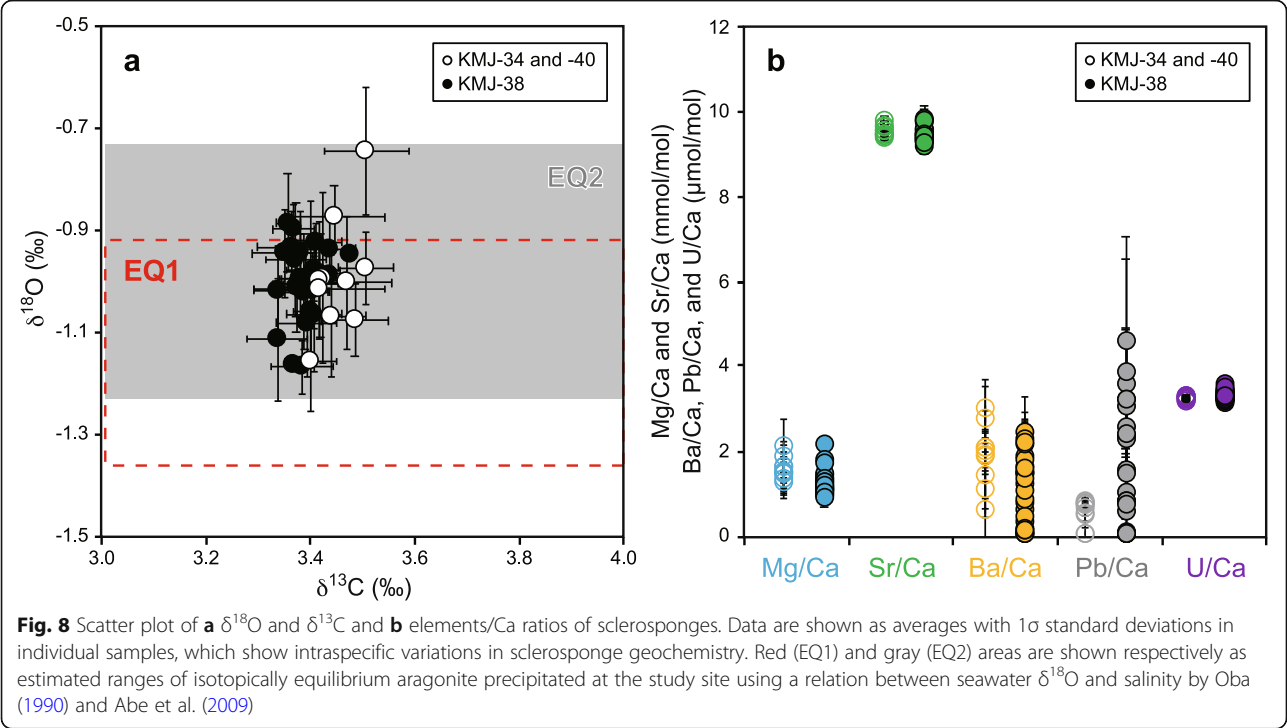
For Mg/Ca, the mechanisms of magnesium incorporation into aragonite are very complicated: loosely bound in the crystal lattice, bound to metal sites of organic compounds, and/or adsorbed onto crystal surface (Amiel et al. 1973). The intraspecific Mg/Ca variations may be due to individual differences in organic phases and the metal binding capacity of sclerosponge tissue layers. For Ba/Ca, the mode of incorporation of barium into the sclerosponge skeleton remains unknown (e.g., Rosenheim et al. 2005b; Allison et al. 2012). Sclerosponges contain a large amount of bacteria living within their tissue (Wörheide 1998). One possibility to explain the intraspecific Mg/Ca and Ba/Ca variations found in this study is that the physiological processes associated with these bacteria may have an effect on the incorporation of Mg^{2+} and Ba^{2+} for calcification at a micro-environmental level (Rosenheim et al. 2005b). Further, the intraspecific variation indicates that

