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Journal

Earth and Planetary Science Letters, 308(3-4)

ISSN

0012-821X

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[et al.](#)

Publication Date

2011-08-01

DOI

10.1016/j.epsl.2011.05.054

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Increased seasonality in the Western Mediterranean during the last glacial from limpet shell geochemistry

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ARTICLE INFO

Article history:

Received 9 December 2010

Received in revised form 23 April 2011

Accepted 31 May 2011

Available online 13 July 2011

Editor: P. DeMenocal

Keywords:

mollusc

seasonality

Gibraltar

palaeoclimate

oxygen isotopes

ABSTRACT

The seasonal cycle is a fundamental aspect of climate, with a significant influence on mean climate and on human societies. Assessing seasonality in different climate states is therefore important but, outside the tropics, very few palaeoclimate records with seasonal resolution exist and there are currently no glacial-age seasonal-resolution sea-surface-temperature (SST) records at mid to high latitudes. Here we show that both Mg/Ca and oxygen isotope ($\delta^{18}\text{O}$) ratios in modern limpet (*Patella*) shells record the seasonal range of SST in the western Mediterranean – a region particularly susceptible to seasonal change. Analysis of a suite of fossil limpet shells from Gibraltar shows that SST seasonality was greater during the last glacial by $\sim 2^\circ\text{C}$ as a result of greater winter cooling. These extra-tropical seasonal-resolution SST records for the last glacial suggest that the presence of large ice-sheets in the northern hemisphere enhances winter cooling. This result also indicates that seasonality in the Mediterranean is not well-represented in most palaeoclimate models, which typically show little change in seasonal amplitude, and provides a new test for the accuracy of climate models.

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1. Introduction

Most biological and physical components of the climate system are controlled as much by seasonal conditions as by the mean climate state. In turn, these components impact the mean climate state so that seasonal and mean climates are intimately linked. Assessing past seasonality during times of different boundary conditions is therefore important to our understanding of the climate system (Denton et al., 2005). Many palaeoclimate proxies, such as foraminiferal Mg/Ca ratios (Barker et al., 2005) and alkenones (Rossell-Mel e et al., 2004), can be biased to a particular season and therefore provide some seasonal information. However, very few extra-tropical records have the resolution to capture the full seasonal cycle and therefore unequivocally reveal the relationships between past seasonality and mean climate.

Producing seasonal-resolution palaeo-SST records outside the tropics (where surface corals are used (e.g. Gagan et al., 2000 and references within)) has proved difficult, but recent work has shown that mollusc shells have significant potential as an archive of seasonal-resolution SST at mid to high latitudes (e.g. Carr e et al., 2005; Jones et al., 2005; Sch one et al., 2004). The $\delta^{18}\text{O}$ of marine mollusc shells is a function both of seawater temperature and of seawater $\delta^{18}\text{O}$ (O'Neil et al., 1969). Where there are no large seasonal changes in seawater

$\delta^{18}\text{O}$, sequential analyses of $\delta^{18}\text{O}$ within a mollusc shell parallel to growth banding can produce a record of the SSTs experienced during the mollusc's lifespan. The absence of seasonal changes in seawater $\delta^{18}\text{O}$ in some regions can be supported by modern observations and by the pattern of local drainage. Ideally, however, use of an additional second palaeothermometer negates the need to make assumptions about past seawater $\delta^{18}\text{O}$ and can provide increased confidence about past SST. This approach has been successfully used in calcitic foraminifera by combining Mg/Ca ratios as an independent palaeothermometer with $\delta^{18}\text{O}$ (e.g. Elderfield and Ganssen, 2000), and in aragonitic corals by using Sr/Ca ratios in conjunction with $\delta^{18}\text{O}$ (e.g. Beck et al., 1997; Gagan et al., 2000). However there has been little success in identifying independent trace element palaeothermometers in the mollusc species so far examined (Carr e et al., 2006; Freitas et al., 2005, 2008; Gentry et al., 2008; Takesue and Van Geen, 2004).

Another potential difficulty in using intertidal and shallow-dwelling marine molluscs in palaeoclimate reconstruction is the global eustatic sea level changes that occur due to the waxing and waning of large ice-sheets during glacial–interglacial cycles. These changes mean that in situ molluscs which grew during glaciations are now significantly beneath sea level (e.g. Sidall et al., 2005). When using intertidal mollusc shells this problem is compounded by their small size and by the destructional nature of most coastal environments, making it difficult to find samples that span a range of time and possible climate conditions. One possible approach to solve this problem of poor preservation (and the approach used in this study) is

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to make use of shells collected by hominins over the last several tens of thousands of years. This may allow the construction of records of seasonality at mid to high latitudes for the Holocene, last glacial and last interglacial periods.

This study investigates 1) whether the stable isotope and elemental composition of *Patella* (limpet) shells allow the reconstruction of seasonal resolution SST and seawater $\delta^{18}\text{O}$, and 2) whether SST seasonality changed during the last glacial using fossil *Patella* shells from Gibraltar.

2. Study site and regional setting

Gibraltar is located at the western edge of the Mediterranean Sea (Fig. 1) where cooler, less saline North Atlantic surface water flows into the Mediterranean Sea and more saline deepwater outflows at relatively shallow depths. The site is ideally located both to investigate the seasonal SSTs of the adjacent North Atlantic waters and to define the characteristics of the initial seawater entering the Mediterranean Sea.

This is a region where seasonally resolved climate records would be of considerable interest. It experiences a strong seasonality in today's climate due to its proximity to the boundary of modern day climate belts. Dry and warm sub-tropical conditions dominate in the summer months, while movement of the major circulation cells and climate belts southward in the winter results in rainfall and lower temperatures. Movement of circulation systems such as the polar front through time could lead to dramatic changes in regional seasonality, with significant implications for climate more generally. For example, the evaporative balance of the Mediterranean is important for ocean circulation (Rogerson et al., 2010), and atmospheric teleconnections exist between the Mediterranean region, North Atlantic (Lionello et al., 2006) and Asian monsoon (Raicich et al., 2003). Changes in seasonality would also have profound implications for human society in the western Mediterranean. Past reconstruction is interesting not only because it may improve our understanding of future possible change, but also because of the importance of the area for human evolution and past societal development.

