Reassessment of ocean paleotemperatures during the Late Ordovician

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SUPPLEMENTARY MATERIALS

Geological Setting

Paleogeographic reconstructions place the Cincinnati Arch of North America in the southern subtropics, approximately 23-27°S, during the beginning of the Late Ordovician (Scotese, 2016). At the time of deposition, an epeiric sea covered much of Laurentia. The Taconic Orogeny along eastern Laurentia created the Appalachian foreland basin. The Cincinnati Arch was a peripheral bulge within that basin (Fig. 1) (Pope et al., 2012). Cool-water subtidal and peritidal carbonates were deposited on the Jessamine Dome of the Cincinnati Arch throughout the Late Ordovician (Kolata et al., 2001). Twenty-eight calcitic brachiopods were analyzed from these Late Ordovician strata.

Burial History

Regional burial history studies using conodont CAI or vitrinite reflectance suggest that these strata experienced burial temperatures lower than 90 °C during the Late Paleozoic. Conodonts with a CAI of up to 1.5 occur within the Cincinnati strata

21 indicating minimal burial (<1 to 2 km), with maximum burial temperatures of < 50 to 90
22 °C for the Upper Ordovician sediments during the Mississippian to the early Permian
23 (Epstein et al., 1977). Between 1.3 and 2 km of overlying Late Paleozoic sediments were
24 eroded during the Mesozoic and Cenozoic (Stearns and Reesman, 1986). This allowed
25 for a maximum burial depth of at most 2.4 km, with maximum burial temperatures of
26 ~85 °C.

27 **Diagenetic Evaluation**

28   A thin section of each sample was examined under standard optical microscopy
29 for breaks in the original crystal fabric, such as filled fractures, corrosion, and secondary
30 mineral phases (e.g., pyrite). Secondly, thin sections were viewed using
31 cathodoluminescence (CL) microscopy with a Technosyn 8200 MKII cold cathode
32 luminoscope. Samples were exposed to a beam current and voltage of 200-300 nA, and
33 10-15 kV, respectively, for 60 seconds (Roark et al., 2017). Enrichment of Mn^{2+} above
34 ~25 ppm in the crystal lattice of calcite causes orange luminescence (Mason, 1987),
35 which typically indicates diagenesis in brachiopod shells (Popp et al., 1986; Grossman et
36 al., 1996). This is because Mn^{2+} is uncommon in oxygenated bottom waters but very
37 common in anoxic ground and pore waters. Thus, unaltered areas of the shells should
38 consist of non-luminescent areas free of visible dissolution and cementation features.
39 Note that Mn^{2+} may not be incorporated in diagenetic calcite precipitated in oxic or iron-
40 free waters, thus it is important to confirm cathodoluminescence in cements and
41 texturally altered grains (Grossman, 1994). Using a gradational scale of
42 cathodoluminescence, the shells were labeled as non-luminescent (NL), slightly

43 luminescent (SL), cathodoluminescent (CL), or some combination. The five categories
44 are NL, NL/SL, SL, SL/CL, and CL (See Figure 6 in Grossman, 2012). Shells were
45 sampled from several NL shell areas or NL/SL areas when NL areas were unavailable.

46 As a supplement to the textural and CL examination, trace elements were used as
47 a secondary criterion of alteration within the brachiopod shells. Diagenetic alteration
48 can lead to an increase in Fe^{2+} and Mn^{2+} and a decrease in Sr^{2+} . These trends are often
49 associated with depletions in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Brand and Veizer, 1980; Brand et al.,
50 2012). For trace element analyses (Fe, Mg, Mn, Na, and Sr), aliquots of $\sim 110\ \mu\text{g}$ of
51 sample powder were reacted in 1.5 ml of 2% HNO_3 solution for > 1 hour prior to
52 analysis on a Thermo Scientific Element XR high-resolution inductively coupled plasma
53 mass spectrometer (HR-ICP-MS) at the R. Ken Williams '45 Radiogenic Isotope
54 Geosciences Laboratory at Texas A&M University. To correct for instrument drift,
55 ~ 0.115 ml of 100 ppb indium standard was added to each solution. Analytical sessions
56 included measurements of internal standards with known elemental concentrations.
57 Samples found with $\text{Mn}^{2+} > 150$ ppm or $\text{Fe}^{2+} > 400$ ppm were considered diagenetically
58 altered and were not used for paleotemperature calculations (Grossman and Joachimski,
59 2020).