Fig. 7 Frequency distributions (histograms) of correlation coefficients among geochemical records of sclerosponges. The Y-axis represents the number of individuals (sample number: N). The r values are divided into nine classes in the X-axis. A trend of the respective relations of two within-skeleton geochemical components is visualized. High frequency with r values of − 0.4–0.4 indicates a little significant relationship in within-skeletal geochemistry

the efficiency for transporting elements into the calcification site may be different among individuals because of the large discrepancy in the cationic radii of Mg^{2+} and Ba^{2+} relative to Ca^{2+} unlike Sr^{2+} (Gaetani and Cohen 2006).

The Pb/Ca profiles along a growth direction shows historical changes associated with environmental lead

pollution (e.g., Lazareth et al. 2000; Swart et al. 2002; Ohmori et al. 2014). Skeletal Pb/Ca in a *Acanthochaetetes wellsi* (high-Mg calcite) collected from the same locality as our study (Kume Island, Japan) varied roughly from 200 to 1000 nmol/mol for 2000–2007 (Ohmori et al. 2014) and that in a *Ceratoporella nicholsoni* (aragonite) from the

Fig. 8 Scatter plot of **a** $\delta^{18}O$ and $\delta^{13}C$ and **b** elements/Ca ratios of sclerosponges. Data are shown as averages with 1σ standard deviations in individual samples, which show intraspecific variations in sclerosponge geochemistry. Red (EQ1) and gray (EQ2) areas are shown respectively as estimated ranges of isotopically equilibrium aragonite precipitated at the study site using a relation between seawater $\delta^{18}O$ and salinity by Oba (1990) and Abe et al. (2009)

Caribbean Sea varied roughly from 90 to 120 nmol/mol for 1999–2001 (Rosenheim et al. 2005b). Considering the Pb/Ca averages of our samples (1648 ± 421 nmol/mol), interspecific variations are large. Sclerosponges incorporate ~ 10 times higher Pb than corals because pumping and filtering particulates, which absorb heavy metal species, are the only source of nutrition for sclerosponges (e.g., Hartman and Goreau 1966; Willenz and Hartman 1989). Therefore, it is inferred that the amounts, size, and/or species of filtered particles may be considerably different among individuals and species.

Differences in the geochemistry among micro-scale skeletal structures may reflect variations in the composition of the precipitation fluid, the incorporation of ions into the skeleton, and/or kinetic effects (Gabitov et al. 2008). In most cases, apparent relationships among elements/Ca and isotope data of all samples were not founded, yielding a very weak correlation coefficient ranging from – 0.38 to 0.29 (Table 2). This may indicate that the millimeter scale

analyses carried out in this study smoothed the heterogeneity of skeletal geochemistry, which results in a smoothing of environmental signals to no small extent through the living tissue layer. Meanwhile, there significantly exist weak correlations between Sr/Ca and $\delta^{18}O$ ($r = 0.47$), Mg/Ca and Pb/Ca ($r = -0.56$), and Ba/Ca and U/Ca ($r = -0.69$), but their relationships can explain only 22–48% in the respective variance. The former may reflect a difference in skeletal growth rate among the individual samples because both sclerosponge Sr/Ca and $\delta^{18}O$ strongly correlated negatively with seawater temperature. At this point, no clear reason underlying the latter two can be inferred. However, the negative relation between Mg/Ca and Pb/Ca found in this study can be explained by an indication that sclerosponges would acquire more Mg^{2+} nutritionally with a decrease in pumping of ambient water and particulates with adsorbed Pb species (Willenz and Hartman 1989; Rosenheim et al. 2005b). The significant negative correlation of the comparatively high r value of – 0.69 between Ba/Ca and U/Ca in

Table 2 Correlations between average values of sclerosponge geochemistry[*]