In the modern era, average annual rainfall at Gibraltar is 775 mm (1984–2005), the majority of which falls during the winter months (UK Meteorological Office, 2006). Monthly average SSTs from 1990 to 2008 range between 15.5 and 23.3 °C giving an average SST seasonality of 7.8 ± 1.1 °C (2 s.d.) (NOAA CIRES ESRL/PSD Climate Diagnostics Branch, Boulder, Colorado, 2006; <http://www.cdc.noaa.gov>). Sea surface salinity (SSS) measurements for the region from World Ocean Atlas 2005 show a small range in monthly average SSS from 36.4 to 36.6 psu (Antonov et al., 2006).

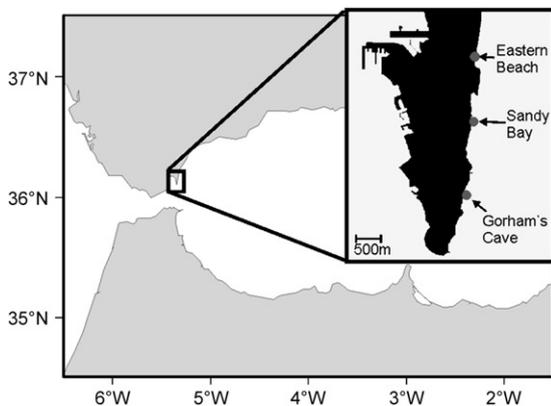


Fig. 1. Map of Gibraltar shell and water collection sites and Gorham's Cave.

In Gibraltar, Neanderthals and Anatomically Modern Humans have gathered molluscs for food for the last ~120 kyrs BP, transporting them inland to cave sites where they have been discovered in recent excavations at sites such as Gorham's Cave (Fa (in press); Finlayson et al., 2006; Stringer et al., 2008). The predominant limpet species found within the caves are the intertidal *Patella vulgata*, *Patella caerulea* and *Patella ferruginea* (Fa (in press)) (the latter is now highly endangered and could not be sampled for modern calibration). Gorham's Cave is a site of particular archaeological interest as it has yielded evidence of the most recent existence of living Neanderthals at 28,000 years BP (Finlayson et al., 2006) making it a highly relevant site at which to investigate climate and its possible influence on the behaviour and extinction of Neanderthals, and the behaviour of early Anatomically Modern Humans (early individuals of *Homo sapiens*).

3. Sampling and analytical techniques

3.1. Seawater sampling and temperature

Coastal water samples were collected approximately every two weeks from March 2006 to November 2007 for $\delta^{18}\text{O}$ analysis. All samples were collected on the open eastern coastline of Gibraltar at Sandy Bay, with the exception of the sample collected on 17/09/2007 at Eastern Beach, a short way to the north (Fig. 1).

In situ seawater temperature measurements are not available at this location so the NOAA Optimum Interpolation (OI) sea surface temperature (SST) data (NOAA CIRES ESRL/PSD Climate Diagnostics Branch, Boulder, Colorado, 2006; <http://www.cdc.noaa.gov>) has been used for comparison with molluscan reconstructed SST records. Weekly SST gridded data is available for a $1 \times 1^\circ$ size grid using the optimum interpolation analysis based on in situ and satellite measurements of SST. The dataset is of use in investigating whether the molluscan reconstructed SST records are representative of the regional water mass properties rather than simply reflecting the variability of immediate coastal waters, which may be more influenced by freshwater inputs or local extremes of temperature in the shallower waters.

3.2. Shell sampling and micromilling

Four modern *Patella rustica* and *P. caerulea* shells were collected from the east Gibraltar coastline (36°07'39"N, 5°20'27.6"W) in November 2005 and November 2007. The mollusc body tissues were removed and the shells soaked in ~15% hydrogen peroxide to remove any remaining organic matter. Based on their preservation and size, 34 fossil shells (*P. caerulea*, *P. vulgata*, *P. ferruginea*) were selected for radiocarbon dating from amongst those excavated from Gorham's Cave. Of these, 14 shells spanning the period 40–19 kyrs BP were analysed to produce oxygen isotope profiles and 10 of these were analysed to produce Mg/Ca ratio profiles. Historical and contemporary empirical data from sites around the world have often shown reductions in body size in *Patella* and similar species through time (Keough et al., 1993; Roy et al., 2003). A significant, although not the sole, contributor to this observed size reduction has been the sustained exploitation of these species over time by humans for food or fish bait. Therefore the duration of the SST records that can be generated from modern *Patella* shells is usually less than those that can be generated from the fossil *Patella* shells. Of the species analysed in this study, *P. caerulea* have been found to be particularly fast-growing and the individuals sampled produced records spanning only 1–2 years compared with the other species which have the potential to record many more years of SST data, although growth rates of all the species can be very variable. With one exception, all the fossil *Patella* shells analysed were the longer-lived *P. ferruginea* and *P. vulgata*.

All shells were cut in half along the direction of maximum growth and, using a New Wave Research Micromill, successive samples of the outer calcite layers ($m+2$ and $m+3$ as shown in Fenger et al., 2007) of each *Patella* shell were milled, parallel to visible growth lines from the shell edge towards the umbo (Fig. 2). Samples were milled, using a tungsten carbide drill bit, at increments varying from 50 to 450 μm , depending on shell thickness and size, and to a depth of 300 μm . Care was taken not to sample the outer surfaces of the shell to avoid contamination from adhering sediment or organic matter.

3.3. Mass spectrometry techniques

Seawater samples were analysed for $\delta^{18}\text{O}$ using headspace equilibration on a Thermo Scientific GasBench II continuous flow preparation system passing into a Thermo Scientific Delta V Advantage Isotope Ratio Mass Spectrometer (IRMS). Repeat measurements of the external water standards IA-R052 and IA-R053 indicate a 1 s.d. precision of 0.05‰ and 0.04‰ respectively ($n=10$). Splits of the milled shell samples were analysed for $\delta^{18}\text{O}$ and Mg/Ca ratios. Oxygen isotope measurements were made using a Thermo Scientific Kiel IV carbonate preparation system, interfaced to a Thermo Scientific Delta V Advantage IRMS, with a standard deviation of NBS-19 of 0.07‰ (1 s.d.; $n=800$). For Mg/Ca ratio analysis, the calcite sample was dissolved in 2% HNO_3 to create a solution close to 10 ppm Ca. These solutions were aspirated using a Cetac Aridus desolvation unit and a PFA microflow nebulizer into a Thermo-Finnigan Element2 HR-ICP-MS. The analysis method uses a peak-hopping method (Rosenthal et al., 1999) normalising trace element signals to Ca. The standard deviation of the matrix-matched standards (2 s.d.; $n=197$) was 2.9% for Mg/Ca ratios.

