Stable Ca and Sr isotopes support volcanically-triggered

biocalcification crisis during Oceanic Anoxic Event 1a

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SUPPLEMENTARY MATERIALS

Lithology

Analytical Methods

δ¹³C Segmentation and Stratigraphic Correlation

Supporting Elemental and Isotopic Results

Sr Isotope Equilibration Sensitivity Analysis

Figures

- Figure S1 Stratigraphic height vs. CaCO₃ abundance, Mg/Ca, Sr/Ca, Mn/Sr, and δ^{18} O in bulk carbonate samples from ODP Hole 866A
- Figure S2 Cross-plots of isotopic data
- Figure S3 Cross-plots of isotopic and elemental ratios
- Figure S4 Comparison of $\delta^{44/40}$ Ca data for Hole 866A reported here and elsewhere
- Figure S5 $-\frac{87}{\text{Sr}}$ records of porewater and bulk carbonate from ODP Hole 866A
- Figure S6 Sensitivity analysis for Sr isotope equilibration between recrystallizing carbonate sediments and seawater
- Figure S7 Stratigraphic correlation of various geochemical proxy data for the entire study interval

Tables

Table S1 – Elemental and isotopic data presented in this study Table S2 – Statistical data for linear regressions provided in Fig. 2

Lithology

Samples analyzed in this study are from Hole 866A drilled on the flanks of Resolution Guyot in the Mid-Pacific (21°N, 174°E). Cyclic packstone–wackestones and oolitic/peloidal grainstones dominate the lithology, with lesser amounts of dolomitic packstone (Sager et al.,1993; Jenkyns and Strasser, 1995). Skeletal fragments of rudists, gastropods, and corals occur as sand-sized or larger grains (Sliter, 1995; Swinburne et al., 1995). Petrologic and elemental analyses reveal calcite as the primary mineralogy (Jenkyns and Strasser, 1995), although parts of the core below the study interval (>1200 mbsf) show evidence for dolomitization (Flood and Chivas, 1995).

Thermal gradients have convected large volumes of seawater through the carbonates (Paull et al., 1995). This mechanism may have supplied Mg necessary for dolomitization lower in the section (Food and Chivas, 1995), but the results presented here for the overlying limestone do not reveal significant secondary incorporation of seawater Ca and Sr. Limestone at the base of Hole 865, drilled on Allison Guyot, shows evidence for radiogenic Sr isotope equilibration with basaltic basement rocks (Paull et al., 1995). However, the Hole 866 rocks analyzed here, as well as stratigraphically equivalent rocks at Hole 865, display ⁸⁷Sr/⁸⁶Sr ratios consistent with the global record, and no evidence exists for alteration by younger fluids (Paull et al., 1995). While researchers have raised concerns about meteoric water diagenesis at Hole 866A (Röhl and Strasser, 1995), other studies suggest minimal alteration, or at least negligible impact on bulk sediment δ^{13} C values and ⁸⁷Sr/⁸⁶Sr ratios (Jenkyns and Wilson, 1999).

Analytical Methods

We analyzed a subset of samples previously investigated by Mills et al. (2017). Rocks were powdered in a shatterbox equipped with an alumina ceramic grinding container. Approximately ~200 mg of powder was dissolved in 10 mL of ultrapure 5% HNO₃ in acid-

cleaned centrifuge tubes for 12 hrs. The mixtures were centrifuged, and the supernatants were passed through 0.45 μ m polypropylene syringe filters, collected in Teflon beakers, dried at 90 °C, and re-dissolved in 15 mL of 5% HNO₃ for elemental and isotopic analyses.

Subsamples of the solutions taken for elemental analysis were diluted to minimize matrix effects. Concentrations of Ca, K, Mg, Na, Mn, and Sr were measured using a Thermo Scientific iCAP 6500 ICP-OES. K was not detected in the samples. Repeated analyses of NIST-1643f yielded results within $\pm 5\%$ of reported concentrations. In addition, Ca and Sr concentrations measured by ICP-OES were within $\pm 5\%$ of those determined by isotope dilution, as part of the double-spike methodologies presented below. Calcium concentrations were used to estimate the abundance of calcium carbonate (wt%), assuming stoichiometric CaCO₃.