	$\delta^{18}O$	Mg/Ca	Sr/Ca	Ba/Ca	Pb/Ca	U/Ca
$\delta^{13}C$	*0.27*	*0.22*	*0.17*	*0.22*	*-0.35*	*-0.11*
$\delta^{18}O$		*-0.06*	**0.47**	*0.29*	*-0.04*	*-0.06*
Mg/Ca			*-0.11*	*0.18*	**-0.56**	*0.02*
Sr/Ca				*0.16*	*-0.01*	*-0.12*
Ba/Ca					*-0.38*	**-0.69**
Pb/Ca						*0.19*

[*]Coefficent values in italics and bold fall outside ($p > 0.01$) and inside ($p < 0.01$) the 99% confidence intervals, respectively

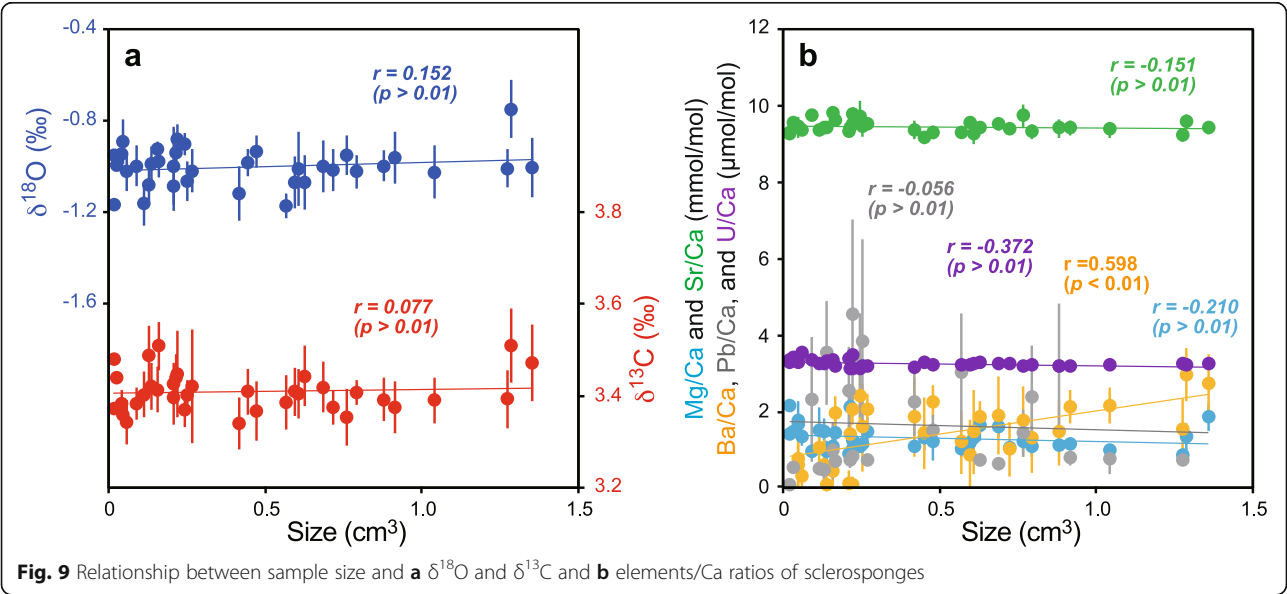**Table 3** Average elemental ratios and partition coefficients for aragonite sclerosponges

