

## Surface temperatures coupled with carbon dioxide concentrations during the Paleozoic Era

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### SUPPLEMENTARY INFORMATION

#### Appropriateness of the inorganic $\Delta_{47}$ -temperature calibration for brachiopods and molluscs

Ghosh *et al.* (2006)<sup>1</sup> determined the relationship between  $\Delta_{47}$  and temperature (Eq 4) by analyzing the  $\text{CO}_2$  extracted from synthetic calcites grown in the laboratory at known, controlled temperatures. In addition, they analyzed natural surface-dwelling corals (*Porites*) and deep-sea corals (*D. dianthus*), which grew at known, approximately constant temperatures<sup>1</sup>. Their results indicate that the vital effects that influence the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of surface-dwelling and deep-sea corals do not influence the  $\Delta_{47}$  values of the  $\text{CO}_2$  extracted from that carbonate<sup>1</sup>. This result is consistent with models for vital effects<sup>2,3</sup>, which describe the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  offsets as reservoir effects, rather than kinetic fractionations. Recent calibration work<sup>4</sup> reveals that fish otolith carbonate, which also suffers from vital effects in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , does not exhibit a significant offset from the Ghosh *et al.* (2006)<sup>1</sup> calibration of the relationship between growth temperature and the  $\Delta_{47}$  of  $\text{CO}_2$ .

As part of the current study, we analyzed naturally occurring brachiopods and molluscs (the two phyla from which we obtained Paleozoic temperatures based on carbonate clumped isotope thermometry) that grew at known temperatures in the modern ocean (see Supplementary Table 1 and Supplementary Figure 1). The  $\Delta_{47}$  values of  $\text{CO}_2$  extracted from brachiopod carbonate are plotted vs. mean annual temperatures<sup>5</sup>, whereas the  $\Delta_{47}$  values of  $\text{CO}_2$  extracted from mollusc carbonate,

Supplementary Table 1. Stable isotopic compositions of brachiopods and molluscs grown at known temperatures

Sample ID	Species	Lat.	Lon.	Depth (m)	Growth T (°C)*	$\delta^{18}\text{O}$ (‰; PDB)	$\delta^{13}\text{C}$ (‰; PDB)	$\Delta_{47}$ (‰ ± 1 Std. Err.)
<i>Brachiopods</i>								
BR 22	<i>Tichosina floridensis</i>	25.2°N	83.9°W	118	21.5	1.05	2.82	0.65 ± 0.007
RB 31	<i>Thecidellina blochmanni</i>	22.3°S	40.3°E	55	24.5	-1.16	1.60	0.64 ± 0.011
BR 14	<i>Terebratulina septentrionalis</i>	42.3°N	65.8°W	118	10.0	2.41	1.66	0.72 ± 0.012
<i>Molluscs</i>								
S-1	<i>Arctica islandica</i>	69.7°N	18.9°E	5-10	8.8	2.68	1.59	0.71 ± 0.005
S-6	<i>Chlamys islandica</i>	46.0°N	56.0°W	70	3.6	2.32	1.49	0.74 ± 0.008
S-7	<i>Paphya crassiscula</i>	17.8°S	146.1°E	0-2	28.0	-1.07	1.46	0.64 ± 0.012

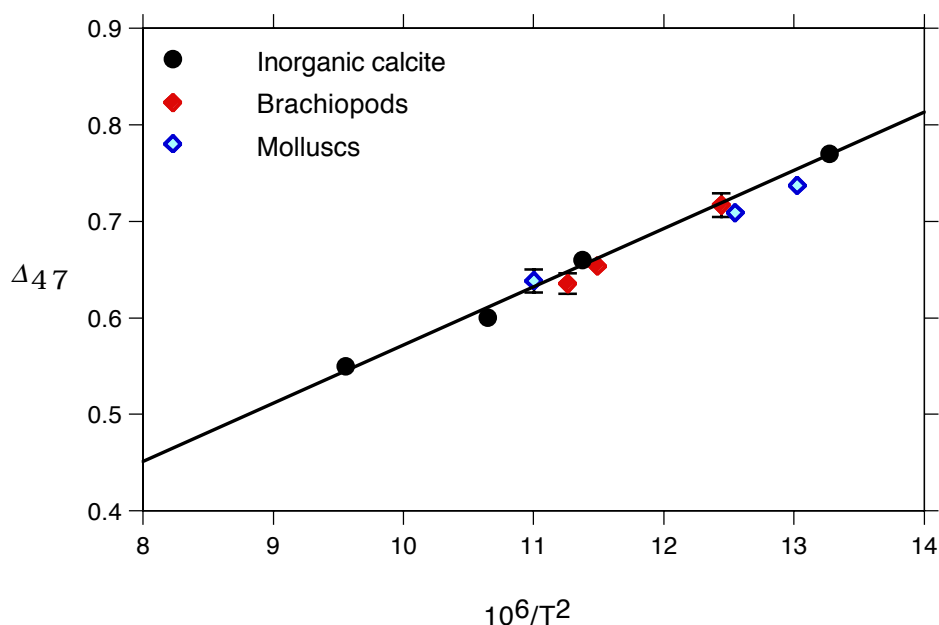
\* Brachiopod growth temperatures are mean annual temperatures, and mollusc growth temperatures are the mean of the warmest six months of the year<sup>6</sup>. Growth temperatures were taken from Levitus and Boyer (1994)<sup>5</sup>.

which records temperatures in the warmest 6 months of the year<sup>6</sup>, are plotted vs. the mean of the warmest 6 months<sup>6</sup>. Our modern calibration materials agree very well (mean deviation of  $\pm 0.009$  ‰ in  $\Delta_{47}$  of  $\text{CO}_2$ ) with the Ghosh *et al.* (2006)<sup>1</sup> temperature relationship for synthetic calcites.