3.4. Radiocarbon dating of *Patella* shells

In addition to dating the fossil *Patella* shells, modern *Patella* and *Mytilus* were also analysed for radiocarbon content to investigate whether *Patella* incorporate old carbon into their shells from the limestone rocks on which they graze. By comparing the radiocarbon content of live-collected *Patella* with live-collected *Mytilus*, which are filter-feeders, an assessment can be made of the potential uncertainty

that old carbon incorporation could introduce to radiocarbon dates produced from fossil shells. Two *P. rustica* and one *P. caerulea* living at different heights above mean sea level were collected from Sandy Bay in November 2007 and two living *Mytilus galloprovincialis* (intertidal and 5 m depth) were collected in November 2005 for comparison.

A 30–100 μg section was cut from each modern and fossil *Patella* or *Mytilus* shell then rinsed several times in distilled 15 M Ω water and 15% hydrogen peroxide to remove organic matter. The samples were analysed at the NERC Radiocarbon Laboratory in East Kilbride. Radiocarbon dates of the fossil shells were calibrated using Fairbanks et al. (2005) because, while recognising that this curve may still require revision, it covers the entire period of interest whereas the more established marine radiocarbon calibration curve (Hughen et al., 2004) does not extend beyond 21,000 ^{14}C years. A correction was applied for the Mediterranean Sea reservoir age of 390 years (Siani et al., 2000, 2001) which is assumed to be invariant.

4. Results

The average seawater $\delta^{18}\text{O}$ during the period from March 2006 to November 2007 was $1.27\text{‰} \pm 0.30\text{‰}$ VSMOW (2 s.d.). The minimum seawater $\delta^{18}\text{O}$ observed is 0.99‰ and the maximum is 1.67‰ (Fig. 3). Despite the relatively large variability in individual values, seasonal averages of seawater $\delta^{18}\text{O}$ are consistent (ranging from 1.21 to 1.38‰) with the exception of fall 2007 (1.08‰). There is also no clear pattern of seawater $\delta^{18}\text{O}$ variation with time of collection or with wave or wind conditions. The $\delta^{18}\text{O}$ values are more positive than previous open-ocean measurements made near Gibraltar of 0.7–0.9‰ VSMOW (Pierre, 1999). If freshwater inputs were playing an important role in controlling seawater $\delta^{18}\text{O}$ at this location, winter $\delta^{18}\text{O}$ values would be more negative as the majority of rainfall over Gibraltar occurs in these months. Similarly, if evaporation strongly affected seawater $\delta^{18}\text{O}$ then values would be more positive in the summer. No indication of higher $\delta^{18}\text{O}$ in summers relative to winters is observed. Alternative mechanisms must be responsible for the year-round positive values of seawater $\delta^{18}\text{O}$ and the inter-sample variability. One possibility may be upwelling and mixing of saline Mediterranean Deep Water and Levantine Intermediate Water with more positive $\delta^{18}\text{O}$ of 1.3–1.6‰ into surface waters in the Gibraltar Strait but further assessment of this control will require a larger dataset.

All modern *Patella* shells exhibit clear cycles in $\delta^{18}\text{O}$ in the milled carbonate subsamples, with consistent absolute values and ranges (Table 1). Mg/Ca ratios also show clear cyclicity and correlation with paired $\delta^{18}\text{O}$ values in three of the four modern *Patella* shells (Figs. 4 and 5). In the fourth modern shell, *P. rustica* 1, Mg/Ca ratios show no apparent correlation to shell $\delta^{18}\text{O}$ or SST. The consistent Mg/Ca- $\delta^{18}\text{O}$ behaviour also appears to break down in the second year of growth of *P. caerulea* 1 (Fig. 4).

Twelve of the 14 fossil *Patella* shells analysed show clear seasonal cycles in $\delta^{18}\text{O}$. Of the 10 shells analysed for Mg/Ca ratios one shell showed no clear correlation between the cycles in $\delta^{18}\text{O}$ and Mg/Ca ratios and so was not considered when producing SST estimates. The other nine shells yielded clear cycles in Mg/Ca ratios which are well-correlated with $\delta^{18}\text{O}$, examples of which can be seen in Fig. 6. Maximum, minimum and average $\delta^{18}\text{O}$ and Mg/Ca ratios for each fossil shell are listed in Table 1. The complete dataset from all modern and fossil *Patella* shells can be found in Supplementary Information.

Radiocarbon analysis of modern *Mytilus* and *Patella* shells reveals interesting differences (Supplementary Information). While the two *M. galloprovincialis* shells analysed show the same % modern ^{14}C within error ($\sim 105\%$ modern ^{14}C), there is considerable variability between the three *Patella* shells, with the % modern ^{14}C ranging from 87 to 101% which equates to an age offset of up to 1500 years. This difference is likely to be a result of the different feeding strategies of the two molluscs. *Mytilus* are filter feeders so the only sources of

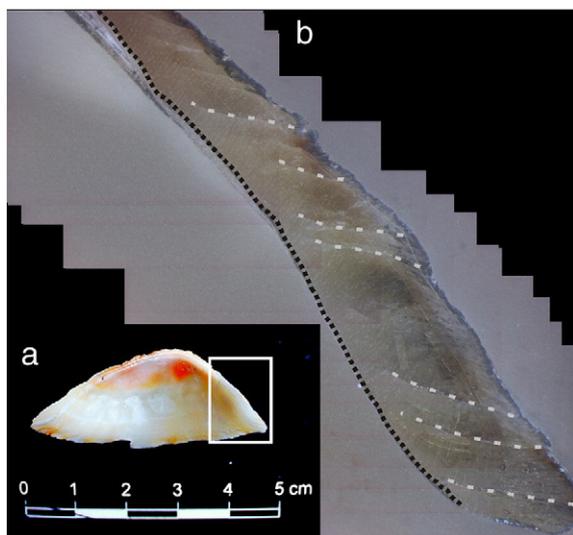


Fig. 2. a) Photograph of a *Patella* shell sliced along the maximum growth axis. The area within the white box is shown at higher resolution in section b). b) The black dotted line marks the boundary between the outer calcite $m+2$ and $m+3$ layers which were subsampled and the inner aragonite and calcite layers (for more details of mollusc layering see Fenger et al., 2007). Some of the major growth lines in the shell have been highlighted using dotted white lines. Subsamples were taken parallel to these growth lines at increments of between 50 and 450 μm using a New Wave Research Micromill.