	Species	Site	Depth (m)	Mg/Ca (mmol/ mol)	Sr/Ca (mmol/ mol)	Ba/Ca (μmol/ mol)	Pb/Ca (nmol/ mol)	U/Ca (μmol/ mol)
This study								
Avg. (95% CL)	*A. willeyana*	Kume Is., Japan	30–40	1.31 ± 0.11	9.45 ± 0.05	1.42 ± 0.26	1648 ± 421	3.26 ± 0.03
$D_{Me, Arag}$				3.62-4.27 x 10^{-4}	1.09-1.11	0.007-0.017		2.28-2.35
Rosenheim et al. (2005)								
Avg. (±1σ)	*C. nicholsoni*	Jamaica	22	0.85-0.92	9.45-9.89	3.60-4.14	8.13-91.9	3.20-3.37
$D_{Me, Arag}$				1.81 x 10^{-4}	1.10	0.098		
Average (±1σ)	*C. nicholsoni*	Bahamas	143	0.77-0.90	10.15-10.74	3.16-3.66	52.10-289	3.07-3.28
$D_{Me, Arag}$				1.6 x 10^{-4}	1.17	0.86	171.85	2.98
Fallon et al. (2005)								
Avg. (1980-1994)	*A. willeyana*	Otta Island, Micronesia	25	0.9-1.2	9.5-12.0	2.7-4.1		3.1-3.6
Allison et al. (2012)								
Avg. (-2004, several yrs)	*A. willeyana*	Nomuka Ika, Tonga	9.5	0.3-1.1	8.5-12.5	2.5-8.0		

our sclerosponge samples possibly reflects a significant positive relation between Ba/Ca and sample size (a parameter presumably related to biological and skeletal growth rate) (Fig. 9) and the significant negative relationship between U/Ca and seawater carbonate ion concentration (relating to pH and aragonite saturation degree) for deep-sea azooxanthellate corals (Anagnostou et al. 2011).

Compared with equilibrium aragonite for stable isotopes

To evaluate the fidelity of *A. willeyana* as a paleoenvironmental proxy, we compared our data with the $\delta^{13}C$ and $\delta^{18}O$ values of aragonites that are inorganically precipitated in isotopic equilibrium with seawater at the sclerosponge growth site: "equilibrium aragonite."

The $\delta^{18}O$ values were calculated using an equation (1000 × ln α = 17.88($10^3/T$) − 31.14) derived from laboratory synthesis experiments of aragonite at water temperatures of 0–40 °C (Kim et al. 2007). Therein, α is the fractionation factor between aragonite and water; T is in degrees Kelvin. Although showing good consistency with the climatological data products (Fig. 2), the in situ observational data of this study (October 2015 to November 2016) are temporally limited relative to the growth periods (a few years) of investigated skeletal portions. Based on skeletal growth characteristics for *A. willeyana* reported from earlier works (see the "Materials and methods" section), for this study, the investigated skeletal increments of our sclerosponges were

Fig. 9 Relationship between sample size and **a** $\delta^{18}O$ and $\delta^{13}C$ and **b** elements/Ca ratios of sclerosponges

assumed to be precipitated for 2013–2016. Consequently, the annual mean seawater temperature (25.4 °C) and the variation (± 0.9 °C, 2σ) for 2013–2016 were estimated from JODC and Integrated Global Ocean Services System gridded data (26°–27° N, 126°–127° E: Reynolds et al. 2002). The seawater δ18O values of 0.26 ± 0.05‰ or 0.43 ± 0.08‰ were estimated respectively from JODC salinity data using a relation for the East China Sea – Kuroshio Current region (Oba 1990) (case 1) or for Ishigaki Island in the southern Ryukyus (Abe et al. 2009) (case 2). These estimations are consistent with δ18O values (0.18‰ in November 2009, 0.25–0.29‰ in October 2015, 0.35‰ in March 2016) of seawater samples collected at water depths of 34–40 m in this study area. Consequently, the δ18O values of equilibrium aragonites precipitated at the study site for 2013–2016 are expected to fall within a range of – 0.92‰ to – 1.37‰ (case 1: shown as EQ1 in Fig. 8) or from – 0.73‰ to – 1.23‰ (case 2: shown as EQ2 in Fig. 8) at 95% confidence intervals.

