Middle Holocene daily light cycle reconstructed from the strontium/calcium ratios of a fossil giant clam shell

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Insolation is an important component of meteorological data because solar energy is the primary and direct driver of weather and climate. Previous analyses of cultivated giant clam shells revealed diurnal variation in the Sr/Ca ratio, which might reflect the influence of the daily light cycle. We applied proxy method to sample from prehistoric era, a fossil giant clam shell collected at Ishigaki Island in southern Japan. The specimen was alive during the middle Holocene and thus exposed to the warmest climate after the last glacial period. This bivalve species is known to form a growth line each day, as confirmed by the analysis of the Sr enrichment bands using EPMA and facilitated age-model. We analyzed the Sr/Ca, Mg/Ca and Ba/Ca ratios along the growth axis, measuring a 2-μm spot size at 2-μm interval using NanoSIMS. The Sr/Ca ratios in the winter layers are characterized by a striking diurnal cycle consisting of narrow growth lines with high Sr/Ca ratios and broad growth bands with low Sr/Ca ratios. These variations, which are consistent with those of the cultivated clam shell, indicate the potential for the reconstruction of the variation in solar insolation during the middle Holocene at a multi-hourly resolution.

Results

Figure 2a presents a long dataset of Sr/Ca ratios, referred to herein as the “low-resolution analysis”. Measurements were conducted at a 50 μm resolution along the growth axis of the fossil shell from one edge to the other end using NanoSIMS (the solid line in Fig. 1b). The Sr/Ca ratios vary from 1.09 to 2.12 mmol/mol, with a mean of 1.44 ± 0.20 mmol/mol (hereafter, the error assigned to the mean value is 1σ standard deviation). In the low-resolution analysis, there are two apparent periodical variations in Sr/Ca ratios; the maximum values correspond to the dark lines (Fig. 1b). Figures 2b and 2c, respectively, present the associated low-resolution Mg/Ca and Ba/Ca measurements. There is a weak positive correlation between the Mg/Ca and Sr/Ca ratios and broad growth bands with low Sr/Ca ratios. These variations, which are consistent with those of the cultivated clam shell, indicate the potential for the reconstruction of the variation in solar insolation during the middle Holocene at a multi-hourly resolution.

In paleoclimatic studies, valuable information, such as historical seawater temperatures1, salinity2, pH3, and nutrient availability4, has been derived experimentally from analyses of the stable isotopes and of the trace element concentrations of marine calcium carbonates, such as coral skeletons and foraminifera tests. Insolation is a direct consequence of solar energy and a driving force of environmental change5. However, the effect of increasing solar energy is not uniform, resulting in heavy rain or serious drought depending on the locality. Attempts to develop a proxy for insolation6 have included the use of carbonate samples, but these attempts have not been successful. This lack of success is partially attributable to the difficulty in distinguishing the variation in insolation from that of temperature by the analyses conducted at the scale of 100s of μm7 because solar energy is the driver of both meteorological parameters. Therefore, the insolation and temperature are expected to change following a similar pattern. A recent study has reported that the Sr/Ca ratios in cultivated giant clam shells exhibit striking diurnal variation, reflecting the daily light cycle8.

For this study, we applied a proxy method to a fossil giant clam (Tridacna gigas) shell to demonstrate the potential of the use of the Sr/Ca ratio as a proxy for paleo-insolation. The specimen was collected at the Shiraho Coast of Ishigaki Island in the southwestern portion of the Ryukyu Archipelago, southern Japan (Supplementary Fig. S1), and its living age was determined as the middle Holocene using a radiocarbon method (Fig. 1a). The results were compared with those of modern specimens, which were cultivated at the same island8.
maximum (that is the middle point of a dark and opaque area in Fig. 1b) to another contains approximately 350 Sr enrichment bands by EPMA. Figure 2d presents the Sr/Ca results for the “high-resolution analysis”. Measurements were collected at a 2 µm resolution along the growth axis within the dark and opaque area denoted as “W1a” in Fig. 1b, which corresponds to the region with the maximum Sr/Ca ratios in the low-resolution analysis. The Sr/Ca ratio varies from 1.17 to 2.16 mmol/mol, with a mean of 1.51 ± 0.27 mmol/mol. The relatively longer datasets of Sr/Ca ratios collected for sections “W1b” and “W2” in Fig. 1b exhibit similar cyclic variations to W1a (Supplementary Fig. S2), even though the data for section W2 are more irregular. Figures 2e and 2f, respectively, present the associated high-resolution Mg/Ca and Ba/Ca measurements at the position W1a of Fig. 1b. There are apparent periodical variations in the Mg/Ca and Ba/Ca ratios, with seven cycles contained within the section, which is consistent with the Sr/Ca variations, reflecting the clear positive correlation (Supplementary Fig. S3). The relatively longer datasets for the Mg/Ca ratios of sections “W1b” and “W2” in Fig. 1b (Supplementary Fig. S2) are characterized by similar periodical variations to those of W1a, whereas the Ba/Ca ratios of W2 follow no clear cyclic pattern.