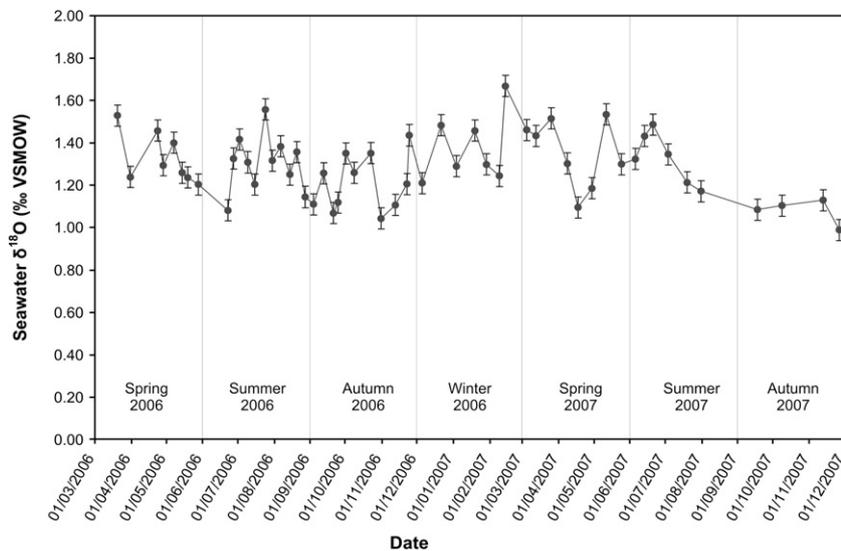


Fig. 3. Seawater $\delta^{18}\text{O}$ measurements from March 2006 to November 2007. Errors on each point are 0.05‰ (1 s.d.). All samples were collected by Darren Fa at Sandy Bay with the exception of the sample collected on 17/09/2007 which is from Eastern Beach. The average seawater during this period was $1.27\text{‰} \pm 0.30\text{‰}$ VSMOW (2 s.d.). There is no clear pattern of seawater $\delta^{18}\text{O}$ variation with either season or time of collection or with wave or wind conditions.

carbon to their shells should be seawater dissolved inorganic carbon (DIC) and marine particulate organic matter (POM), which derives its carbon from seawater DIC. In contrast, *Patella* species are grazers and the rasping and grinding of the *Patella radula* on the host Jurassic limestone rocks of Gibraltar during grazing will result in the incorporation of 'dead' carbon containing no ^{14}C . A similar age offset of ~600 years has been observed in Hawaii, between limpets living on limestone and those living on volcanic rocks (Dye, 1994). This dead carbon effect increases the uncertainty on the radiocarbon dates of the fossil *Patella* shells from Gorham's Cave (see Fig. 7 and Supplementary Information) and limits the precise placement of each shell in relation to millennial scale abrupt climate events (Bond and Lotti, 1995).

5. Discussion

5.1. Fidelity of SST seasonality estimates from modern *Patella* shell $\delta^{18}\text{O}$

The oxygen isotope composition of biogenic calcium carbonate is usually assumed to be primarily a function of water temperature and water $\delta^{18}\text{O}$. The oxygen isotope profiles of the modern *Patella* shells can be converted to SST using the average measured seawater $\delta^{18}\text{O}$ value of 1.27‰ VSMOW (converted to VPDB by subtracting 0.27‰

(Hut, 1987)), and the calcite–water $\delta^{18}\text{O}$ relationship defined by O'Neil et al. (1969):

$$\text{SST}(\text{°C}) = 16.9 - 4.38(\delta_c - \delta_w) + 0.1(\delta_c - \delta_w)^2 \quad (1)$$

where $\delta_c = \delta^{18}\text{O}$ of calcite (‰ VPDB) and $\delta_w = \delta^{18}\text{O}$ of seawater (‰ VPDB). However, in order to match the reconstructed SST with the NOAA SST dataset (Fig. 4) it is necessary to include a constant positive offset to the carbonate data from the O'Neil et al. (1969) relationship of 0.72‰ , otherwise both winter and summer reconstructed SSTs are approximately 3°C too cold. This offset is too large and seasonally consistent to be due to potential differences between the satellite-derived SST record and site-specific intertidal seawater temperatures. A similar positive offset from equilibrium has also been identified in other *Patella* species including an offset of $\approx 1\text{‰}$ in *P. vulgata* (Fenger et al., 2007) and 0.7‰ in *Patella tabularis* (Cohen and Tyson, 1995; Shackleton, 1973). The difficulty in comparing the size of the offset between species is that it is very dependent on the seawater $\delta^{18}\text{O}$ value used. Given the uncertainties in seawater $\delta^{18}\text{O}$ due to the lower spatial and temporal resolution sampling in previous studies, the magnitude of the positive offset is remarkably similar between studies and implies very little or no difference in the size of the vital effect between the *Patella* species. This similarity suggests that the offset is

Table 1
Maximum, minimum and average $\delta^{18}\text{O}$ (‰ VPDB) and Mg/Ca ratios (mmol/mol) for all modern and fossil *Patella* shells.