The δ13C values of the equilibrium aragonites were estimated using DIC δ13C of seawater, the carbon-isotope fractionation factors among CO_2 species (Zhang et al. 1995), and the aragonite–HCO_3^- enrichment factor (2.7 ± 0.6‰; Romanek et al. 1992). Because of the lack of data on DIC δ13C of seawater around the study site, the annual δ13C value of DIC at a water depth of 40 m is assumed to be the medium value (0.68‰) between November and August estimated using two significant relations established west of Okinawa Island (r^2 = 0.810; Takayanagi et al. 2012) and southeast of Okinawa Island (r^2 = 0.997; Suzuki et al. 2009). Consequently, the δ13C values of the equilibrium aragonites are expected to be roughly 3.0–4.2‰ (Fig. 8). It is noteworthy that the estimated δ13C values are approximate because of the limitations and uncertainty of the dataset.

The skeletal δ13C and δ18O values in our 36 sclerosponge samples almost fell within the probable ranges (case 1 and case 2) of the equilibrium aragonites precipitated at the living site (Fig. 8). This result strongly shows that the δ13C and δ18O of *A. willeyana* is not be influenced isotopically by vital physiological effects. Furthermore, no strong correlation exists between the isotope composition and the sclerosponge sample size (r = 0.076 for δ13C and r = 0.150 for δ18O, p > 0.01) (Fig. 9), unlike symbiont corals for which the isotopic variations (the degree of disequilibrium) are related to the skeletal growth rate (e.g., McConnaughey 1989; Felis et al. 2003). δ13C and δ18O values of corals with symbiotic algae are well known to differ greatly from those of equilibrium aragonite because of kinetic and metabolic fractionation effects (e.g., Aharon 1991; McConnaughey 2003). We therefore suggest that the fractionation effects have little influence on the isotopic composition of *A. willeyana*

because the skeletal growth is expected to constant at a very slow rate. Our results are supported strongly by evidence from earlier studies showing that δ18O values of living sclerosponges (seven *C. nicholsoni* from the Caribbean Sea and a *A. willeyana* from the Great Barrier Reef) are in good agreement with published values from synthetic aragonite and near-equilibrium values of mollusks and foraminifers (Böhm et al. 2000) and that sclerosponges (three *C. nicholsoni* from the Caribbean Sea and a *A. wellsi* from New Caledonia) precipitate $CaCO_3$ skeletons close to isotopic equilibrium for δ13C values (Böhm et al. 1996).

Partition coefficients of elements/Ca

Partition coefficients, apparent distribution coefficients ($D_{Me, Arag}$), were estimated using element/Ca ratios between seawater and aragonitic skeleton of sclerosponge, except for Pb/Ca (Table 3). As it is known that the $D_{Sr, Arag}$ of inorganic aragonite depends on water temperature (e.g., Kinsman and Holland 1969; DeCarlo et al. 2015), sclerosponge Sr/Ca can be useful for a proxy of seawater temperature (e.g., Rosenheim et al. 2004; Haase-Schramm et al. 2005; Waite et al. 2018). The $D_{Sr, Arag}$ from our *A. willeyana* samples was 1.09–1.11 (almost unity), which is consistent with that of *C. nicholsoni* from the Caribbean Sea (Rosenheim et al. 2005b) (Table 3) and experimentally precipitated abiogenic aragonite (Gaetani and Cohen 2006; DeCarlo et al. 2015). The average Sr/Ca of ~ 9.5 mmol/mol in our sclerosponges was identical to an estimation of inorganic aragonite of 9.42–9.50 mmol/mol at 25.4 ± 0.9 °C calculated by using the experimentally established relationship (Gaetani and Cohen 2006) and almost consistent with previously reported values for the same species in the Pacific Ocean (Fallon et al. 2005; Grottoli et al. 2010; Allison et al. 2012). Furthermore, high-resolution Sr/Ca records of aragonitic skeleton for *A. willeyana* (Fallon et al. 2005) and *C. nicholsoni* (Rosenheim et al. 2004) using LA-ICP-MS have been shown to be seasonal variations, yielding significant calibrations for seawater temperature. Therefore, these lines of evidence suggest that *A. willeyana* sclerosponge Sr/Ca can be a robust indicator of seawater temperature.