Table 1 lists the basic statistics of the fossil clam shell chemistry data of this study (periods W1a, W1b and W2) together with those of the cultivated samples from the same island. The growth rate of each period was calculated by multiplying the number of data points per day by the analytical interval of 2 µm. The first listed modern clam shell specimen is characterized by a growth rate of 21 ± 5 µm/day, which is almost double that of the other modern specimen, 10 ± 3 µm/day (Table 1). The growth rate of the Holocene fossil sample collected for this study varied from 12 ± 4 to 16 ± 3 µm/day, which is within the range of the modern clam shells. The mean Sr/Ca ratio of the fossil clam was 1.51 ± 0.27 mmol/mol for the W1a period.

Figure 1 | (a) Whole section of the analyzed fossil giant clam shell. The individual radiocarbon ages are given for the two samples (portions of the outer and middle layers). (b) The portion of the shell outer layer mounted in an Araldite resin disk, together with a carbonate standard. The dotted and solid lines, respectively, portray the results of EPMA and NanoSIMS analyses along the growth axis. W1a, W1b and W2 represent sections of the “high-resolution analysis”. (c) Strontium concentration map of the sample enlarged from the square marked in (b).

Figure 2 | (a) Low-resolution analyses of the Sr/Ca ratio, (b) Mg/Ca ratio, and (c) Ba/Ca ratio along the growth axis of the clam shell, marked by the solid line in Fig. 1b. (d) High resolution analyses of Sr/Ca ratio, (e) Mg/Ca ratio, and (f) Ba/Ca ratio along the growth axis in the section marked by W1a in Fig. 1b.
1.53 ± 0.29 mmol/mol for W1b, and 1.26 ± 0.14 mmol/mol for W2. The results for the first winter (W1a and W1b) indicate a similar level of variation as that observed for the modern, cultivated samples (1.54 ± 0.20 and 1.51 ± 0.26 mmol/mol), whereas the second winter (W2) is characterized by a relatively small Sr/Ca ratio and low level of variation.

**Discussion**

Both the low- and high-resolution measurements of the Sr/Ca ratios of a fossil giant clam shell were characterized by cyclic patterns at varying time scales, similar to those observed for the cultivated clam shells from the same island. The daily maximum and minimum Sr/Ca ratios, together with dynamic range of the fossil sample results, are consistent with those of the cultivated samples within the 1σ error, except for the second winter (Table 1). The similarity between the variations in the Sr/Ca ratios of the fossil and modern samples suggests that the same mechanisms control aragonite growth and the incorporation of these elements.

An important feature commonly observed from fossil and modern samples is the presence of daily bands with alternating high and low Sr/Ca ratios. In the W1a section, for example, one cycle has approximately eight or nine data points, whereas the troughs consist of a greater number of data points (Fig. 2d). These variations are consistent with the Sr concentration map observed by EPMA (Fig. 1c). The wider bands of Sr depletion are likely to represent daytime because the clam shell calcification rate is expected to be enhanced by the photosynthetic activity of the symbiotic dinoflagellates. By contrast, the narrower enrichment bands are assigned to nighttime. The autocorrelation analysis of the Sr/Ca data (Supplementary Fig. S4) suggests that the periodic variation over a 20 μm shell distance might represent the mean daily growth bandwidth. Thus, the 2 μm spatial resolution of the NanoSIMS analysis might capture a few hours of time.