Shell	Age (yrs BP)	Min $\delta^{18}\text{O}$ (‰ VPDB)	Max $\delta^{18}\text{O}$ (‰ VPDB)	Average $\delta^{18}\text{O}$ (‰ VPDB)	Min Mg/Ca (mmol/mol)	Max Mg/Ca (mmol/mol)	Average Mg/Ca (mmol/mol)
Limpet 1	Modern	0.37	1.93	1.34	17.65	25.28	20.91
Limpet 2	Modern	0.54	2.46	1.54	16.40	25.20	20.56
Limpet 0	Modern	0.66	2.22	1.57	17.26	29.62	20.84
Limpet 30	Modern	0.13	1.92	1.03	17.31	25.55	22.04
JG-19	19,127	2.80	4.84	3.80	11.71	18.38	14.49
JG1-a1a	24,513	2.66	5.17	4.12	11.26	18.39	14.21
JG1-B3	24,808	2.64	4.74	3.88	12.03	18.76	14.22
JG3-AA7v	27,522	2.18	5.09	4.02	12.43	28.05	15.69
JG4-58	28,650	1.87	4.20	3.04	13.98	22.02	17.26
JG3-AA7f	28,903	1.75	4.07	3.33	14.73	22.60	16.96
JG4-66	36,484	1.28	3.73	2.83	16.29	22.30	17.86
JG1-C3	36,561	1.67	3.75	2.77	14.17	25.63	17.96
JG4-A8	38,588	1.89	3.84	3.10	11.34	19.04	14.47

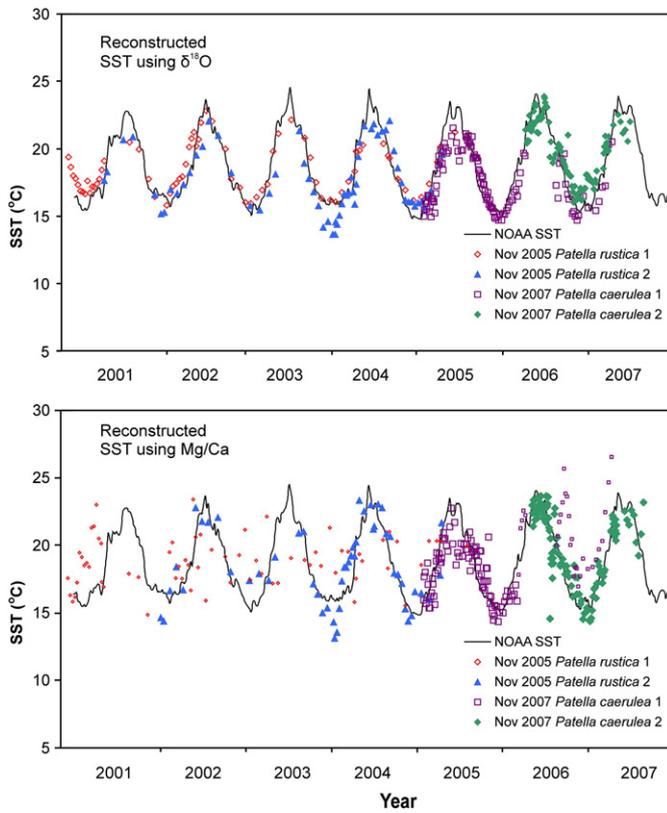


Fig. 4. Comparison of observed weekly NOAA SST with that reconstructed from *Patella* shell $\delta^{18}\text{O}$ and Mg/Ca ratios. *P. rustica* 1 and 2 were collected in November 2005 and *P. caerulea* 1 and 2 were collected at 0 cm and 30 cm respectively above low tide in November 2007. The timescale for each record was constructed by matching the peaks and troughs of the $\delta^{18}\text{O}$ time series to seasonal variations in the instrumental SST record. The $\delta^{18}\text{O}$ and Mg/Ca ratios of the individual *Patella* shells capture more than 80% of the monthly annual cycle in SST. Upper panel: SST reconstructed using a positive offset from equilibrium in the shells of 0.72‰, a seawater $\delta^{18}\text{O} = 1.27\text{‰}$ VSMOW (from Fig. 3), converted to VPDB by subtracting 0.27‰ (Hut, 1987), and $\text{SST} (\text{°C}) = 16.9 - 4.38 (\delta^{18}\text{O}_{\text{shell}} - \delta^{18}\text{O}_{\text{seawater}}) + 0.1 (\delta^{18}\text{O}_{\text{shell}} - \delta^{18}\text{O}_{\text{seawater}})^2$ (O’Neil et al., 1969); Lower panel: SST reconstructed using the relationship between Mg/Ca ratios and SST described in Fig. 5. Data which are uncertain and so not used when constructing the Mg/Ca-SST calibration are shown with smaller symbols. These data are the second year of growth (only observed in this one shell) of *P. caerulea* 1 and the data from *P. rustica* 1.

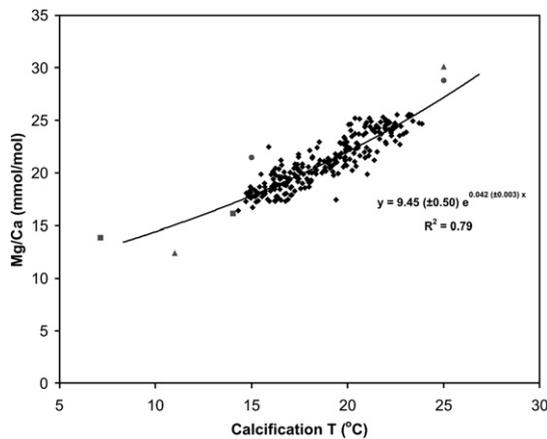


Fig. 5. Mg/Ca-SST relationship for modern limpets in this study: data from this study are shown as diamonds and plotted against calcification temperature. The best fit through this data is $\text{Mg/Ca} (\text{mmol/mol}) = 9.454 (\pm 0.498) \exp (0.042 (\pm 0.003) \text{SST} (\text{°C}))$ and is shown as the curve. Maximum and minimum coarse resolution Mg/Ca ratios and suggested SST from *P. vulgata* from England (Fenger et al., 2007) and from *P. caerulea* from Italy (Schifano, 1982; Schifano and Censi, 1986) are plotted as squares, circles and triangles respectively for comparison and match well to the best fit of the data in this study.

not due to micro-environmental effects, such as desiccation stress, but is rather a result of a calcification process seen in all *Patella* species so far analysed. While the exact mechanism responsible for this consistent positive offset from equilibrium remains unclear (Fenger et al., 2007) a 0.72‰ positive offset was used when reconstructing SSTs from shells of all modern and fossil *Patella* in this study.