The value of $D_{Mg, Arag}$ estimated from our samples shows that *A. willeyana* sclerosponge Mg/Ca ratios are several orders (10^{-3} to 10^{-4}) of magnitude smaller than those of seawater (Table 3). The value is about twice that of the species *C. nicholsoni* (Rosenheim et al. 2005b), but about one order of magnitude less than experimentally precipitated inorganic aragonite (Gaetani and Cohen 2006). The $D_{Ba, Arag}$ estimated from our samples shows that Ba/Ca ratios in *A. willeyana* sclerosponge are variable and about two orders of magnitude less than those of seawater. The $D_{Ba, Arag}$ value estimated in this study is about several orders (10^{-1} to 10^{-2}) of

magnitude less than those for the species *C. nicholsoni* (Rosenheim et al. 2005b) and inorganic aragonite (Gaetani and Cohen 2006; Mavromatis et al. 2018). Rosenheim et al. (2005b) also reported that *C. nicholsoni* sclerosponges showed large variations in their $D_{Ba, Arag}$ values of about 0.1–0.9 (Table 3). Such a small $D_{Ba, Arag}$ value of < 1 for sclerosponge samples can be reasonably explained by the lower incorporation of an incompatible trace metal because of the large difference of ~ 25% in ionic radius between Ba^{2+} and Ca^{2+}, as was true also for other aragonite materials such as synthetic aragonite (Mavromatis et al. 2018), speleothems (e.g., Wassenburg et al. 2016), bivalves (e.g., Poulain et al. 2015), and fish otoliths (e.g., Bath et al. 2000) in contrast to corals, which were greater than unity (e.g., Gonneea et al. 2017). However, such a different value of ~ 0.01 to ~ 0.9 (Table 3) indicates that physiological processes for the incorporation of Ba^{2+} into aragonitic sclerosponges for calcification differ greatly not only among individuals but also among species. Perhaps for this reason, significant correlations exist between the Ba/Ca and the sclerosponge sample size found in this study (r = ~ 0.6, p < 0.01) (Fig. 9). Furthermore, results of a study of element partitioning during aragonite precipitation suggest that the calcifying fluid from which coral skeleton precipitates is depleted in Mg and Ba, unlike Sr. Results also suggest that seasonal fluctuations exist in the mass fraction of aragonite precipitated from the fluid (precipitation efficiency) (Gaetani and Cohen 2006), which can qualitatively explain our results showing lower $D_{Mg, Arag}$ and $D_{Ba, Arag}$ values and a value of $D_{Sr, Arag}$ that is almost equal to unity for *A. willeyana* sclerosponge. Quantitative verification of these results requires additional experimental work.

For U/Ca, the average value (~ 3.3 μmol/mol) of our *A. willeyana* sclerosponges was consistent with those of the same species (Fallon et al. 2005) and with *C. nicholsoni* (Rosenheim et al. 2005b) (Table 3). The value of $D_{U, Arag}$ (2.3–2.4) estimated in this study was slightly lower than that (2.98) reported for *C. nicholsoni* (Rosenheim et al. 2005b) and much higher than the experimentally determined value (0.31 ± 0.06) of inorganic aragonite precipitation at 25.5 °C (DeCarlo et al. 2015). Degradation of tissue layers and/or bacteria can influence the pH and carbonate species system of the calcifying fluid, thereby altering the U/Ca ratios in sclerosponge skeleton at different levels, which possibly caused differences in U/Ca among sclerosponge species. Although coralline aragonite U/Ca records are apparently correlated with temperature (e.g., Min et al. 1995; Shen and Dunbar 1995), several recent studies demonstrated that the U/Ca ratios of azooxanthellate deep sea coral (Anagnostou et al. 2011) and experimentally precipitated aragonite from seawater (DeCarlo et al. 2015)