Carbon and oxygen isotope ratios were measured using a Gas Bench connected to a Delta V Plus Isotope Ratio Mass Spectrometer (IRMS). Powders were purged with He for 7 minutes and then reacted overnight at 30 °C with 103% anhydrous H₃PO₄. Results were calibrated against NBS-18, NBS-19, and one internal CaCO₃ standard. Data are reported in δ -notation (δ ¹³C and δ ¹⁸O) relative to Vienna Peedee Belemnite (VPDB). The uncertainties (2σ _{SD}) for δ ¹³C and δ ¹⁸O are ±0.12‰ and ±0.30‰, respectively.

Calcium and strontium isotope ratios were measured using a Thermo-Scientific Triton Thermal Ionization Mass Spectrometer (TIMS) equipped with $10^{11} \Omega$ amplifier resistors. Wang et al. (2019) recently reviewed the methods. In brief, a ⁴³Ca-⁴²Ca double-spike technique was used to measure ⁴⁴Ca/⁴⁰Ca ratios (Lehn et al., 2013). Procedural blanks quantified with an ⁴²Ca isotope dilution method were negligible (~50 ng, n = 6) compared to the amount of sample Ca that was spiked and processed through column chemistry (50 µg). Radiogenic and stable Sr isotope ratios (⁸⁷Sr/⁸⁶Sr and ⁸⁸Sr/⁸⁶Sr) were measured following Andrews et al. (2016) and Andrews and Jacobson (2017). ⁸⁷Sr/⁸⁶Sr ratios were measured using multi-dynamic mode, and instrumental mass fractionation was corrected by normalizing ⁸⁸Sr/⁸⁶Sr ratios to a value of 8.3752 using an exponential law. An ⁸⁷Sr-⁸⁴Sr double-spike technique was used to measure fractionated ⁸⁸Sr/⁸⁶Sr ratios. The ⁸⁸Sr/⁸⁶Sr data reduction includes input of corresponding ⁸⁷Sr/⁸⁶Sr ratios. Procedural blanks determined with an ⁸⁴Sr isotope dilution method were negligible (~70 pg, n = 3) compared to the amounts of Sr employed for both analyses (150 ng for ⁸⁷Sr/⁸⁶Sr and 200 ng for ⁸⁸Sr/⁸⁶Sr). ⁴⁴Ca/⁴⁰Ca and ⁸⁸Sr/⁸⁶Sr ratios are reported in δ-notation, with $\delta^{44/40}$ Ca presented relative to the Ocean Scientific International Ltd. (OSIL) Atlantic seawater standard (SW) and $\delta^{88/86}$ Sr presented relative to NIST SRM-987 strontium carbonate standard (NIST-987).

For $\delta^{44/40}$ Ca, at least 6 SW standards and 2 NIST-915b standards were analyzed every 30 samples. For $\delta^{88/86}$ Sr, at least 6 NIST-987 standards and 2 IAPSO seawater standards were analyzed every 40 or fewer samples. During the period of study, repeated analyses yielded $\delta^{44/40}$ Ca_{SW} = 0.000±0.003‰ (2 σ_{SEM} , n=16) and $\delta^{44/40}$ Ca_{915b} = -1.134±0.002‰ (2 σ_{SEM} , n=6). These results point to a remarkably good short-term reproducibility (2 σ_{SD}) ranging between 0.012‰ and 0.005‰. The current long-term values for the laboratory are $\delta^{44/40}$ Ca_{SW} = 0.000±0.002‰ (2 σ_{SEM} , n=661) and $\delta^{44/40}$ Ca_{915b} = -1.135±0.003‰ (2 σ_{SEM} , n=263). These results are consistent with an external reproducibility (2 σ_{SD}) of ±0.05‰, which is the uncertainty adopted for the study. As shown below, the reproducibility of sample unknowns is better than ±0.05‰. During the period of study, repeated measurements of NIST-987 yielded ⁸⁷Sr/⁸⁶Sr = 0.710250±0.000002 (2 σ_{SEM} , n=211). The overall uncertainty (2 σ_{SD}) assigned to ⁸⁷Sr/⁸⁶Sr ratios is ±0.00010. For $\delta^{88/86}$ Sr, at least 6 NIST-987 standards and 2 IAPSO seawater standards were analyzed every 40