The SST records generated from the $\delta^{18}\text{O}$ profiles of the four modern *Patella* shells have been plotted in Fig. 4 against the weekly average NOAA SST dataset. The length scale has been converted to time by stretching to give a best fit between the reconstructed molluscan SSTs and the observed weekly average SSTs using the collection date as a fixed point. There is a very good correlation between the NOAA SST dataset and the $\delta^{18}\text{O}$ -reconstructed molluscan SSTs, although *P. rustica* 2 produces SSTs about 2 °C too cold during winter 2003/2004. The four *Patella* shells record between 82 and 107% of the observed range in monthly average SST around Gibraltar (~7.5 °C). Regular sample intervals are used when milling the shells so if growth slows or ceases for an interval due to biological factors, such as age (Sato, 1995), or environmental factors, such as temperature (Goodwin et al., 2001), then larger amounts of time are averaged (Goodwin et al., 2003). The range in SST recorded by each shell must therefore be considered a minimum. The fact that these modern samples capture >80% of the monthly average SST range, however, suggests that the true seasonality is not much larger than that observed in the shells. Although no clear seasonal cycles in seawater $\delta^{18}\text{O}$ were observed, using an average seawater $\delta^{18}\text{O}$ value to reconstruct SST from shell $\delta^{18}\text{O}$ could also introduce error to seasonality estimates. The 2 s.d. of the measured seawater $\delta^{18}\text{O}$ values (~0.3‰) equates to an uncertainty in reconstructed temperature of ± 1.3 °C, but this should be considered as a maximum uncertainty that could result due to seawater $\delta^{18}\text{O}$ changes because the carbonate will average seawater $\delta^{18}\text{O}$ variability during its growth interval in a way that periodic bottle sampling of seawater does not.

5.2. Mg/Ca ratios as an independent palaeothermometer in *Patella* shells

There has been little success in identifying independent trace-element palaeothermometers in mollusc shells (e.g. Freitas et al., 2008; Gillikin et al., 2005; Vander Putten et al., 2000). Without such an independent palaeothermometer, considerable uncertainties can be introduced to $\delta^{18}\text{O}$ -derived palaeo-SST estimates due to the necessity of assuming a seawater $\delta^{18}\text{O}$ value. However, the results of this study show a consistent relationship between calcification temperatures, calculated from shell $\delta^{18}\text{O}$, and Mg/Ca ratios in the majority of modern *Patella* shells allowing a calibration curve to be constructed (Fig. 5). It is unclear why the Mg/Ca-SST relationship observed in three of the four modern *Patella* shells analysed does not exist in the fourth – *P. rustica* 1. It is also difficult to explain why the consistent Mg/Ca-SST behaviour breaks down in the second year of growth of *P. caerulea* 1 which was the only shell of this very fast growing *Patella* species to show a second year of growth in this study. This was the only modern or fossil *Patella* shell in this study to show any evidence of a potential ontogenetic trend in Mg/Ca (Fig. 6, Supplementary Information). The data from *P. rustica* 1 and the second year of *P. caerulea* 1 were excluded from the modern dataset used to define the Mg/Ca-temperature relationship. The remaining data were used to construct a *Patella* shell Mg/Ca-temperature calibration curve (Fig. 5). Also plotted are the minimum and maximum Mg/Ca ratios at coarse resolution from previous studies (*P. vulgata* (Fenger et al., 2007) and *P. caerulea* (Schifano, 1982; Schifano and Censi, 1986)) paired with minimum and maximum quoted SSTs for each location. This literature data plots close to the constructed calibration curve and implies that there is a consistent Mg/Ca-SST relationship in the *Patella* species so far examined.

The sensitivity of *Patella* Mg/Ca ratios to temperature is ~4% per °C and is broadly comparable with that seen in other biogenic

carbonates. Benthic and planktonic foraminifera, for instance have a Mg/Ca ratio sensitivity of $\sim 10\%$ per $^{\circ}\text{C}$ (Elderfield and Ganssen, 2000; Lear et al., 2002). The sensitivity of Mg/Ca ratios in biogenic carbonate is, in general, significantly higher than that found in inorganic carbonates and its origin remains rather enigmatic. Calibrations for Mg/Ca ratio palaeothermometers, including the much used foraminiferal examples, therefore rely on empirical relationships such as that observed in this study for *Patella*, and exhibit a similar degree of scatter about a single relationship as that seen in this study (Fig. 5).

Further calibration work in a variety of *Patella* species would be useful to further refine the observed relationship and to investigate the possible causes of breakdowns in consistent Mg/Ca-SST behaviour, including biological factors such as life position. Such studies could reinforce *Patella* shell Mg/Ca ratios as a powerful tool in producing seasonal-resolution SSTs.

Fortunately, it is possible to identify and screen for shells where there is a breakdown in Mg/Ca-SST behaviour by looking for marked differences in the $\delta^{18}\text{O}$ and Mg/Ca ratio profiles. The small number of fossil shells where distinct differences were observed between $\delta^{18}\text{O}$ and Mg/Ca ratios were not used for further analysis. In shells where consistent behaviour is seen, Mg/Ca ratios allow the deconvolution of the temperature and seawater $\delta^{18}\text{O}$ signals from the measured shell $\delta^{18}\text{O}$. For the 9 glacial age shells in this study where such analysis is possible, no clear seasonal cyclicity in reconstructed seawater $\delta^{18}\text{O}$ is observed. The lack of seasonal cycles in glacial seawater $\delta^{18}\text{O}$ is in agreement with the lack of cycles in modern direct observations of seawater $\delta^{18}\text{O}$. The average reconstructed seawater $\delta^{18}\text{O}$ for each shell was used to calculate seasonal variations in SSTs from shell $\delta^{18}\text{O}$ profiles using Eq. (1). This negates the need to assume a seawater $\delta^{18}\text{O}$ value, which is otherwise normally the largest uncertainty associated with estimating SST from mollusc $\delta^{18}\text{O}$. The deconvolved average seawater $\delta^{18}\text{O}$ for individual shells range from 1.0 to 2.6‰ VSMOW and differ from seawater $\delta^{18}\text{O}$ predicted from a sea level record (Sidall et al., 2005) by -0.9 to $+0.25\%$, equivalent to a SST discrepancy of up to 4°C . These results highlight the potential errors that can be introduced to palaeo-SSTs made using shell $\delta^{18}\text{O}$ by assuming

seawater $\delta^{18}\text{O}$ values and emphasise the need to continue investigations into independent palaeothermometers within mollusc shells and to further explore the promise of Mg/Ca palaeothermometry in limpets.