The Sr enrichment bands, therefore, can be used for facilitating the age-model determination along the growth axis (dotted line in Fig. 1b). In our study, 350 micro-bands were observed between two maximum values of the Sr/Ca ratio in the low resolution analysis, which correspond to the middle portions of the narrow dark lines (Fig. 1b). Thus, the period between two narrow dark lines (with high Sr/Ca ratios) represents the annual carbonate precipitation. This conclusion is reasonable as suggested in the previous study, which determined the shell growth rate based on the radioactivity from 90Sr deposited in the shell grown during the testing of nuclear weapons. According to the observations, it was also concluded that differentiation of the dark and light annual bands represent the seasonal variation; the dark and opaque areas were assigned to winter growth, whereas the lighter and more translucent areas were assigned to summer growth. The fossil sample analyzed for this study was characterized by a similar pattern: narrower dark lines and wider light bands (Fig. 1b). Therefore, it is inferred that the maximum Sr/Ca ratios in the narrow dark bands represent winter and that the minimum ratios in the wide light bands represent summer (Fig. 2a).

Here, we elucidate the driving mechanisms of the variability’s in minor and trace elements over time. Two steps might build up the aragonite shell: first, the ionic transport of Ca2+ from ambient seawater to the extrapallial fluid (EPF); and second, precipitation from EPF to the shell skeleton. The first step has three transport pathways through the epithelial mantle in a marine bivalve: (1) the intercellular diffusive pathway, (2) the active pathway via Ca2+-ATPase pump, and (3) the major Ca2+-channel pathway (see Supplementary Fig. S5). The intercellular channel for Ca2+ ions might act similarly to those for Mg2+, Sr2+ and Ba2+ ions, whereas the Ca2+-ATPase pump and the Ca2+-channel might be selective for Ca2+ ions. The Ca2+-ATPase pump is activated during the daytime and produces high-calcification rates because it is induced by enzymes that are activated by solar energy. Thus, the Sr/Ca ratio of EPF may be relatively higher at night. The Ca2+-channel hypothesis supports the model by which a reduction of Ca selectivity might occur at high calcification rates because the ion diffusive transport is driven by the Ca2+ gradient. This type of response would result in a higher Sr/Ca ratio in the daytime, which is inconsistent with the observations. The lower solar radiation in winter and the non-insolation at night might produce higher Sr/Ca ratios in association with the reduction in the Ca2+-ATPase pump.

The coincident variations in the Mg/Ca and Ba/Ca ratios, particularly in the high-resolution analysis (Figs. 2d, 2e and 2f), are also explained by the transport-pathway hypothesis because Mg and Ba have markedly similar chemical characteristics. However, the characteristics of the low-resolution analysis differ in that the temporal variation in the Mg/Ca ratio is spiky relative to the Sr/Ca ratio. This larger variation is likely attributed to the stronger biological control over Mg, as suggested by the spatial variation in the aragonite skeleton of a reef-building coral. The Ba/Ca ratio might be affected by reef nutrient contents or salinity, which are influenced by the occasional occurrence of heavy precipitation from summer to late autumn.

In the second step of shell formation, elemental fractionation might be governed by the kinetic process of inorganic precipitation of aragonite under the assumption of a homogeneous EPF composition with time. A laboratory experiment reported that the Sr/Ca exchange coefficient of aragonite increases with an increase in the precipitation rate. Following this relationship, the Sr/Ca ratio would increase during the daytime when the aragonite growth rate is high. However, this result is not supported by our observations, which indicate the opposite relationship during the daytime.
the modern daily mean insolation and the corresponding monthly Holocene. Hence, we applied the empirical formula determined for of a fossil giant clam shell reflect the daily light cycle in the middle climate after the last glacial period in the middle Holocene.19

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**Author contributions**

M.H. performed all of the experimental analyses, including NanoSIMS and EPMA. Y.S. conceived the study and wrote the manuscript. M.H. and Y.S. prepared a revised version. A.I. and N.T. conducted the instrumental control of the NanoSIMS. K.S. and T.W. contributed to field sampling and advised on biominalar implications. All of the authors contributed to the interpretation of the results and to the discussion of the associated geochemistry of the fossil giant clam shell examined in this study.

**Additional information**

Supplementary Information accompanies this paper at http://www.nature.com/scientificreports

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