have significant negative correlation with carbonate ion concentrations because the aqueous chemistry of uranium is influenced by the carbonate ion, which forms complexes with the uranyl ion (Langmuir 1978). The sclerosponge U/Ca is about 2–3 times higher than that of zooxanthellate corals, which may be related to lowering of pH and carbonate ion concentrations in the calcifying fluid. These lines of implication might bring higher $D_{U, Arag}$ values in aragonitic sclerosponges than that of synthetic aragonite. Although the complicated mechanism for the incorporation of uranyl complexes into calcium carbonate has not been resolved, the slight intraspecific variations (± 0.03 μmol/mol, the relative variation is 0.9%) of sclerosponge U/Ca for the *A. willeyana* species examined in this study (Fig. 8) support the possibility of its use as a proxy for ocean environments.

Conclusions

Results of this study are important scientific findings for the hypercalcified demosponge *Astrosclera willeyana*; (1) within-skeletal variation is quite small for $\delta^{13}C$, $\delta^{18}O$, Sr/Ca, and U/Ca (namely, little heterogeneity in the coevally precipitated skeleton); (2) intraspecific variations are quite small for $\delta^{13}C$, $\delta^{18}O$, Sr/Ca, and U/Ca (namely, little individual difference); (3) the aragonite skeleton is precipitated in or very close to isotopic equilibrium with seawater at the living site; (4) the isotopic composition of the skeleton is scarcely affected by kinetic and biological effects; (5) the partition coefficient of Sr/Ca is consistent with that for different species and close to inorganic aragonite.

We believe that sclerosponge U/Ca may be a paleoenvironmental proxy although there are still unknowns relating to uranium into the aragonitic skeleton. Relatively large variations and individual differences in the sclerosponge Mg/Ca, Ba/Ca, and Pb/Ca were shown in this study. To clarify the reasons for controlling factors of incorporation (distribution) of the elements into the sclerosponge aragonite skeleton, further investigations such as ultra-high resolution analyses and culture experiments are needed. Importantly, we suggest that *A. willeyana* $\delta^{18}O$ ($\delta^{13}C$) is very suitable as an environmental proxy to reconstruct seawater temperature and $\delta^{18}O$ (DIC $\delta^{13}C$) for the past. Coupled determination of Sr/Ca and $\delta^{18}O$ in a sclerosponge can potentially enable the construction of independent time series for both seawater temperature and $\delta^{18}O$ ($\fallingdotseq$ salinity) at near-annual resolution by using a millimeter-scale sampling protocol for widely used and convenient methods. Furthermore, in combination with the geochemistry of marine calcified organisms living in shallow waters, such as corals and giant clams, long-lived sclerosponge-based reconstruction of deeper ocean environments can generate a long time series of spatial and vertical changes in coral

reef environments for the past few hundred years, extending beyond the observation data. This study also presents the important implication that even if only a few skeletal fragments and a few sclerosponge samples are collected, one can reconstruct annual average paleoceanographic conditions using well-preserved fossils that have not been altered diagenetically. Regarded from these viewpoints, our results can support contributions toward broad applications not only to climatology and oceanography but also to geology and biogeochemistry.

Abbreviations
JODC: Japan Oceanographic Data Center; VPDB: Vienna Standard Pee Dee Belemnite; VSMOW: Vienna Standard Mean Ocean Water

Authors' contributions
RA designed the study, analyzed the samples and data, and wrote the manuscript. TN, MM, YI, YF, and TS collaborated with RA in the fieldwork and sampling. AK, DO, RU, and RS collaborated with RA in the chemical analyses. The authors read and approved the manuscript.

Availability of data and materials
Please contact the corresponding author for data requests.

Competing interests
The authors declare that they have no competing interests.

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