5.3. Past seasonality in SST at Gibraltar

The combined Mg/Ca ratios and $\delta^{18}\text{O}$ data from the glacial limpet shells show that summer SSTs cool gradually between 40 and 19 kyrs BP and appear to follow the trend of summer insolation with the exception of the *Patella* shell thought to date from Heinrich 4 (Fig. 7). The incorporation of dead carbon into the shells makes assigning shells to specific millennial events difficult but this shell shows much colder SSTs and lighter seawater $\delta^{18}\text{O}$ (Fig. 6) which may correspond to the release of fresh, isotopically light water into the North Atlantic from large ice discharges which disrupts the Atlantic meridional overturning circulation and results in cooling (Broecker, 1994). In contrast, winter SSTs bear no resemblance to the trend in winter insolation (Fig. 7). This results in a range of seasonality during the last glacial, probably reflecting the variable mean climate of this time. The average SST range of the nine glacial samples ($10.0 \pm 1.3^{\circ}\text{C}$ (1 s.d.)) is about 2°C greater than the average SST range of the four modern samples ($7.5 \pm 0.8^{\circ}\text{C}$ (1 s.d.)) and the modern observational monthly SST seasonality ($7.8 \pm 1.1^{\circ}\text{C}$ between 1990 and 2007). Because the limpet records represent a minimum SST range, this is convincing evidence that the seasonal range during the glacial was larger than today's.

Average SSTs from each shell, derived from the $\delta^{18}\text{O}$ and Mg/Ca ratios, are generally in good agreement with downcore alkenone palaeo-SST records from the Alboran Sea and nearby North Atlantic Ocean (Fig. 7) (Cacho et al., 1999, 2000, 2002) showing a 7°C change between full glacial and modern conditions. There are no seasonal-resolution SST records in the Mediterranean for the last glacial with which to directly compare the seasonal-resolution results of this study. However, seasonal estimates of Last Glacial Maximum (LGM) SST have been made throughout the Mediterranean Sea using

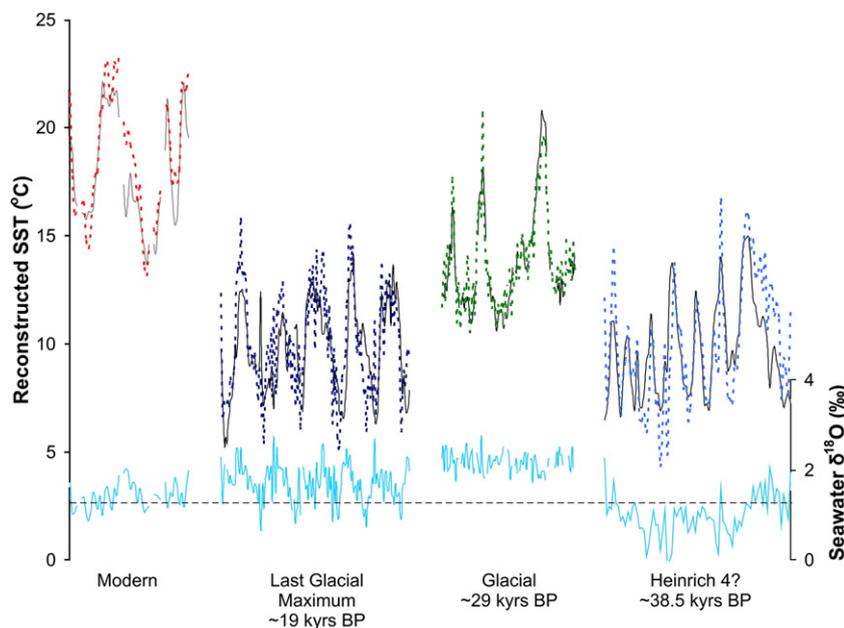


Fig. 6. Reconstructed SST ($^{\circ}\text{C}$) and seawater $\delta^{18}\text{O}$ profiles of one modern and three radiocarbon dated *Patella* shells with an arbitrary length scale. These are typical examples of the shells studied (data and figures for all other shells are provided in the Supplementary material). Quoted ages are calendar ages calibrated (Fairbanks et al., 2005) and corrected for the Mediterranean Sea reservoir age of 390 year (Siani et al., 2000, 2001), but may be up to 1500 years too old due to incorporation of dead carbon from limestone rocks. Dashed coloured lines reflect Mg/Ca-derived SSTs and solid black lines reflect $\delta^{18}\text{O}$ -derived SSTs using the average deconvolved seawater $\delta^{18}\text{O}$ value for each shell. The direction of growth for each shell is from right to left. Light blue lines reflect deconvolved seawater $\delta^{18}\text{O}$ values with the dashed black line showing the average modern seawater $\delta^{18}\text{O}$ of 1.27‰ VSMOW.

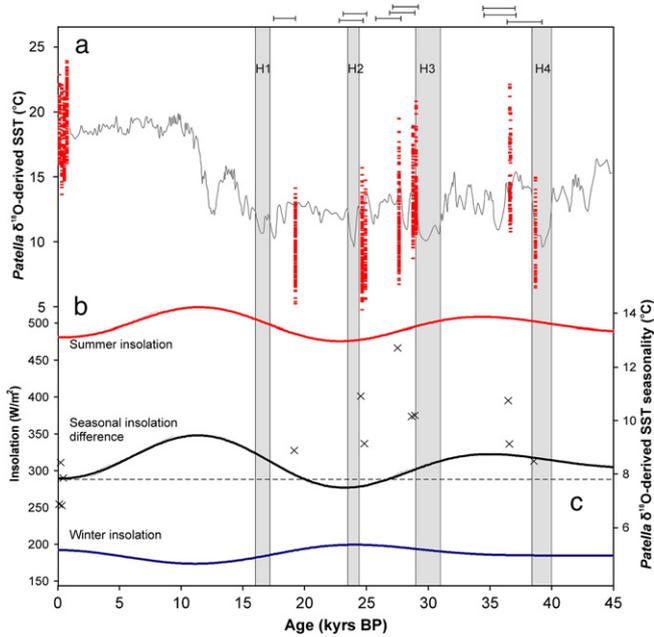


Fig. 7. a) Intra-shell $\delta^{18}\text{O}$ -derived SST data points from each modern and fossil *Patella* shell against time using average seawater $\delta^{18}\text{O}$ reconstructed using Mg/Ca ratios. Also plotted is the mean annual SST reconstructed by Cacho et al. (1999) using alkenones from the nearby Alboran Sea. b) Summer and winter insolation seasonality (W/m^2) and their difference at the latitude of Gibraltar (35°N), with c) the seasonality ($^\circ\text{C}$) of each individual *Patella* shell plotted as a grey cross for comparison. The scales of b) and c) have been drawn such that the dashed line represents both the modern seasonal insolation difference and the mean of modern SST seasonality assessed using the four modern limpets. Note that all glacial limpets exhibit greater seasonality than the modern samples, and that there is no apparent relationship between observed seasonality and the seasonal range of insolation. Heinrich Events 1–4 are shown as grey bars and are labelled H1 to H4.