or fewer samples. During the period of study, repeated analyses yielded $\delta^{88/86}Sr_{NIST987} = 0.000\pm0.001\% (2\sigma_{SEM}, n=17)$ and $\delta^{88/86}Sr_{IAPSO} = 0.397\pm0.002\% (\pm 2\sigma_{SEM}, n=8)$. The current long-term values for the laboratory are $\delta^{88/86}Sr_{NIST987} = 0.000\pm0.001\% (\pm 2\sigma_{SEM}, n=235)$ and $\delta^{88/86}Sr_{IAPSO} = 0.396\pm0.002\% (\pm 2\sigma_{SEM}, n=133)$. After propagating measurement errors for $^{87}Sr/^{86}Sr$ and $^{88}Sr/^{86}Sr$ ratios, the overall uncertainty $(2\sigma_{SD})$ assigned to $\delta^{88/86}Sr$ is $\pm 0.020\%$ ($2\sigma_{SD}$).

Care was taken to ensure that uncertainties determined from the repeated analyses of standards apply to sample unknowns. Duplicates were determined by reanalyzing sample solutions (n = 4), as well as by re-dissolving and processing separate aliquots of powder (n = 6). As shown in Table DR1, duplicates agree with original analyses within the uncertainties. Duplicate measurements are shown in Fig. 1 as crosses.

δ^{13} C Segmentation and Stratigraphic Correlation

Magnetostratigraphy (Tarduno et al., 1995), benthic foraminiferal biostratigraphy (Arnaud-Vanneau and Sliter, 1995), and chemostratigraphy (87 Sr/ 86 Sr and δ^{13} C) have aided correlation of the section (Jenkyns, 1995; Jenkyns and Wilson, 1999). The Cretaceous stage boundaries are taken from Jenkyns and Wilson (1999). The nomenclature and segmentation of the δ^{13} C intervals associated with OAE 1a follow Menegatti et al. (1998) and Bralower et al. (1999), based on study of the Cismon section in Italy. The C1 interval represents the pre-OAE 1a baseline of the δ^{13} C curve, with a mean value of ~2.4‰. The C2 interval starts with a progressive decrease of δ^{13} C, but values oscillate around the baseline with a slightly lower mean of ~1.8‰. The C3 interval points to the minimum δ^{13} C within a relatively organic-rich interval overlying the wackestone of C2. The C4 interval correlates with an abrupt positive shift towards heavier values (~4.5‰) immediately following C3. The C5 interval represents a segment with

invariant δ^{13} C values (~3.6‰). The C6 interval is characterized by another step-like abrupt increase to the maximum values of the entire section (~5.4‰). The C7 interval bears the heaviest mean value of the entire section (~4.0‰). The C8 interval represents the subsequent drop in δ^{13} C overlying C7, towards the upper Aptian.

In Figs. 3 and S7, the δ^7 Li values shown for Resolution Guyot are from Lechler et al. (2015). The nannoconid abundance data and ¹⁸⁷Os/¹⁸⁸Os ratios shown for the Cismon site are from Erba and Tremolada (2004) and Bottini et al. (2012), respectively. Atmospheric *p*CO₂ values reconstructed from analysis of the Cau section are from Naafs et al. (2016). The δ^{13} C segmentation criteria for these sections are mutually consistent. These δ^{13} C segments are unchanged from the original publications and were used in our study to correlate the three sections shown in the figures.