Previous work on brachiopods and molluscs has shown that these organisms generally precipitate carbonate shells in isotopic equilibrium with the waters in which they form<sup>7,8</sup>, without any apparent vital effects. Given this previous evidence for equilibrium carbonate growth in molluscs and brachiopods, and our new calibration results, we suggest that vital effects are unlikely to influence the temperature estimates obtained for fossil molluscs and brachiopods based on carbonate clumped isotope thermometry.

### Calcification depths

The Silurian brachiopods and mid-Pennsylvanian molluscs analyzed in this study were collected from sedimentary rocks which were originally deposited in tropical, shallow-marine environments<sup>9,10</sup>. Although the exact growth depths of the analyzed samples are not known for certain, a study involving the Lower Silurian (Llandovery) carbonate succession of Anticosti Island suggests that the brachiopod species used in this study (*Pentamerus spp.*) lived at depths significantly below the surface (~20-90 meters)<sup>9</sup>. We suggest, therefore, that the temperatures we present here provide minimum estimates of the actual sea surface temperatures.



**Supplementary Figure 1.** Values of  $\Delta_{47}$  of  $\text{CO}_2$  extracted from calcium carbonate grown from aqueous solution (black circles)<sup>1</sup>, brachiopods (red diamonds), and molluscs (blue open diamonds) plotted vs.  $10^6/T^2$ , where T is the known growth temperature in kelvins. Error bars represent 1 standard error on individual analyses.

### Trace and minor element data for Mid-Pennsylvanian molluscs from the Boggy Formation, Oklahoma

Early Silurian brachiopod samples were visually examined under a binocular microscope to determine their extent of preservation<sup>9</sup>. Our suite includes equal numbers of samples that appear to have excellent preservation and samples that appear to be moderately altered (i.e., so we can systematically examine the effects of alteration on the isotopic record). Carboniferous (mid-Desmoinesian, i.e., Middle Pennsylvanian) aragonitic mollusc samples are relatively well preserved because the formation was sealed by asphalt by the end of mid-Virgilian time<sup>10</sup>, limiting interaction with meteoric or marine waters (but not formation waters). All analyzed mollusc samples are dominated by primary aragonite, although some calcite replacement is observed<sup>11,12</sup>. We monitored the extent of sample alteration in this suite based on x-ray diffraction measurements of the calcite/aragonite ratio, and through analyses of the concentrations of elements that are added to fossil carbonate during alteration (e.g., Fe and Mn).

Trace and minor element data for Mid-Pennsylvanian molluscs from the Boggy Formation are presented in Supplementary Table 2<sup>11,12</sup>. (Trace and minor element data for sample B0-01 were not available.) The low-Fe, low-Mn, aragonite-rich sub-set of this suite (samples B81-21, B81-18 and B81-06x) most closely preserves their depositional isotopic compositions. The trace and minor element data for sample B0-04 also meet our criteria for a pristine sample; however, based on the position of B0-04 in our  $\delta^{18}\text{O}$  vs.  $\delta^{13}\text{C}$  of carbonate plot (Figure 1a), we consider it likely that this sample underwent post-depositional alteration that did not have obvious effects on these indices (Table 1). If sample B0-04 had been included in our “unaltered” sub-set, the results would yield nominal growth conditions of  $24.6 \pm 1.4^\circ\text{C}$  and seawater  $\delta^{18}\text{O}$  of  $-1.3 \pm 0.6\text{‰}$ . These averages are similar to those reported in the body of our manuscript and would not significantly change our interpretations.

Supplementary Table 2. Trace and minor element data for the Boggy Formation samples.<sup>12</sup>

Sample ID	Aragonite (%)	Ca (ppm)	Mg (ppm)	Sr (ppm)	Mn (ppm)	Na (ppm)	Al (ppm)	Fe (ppm)
B81-10	90	365,810	230	1,380	80	3,500	10	320
B81-18	100	338,390	80	1,520	20	4,720	10	60
B81-21	95	378,640	190	1,450	20	4,380	0	80
B81-27	81	370,590	130	2,020	20	3,270	20	40
B81-09	69	372,140	330	1,620	110	3,020	10	500
B81-40	92	316,840	210	1,800	40	2,640	10	130
B81-06x	Arag*	311,900	80	2,150	20	3,650	30	60
BO-04	Arag*	347,200	70	1,670	10	3,420	30	20

\* No % data available. The sample was identified as aragonite.

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