foraminiferal assemblages (Hayes et al., 2005). Comparison of these estimates with the reconstructed SST from a *Patella* shell dated at 19 kyrs BP (shown in Figs. 6 and 7) shows that the *Patella* shell records greater SST seasonality with warmer summers ($\sim 16.5^\circ\text{C}$) and colder winters ($\sim 7.5^\circ\text{C}$) than observed in reconstructions using foraminiferal assemblages (13–15 $^\circ\text{C}$ summer SSTs and 9–11 $^\circ\text{C}$ winter SSTs). Part of this discrepancy is likely to be a result of the higher resolution (sub-monthly) record from the *Patella* shells with respect to the seasonal averages produced using other proxies. Another possible explanation for the observed difference is that there may be changes in the depth habitat and season of growth for microfossil species during climate states very different from today. This shows the importance of developing season-resolution SST proxies for the mid to high latitudes, because important climate information such as winter SST minima can be lost when using proxies that are biased to a single season, rather than capturing the full seasonal cycle.

The increased cooling of glacial winter SSTs in the Western Mediterranean that we observe is, however, supported by terrestrial evidence in Southern Europe. LGM air temperatures reconstructed using pollen records on the coast of the Alboran Sea, indicate a cooling of 9°C in annual air temperatures but a much greater cooling of 15°C in the air temperature of the coldest month (Peyron et al., 1998).

Differences between summer and winter insolation are not a good predictor for changes in observed seasonality in the Mediterranean. At the LGM, for instance, the seasonal range of insolation was smaller than that of today (Fig. 7), but observed SST seasonality (based on two samples) is 2.1°C larger than today. This implies that regional climate feedbacks rather than insolation are controlling SST in the Mediterranean region. This is especially true of the *Patella* shell thought to date from Heinrich 4. It appears that the presence of Northern Hemisphere ice sheets and their influence on the North Atlantic ocean circulation

results in greater cooling of winter temperatures during the last glacial. At that time, the polar front extended southwards, eventually reaching a latitude south of 40°N on the Iberian coast at the LGM (Ruddiman and McIntyre, 1981; Siani et al., 2001). Evidence for a southward movement of the polar front is also available from reconstructions of wind patterns in the Mediterranean (Florineth and Schlüchter, 2000). The southward movement of the polar front would allow a southward extension of winter sea ice during the last glacial. The presence of winter sea ice at lower latitudes could explain the greater cooling of winter temperatures compared to summer temperatures seen both in the west Mediterranean Sea LGM SST records of this study and also in the LGM seasonal air temperature evidence in Europe (Atkinson et al., 1987; Isarin et al., 1998; Peyron et al., 1998).

These *Patella* SST records indicate that both the absolute SST and the seasonal distribution of SST in current model outputs for the LGM (Kageyama et al., 2006) are not well represented. Six models run during PMIP2 (Braconnot et al., 2007) show a cooling of $\sim 3.5^\circ\text{C}$ in summer SST and $\sim 3^\circ\text{C}$ in winter SST at 21 kyrs BP relative to present-day model runs (Supplementary Fig. 1). This is in stark contrast to the results of this study, showing an average increase in seasonal SST range of $\sim 2^\circ\text{C}$ and a cooling of $\sim 7^\circ\text{C}$ in summer SST and up to 9°C in winter SST. This highlights the need to test models not only against mean palaeoclimate but against seasonal-resolution data from the past. This is particularly true for the many regions of the world where changes in seasonality may be large, or may play a substantive role in climate processes that control mean climate.

6. Conclusions

1. When seawater $\delta^{18}\text{O}$ is known or can be estimated, *Patella* shell $\delta^{18}\text{O}$ records allow the reconstruction of greater than 80% of the monthly average range in SST albeit with a positive offset from equilibrium of 0.72‰ . This positive offset is consistent with previous studies of *Patella* species.
2. A consistent relationship between Mg/Ca ratios and SST is observed in the majority of modern *Patella* shells. Applying this relationship to fossil shells allows independent estimation of past SST and therefore of the average seawater $\delta^{18}\text{O}$. It is possible to screen for shells in which the Mg/Ca–SST relationship breaks down since no correlation is observed between the $\delta^{18}\text{O}$ and Mg/Ca ratio records in such shells.
3. Analysis of fossil *Patella* shells from Gorham's Cave on Gibraltar spanning the last glacial period allows the reconstruction of the first extra-tropical seasonal-resolution SST records for the last glacial. Individual shells show a gradual cooling of summer and winter SSTs from 40 to 19 kyrs. The average range in SST during the glacial was $\sim 10.0^\circ\text{C}$ which is $\sim 2^\circ\text{C}$ greater than today. Mean SSTs from the *Patella* shells are generally in good agreement with existing proxy data from the region.
4. The *Patella* shell records suggest that both absolute SSTs and the range in seasonal SSTs in current climate models are not well-represented in the western Mediterranean region. This highlights the need for further seasonal-resolution SST records at mid to high latitudes for regions where discrepancies exist between proxy data and palaeoclimate model outputs to better understand the role that seasonality plays in controlling mean climate.

Supplementary materials related to this article can be found online at [doi:10.1016/j.epsl.2011.05.054](https://doi.org/10.1016/j.epsl.2011.05.054).

Acknowledgements

This work was funded with a Natural Environmental Research Council (NERC) studentship and a NERC facilities grant for radiocarbon analyses. Radiocarbon samples were prepared to graphite at the NERC Radiocarbon Facility and analysed at the SUERCAMS in East Kilbride. We

would like to thank Geoff Bailey and Naomi Belshaw for initially putting Oxford and Gibraltar scientists in touch with one another. We also thank Cees-Jan de Hoog for assistance in trace element analysis and Mike Floyd for producing Supplementary Fig. 1.

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