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61 **Standardization of Isotopic Analyses**

62 Fossil brachiopod samples were run from May 2019 to September 2020.
63 Brachiopod samples were run with the four ETH standards in a sample-to-standard ratio

64 of 1:1. The collected data for carbonate standards and unknowns were inputted into
65 Easotope (John and Bowen, 2016) to calculate $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and Δ_{47} values. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
66 values are reported versus VPDB, and Δ_{47} values are standardized within the "Carbon
67 Dioxide Equilibrium Scale" (CDES) (Dennis et al., 2011). These calculations used (1)
68 acid digestion fractionation factors for both $\delta^{18}\text{O}$ (Kim et al., 2007) and Δ_{47} values
69 (Petersen et al., 2019), (2) ^{17}O correction (Brand et al., 2010), and (3) non-linearity
70 corrections related to the IRMS on which the analyses were performed (Dale et al.,
71 2014; Meckler et al., 2014). Propagation of uncertainty was computed using the Python
72 package *D47crunch* as recommended in Daëron, 2021.

73 Replicates were screened using multiple protocols as a means of QA/QC.
74 Replicates with $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ values falling outside $\pm 2\sigma$ the mean of that sample were
75 discarded regardless of the Δ_{47} value. Peirce's criterion was then used to determine
76 outliers in the remaining Δ_{47} data set, which were then removed (Ross, 2003).

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78 **Reordering Assessment Model**

79 The Monte Carlo simulation at the center of the reordering assessment model
80 utilizes the Python package *isotopylog*. This package allows for the prediction of Δ_{47}
81 evolution when a specified activation energy distribution is subjected to time-
82 temperature history. The specified activation energy distribution changes based on which
83 reordering model is selected. This work uses the reordering model presented in
84 Hemingway and Henkes (2021) as it presents Δ_{47} reordering as a system of disordered
85 kinetic processes with multiple pseudo-first-order reactions co-occurring. Previous

86 reordering models (Henkes et al., 2014; Stolper and Eiler, 2015) are specific cases of
87 disordered kinetics within the framework of this disordered kinetics model.

88   The Monte Carlo simulation first produces a random temperature from a
89 statistically normal temperature distribution which provides a suitable representation of
90 the original environment based on a modern analog. However, as shown in Figure S3, at
91 a maximum burial temperature of $\leq 150^{\circ}\text{C}$, temperatures back-calculated using our
92 method show minimal deviation ($\leq 2^{\circ}\text{C}$) from the initial simulated temperatures
93 regardless of initial simulation temperature ($15 - 35^{\circ}\text{C}$).

94   The randomly produced initial temperature is then converted into Δ_{47} space using
95 a specified temperature calibration. We use the recalculated Kele et al. (2015) calibration
96 from Bernasconi et al. (2018). The same Δ_{47} temperature calibration must be used in the
97 Monte Carlo simulation and the calculation of temperatures from measured materials.
98 Using two different temperature calibrations will introduce significant error to the back-
99 calculated temperatures, the magnitude of which is dependent on the temperature
100 calibration used.

101   The Monte Carlo simulation then prepares an activation energy (E_a) distribution
102 based on published data on Δ_{47} reordering (Passey and Henkes, 2012; Henkes et al.,
103 2014; Stolper and Eiler, 2015; Brenner et al., 2018; Hemingway and Henkes, 2021).
104 This study used the ‘all calcite average’ μ_E and σ_E values presented in Hemingway and
105 Henkes (2021). A randomized E_a error factor (<1 to 10%) was then added to the μ_E and
106 σ_E values of the E_a distribution to calculate differences in E_a attributed to trace element

107 contents, ionic impurities, and/or crystallographic defects (Henkes et al., 2014;
108 Hemingway and Henkes, 2021).

109   The model then inputs the specified time-temperature history and produces a
110 series of 500 linearly approximated steps between each of the defined time-temperature
111 points to create a continuous time path for the *geologic_history* tool of *isotopylog*. This
112 tool then simulates the evolution of the Δ_{47} bond signal based on the previously defined
113 E_a distribution and time-temperature history. This process is iterated 1000 times, and the
114 results of each iteration is exported to an Excel^{TM} file.

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126 **SUPPLEMENT FIGURES**

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128 **Figure S1.** Time-temperature diagram for the Late Ordovician strata in the Cincinnati

129 Arch region (Stearns and Reesman, 1986; Ryder, 1987).

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131 **Figure S2.** Time-temperature diagram for the Late Ordovician strata in the Anticosti
132 Island region (Bertrand, 1990).

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141 **Figure S3.** Difference between initial and back-calculated temperatures ($\Delta T_I - T_B$) using
 142 the ΔT_c from a simulation with an initial temperature (T_0) of 25 ± 2 °C ($N = 1000$), as a
 143 function of different hypothetical sample T_0 values and burial temperatures. Each
 144 symbol characterizes a different hypothetical T_0 and the same burial history (Fig. S1).
 145 Note that the uncertainty in back-calculated temperature related to assignment of the
 146 initial temperature is small (± 2 °C) at burial temperatures below 150 °C.

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151 **Figure S4.** Simulated reordering of Δ_{47} versus maximum burial temperature using the
 152 burial history shown in Figure S1. As in Figure S3, each symbol characterizes a different
 153 hypothetical initial temperature (T_0). Note that the Δ_{47} values converge near the
 154 equilibrium value at high temperature.

155 **Figure S5.** Histograms showing (A) measured brachiopod $T(\Delta_{47})$ from Bergmann et al.
 156 (2018), (B) back-calculated brachiopod $T(\Delta_{47})$ from Bergmann et al. (2018), (C)
 157 measured brachiopod $T(\Delta_{47})$ from this study, and (D) back-calculated brachiopod $T(\Delta_{47})$
 158 from this study. Gray bars represent data outside 2σ of the mean.

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161 **Figure S6.** Histograms showing (A) Monte Carlo simulation of initial $T(\Delta_{47})$ values
 162 (mean = 30 °C, $2\sigma = 2$ °C, $N = 1000$), (B) impact of reordering on $T(\Delta_{47})$ values (mean =
 163 30.6 °C, $2\sigma = 3.8$ °C), using the model of Hemingway and Henkes (2021), and (C) back-
 164 calculated $T(\Delta_{47})$ (mean = 29.7 °C, $2\sigma = 3.8$ °C) using ΔT_c correction of 0.9 °C
 165 produced from the Monte Carlo simulation.

Table S1. Trace element data and cathodoluminescence for measured brachiopods. CL = cathodoluminescent, SL = slightly luminescent, and NL = nonluminescent.

Sample	Fe (ppm)	Mg (ppm)	Mn (ppm)	Na (ppm)	Sr (ppm)	CL rating
65983	165	1338	112	487	384	CL
OKP-1	228	1697	64	569	1777	SL
OKH-1	139	1472	64	431	311	NL/SL
66378	47	1104	20	523	292	NL
27542	215	1220	227	459	327	CL
68984	64	1049	26	711	716	NL
CCSP-1	117	929	20	474	375	NL
CCSP-2	166	1260	124	475	305	SL/CL
27638	67	1140	40	560	562	NL
2142-1	30	1261	10	616	508	NL
27724	47	1082	78	585	790	NL
51149	74	888	97	487	1513	NL
51000	25	1100	22	492	350	NL/SL
63678	50	1019	44	539	367	NL
69459	193	1658	101	575	1191	NL
78682-2	72	1198	9	538	714	NL
63696	24	1182	69	562	314	NL
78700	48	1662	11	621	513	NL
27909-1	9	1064	7	599	284	NL
27921	20	1282	26	656	436	NL
MCP-1	55	1233	33	474	599	N/SL
MCP-5	188	1511	156	643	442	NL
MCH-1	237	1209	43	518	692	SL
MCH-3	315	1150	208	459	139	CL
27969-1	99	1721	114	659	594	NL/SL
68818	41	999	7	523	349	NL
68980	120	1335	125	455	212	NL/SL
68766	27	920	10	427	188	NL/SL

Table S2. Back-calculated Δ_{47} temperatures of analyzed brachiopods (‰) with reconstructed water $\delta^{18}\text{O}$ values.

Sample	Age (Ma)	Original Δ_{47} T (°C)*	95% CI	H ₂ O $\delta^{18}\text{O}_{\text{water}}$		Δ_{47} T (85 °C)*	H ₂ O $\delta^{18}\text{O}_{\text{water}}$		Δ_{47} T (60 °C)*	H ₂ O $\delta^{18}\text{O}_{\text{water}}$	
				**	95% CI		(85 °C)^			(60 °C)^	
OKH-1	446.5	32	11	-0.6	2.3	31	-0.7		32	-0.6	
OKP-1	446.5	33	8	-0.3	1.6	32	-0.4		33	-0.3	
66378	446.7	31	6	-2.0	1.2	31	-2.2		31	-2.0	
68984	446.8	28	13	-1.8	2.5	27	-1.9		28	-1.8	
CCSP-1	446.9	57	8	3.3	1.6	56	3.2		57	3.3	
27724	447	34	6	-0.2	1.2	33	-0.4		34	-0.2	
27638	447	34	9	0.0	1.8	33	-0.2		34	0.0	
2142-1	447	35	14	-1.4	2.8	34	-1.6		35	-1.4	
2142-2	447	40	10	0.3	2	39	0.1		40	0.3	
51149	447.2	49	6	2.2	1.2	48	2.0		49	2.2	
51000	447.3	33	15	-1.0	2.9	32	-1.2		33	-1.0	
63678	447.3	35	11	-0.2	2.2	35	-0.5		36	-0.3	
69459	447.4	33	6	0.0	1.2	32	-0.2		33	0.0	
78682	447.5	25	16	-2.3	3.1	24	-2.5		25	-2.3	
78700	447.6	32	11	-1.1	2.2	31	-1.3		32	-1.1	
63696	447.6	40	7	0.6	1.5	39	0.5		40	0.6	
27909	447.7	34	11	-0.9	2.2	33	-1.0		34	-0.9	
MCH-1	447.8	30	12	-1.2	2.4	29	-1.4		30	-1.2	
MCP-5	447.8	37	9	0.3	1.7	36	0.0		37	0.2	
27969-1	447.8	39	13	0.6	2.6	38	0.4		39	0.6	
MCP-1-1	447.8	41	9	1.0	1.8	40	0.9		41	1.0	
27921	447.8	42	11	1.3	2.1	41	1.1		42	1.3	
27969-2	447.8	55	10	3.1	2	54	3.0		55	3.1	
MCP-1-2	447.8	61	6	4.8	1.3	61	4.6		61	4.8	
68818	447.9	38	8	0.4	1.6	37	0.2		38	0.3	
68980	448.5	49	8	2.6	1.6	48	2.5		49	2.6	
68766	449	26	11	-3.0	2.2	25	-3.1		26	-3.0	

*Calculated using Bernasconi et al. (2018) temperature calibration

^Calculated using Kim and O'Neil (1997) calcite-H₂O relationship

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