Supporting Elemental and Isotopic Results

Fig. S1 plots CaCO₃ abundances, as well as Mg/Ca, Sr/Ca, and Mn/Sr ratios, versus stratigraphic height. On average, the samples have high CaCO₃ abundances (~95 wt%). Mg/Ca ratios are slightly elevated lower in the section and decrease upwards. Sr/Ca ratios average ~0.4 nmol/µmol before decreasing to 0.2 nmol/µmol upsection. Mn/Sr ratios are low and modestly decrease upsection from 0.3 to 0.2 mol/mol.

Figs. S2 – S3 cross plot various parameters. Both ordinary least squares (OLS) and standardized major axis (SMA) linear regression models were employed to evaluate the statistical significance of apparent correlations. Unlike the OLS model, the SMA model considers that both x and y variables have error. All regression statistics presented here are from the SMA model, but no differences between the two models were observed. No significant correlations exist, with the exception of the following: $\delta^{44/40}$ Ca vs. $\delta^{88/86}$ Sr ($R^2 = 0.66$, p =

7.7×10⁻⁸), $\delta^{44/40}$ Ca vs. Sr/Ca ($R^2 = 0.40$, $p = 1.3 \times 10^{-4}$), and $\delta^{88/86}$ Sr vs. Ca/Sr ($R^2 = 0.31$, $p = 1.0 \times 10^{-3}$).

Sr Isotope Equilibration Sensitivity Analysis

Previous investigations have shown that Sr isotope equilibration between recrystallizing carbonate sediments and pore fluids only shifts ⁸⁷Sr/⁸⁶Sr ratios by 10 - 50 ppm (e.g., Richter and DePaolo, 1988; Richter and Liang, 1993). Negligible effects are predicted for $\delta^{88/86}$ Sr because the mixing end-members have less contrast in stable Sr isotope space. To illustrate this point, a simple two-component mixing model is employed to examine how shifts in carbonate $\delta^{88/86}$ Sr values ($\Delta^{88/86}$ Sr) correspond to shifts in carbonate ⁸⁷Sr/⁸⁶Sr ratios ($\Delta^{87}Sr/^{86}$ Sr). The equations are:

$$\delta^{88/86} Sr_{carb_altered} = \frac{(\delta^{88/86} Sr_{carb_initial} - \delta^{88/86} Sr_{fluid})^{*87} Sr/^{86} Sr_{carb_altered}}{(\delta^{87} Sr/^{86} Sr_{carb_initial} - \delta^{87} Sr/^{86} Sr_{fluid})}$$
(1)

$$\delta^{88/86} Sr_{carb_altered} = \delta^{88/86} Sr_{carb_initial} + \Delta^{88/86} Sr$$
(2)

$${}^{87}Sr/{}^{86}Sr_{carb_altered} = {}^{87}Sr/{}^{86}Sr_{carb_initial} + \Delta^{87}Sr/{}^{86}Sr \quad , \tag{3}$$

where *carb_initial* refers to the initial carbonate before recrystallization, *carb_altered* denotes the altered carbonate after recrystallization, and *fluid* refers to pore water. Two example calculations are presented. In one case (Fig. S6-A), 87 Sr/ 86 Sr_{carb_initial} values are set to the range of ratios measured for the present dataset and all other parameters are set to modern values. In the second case (Fig. S6-B), 87 Sr/ 86 Sr_{carb_initial} is set to the average for the present dataset, 87 Sr/ 86 Sr_{fluid} is allowed to range from 0.7082 to 0.7092, and the remaining two parameters are set to modern values. As Figs. S6-A and B show, Δ^{87} Sr/ 86 Sr values ranging up to 100 ppm yield $\Delta^{88/86}$ Sr values no higher than 0.03‰, which is only 0.01‰ higher than the long-term external reproducibility of the stable Sr isotope method and smaller than the total range of $\delta^{88/86}$ Sr variation measured for the samples (0.12‰).



Figure S1 Stratigraphic height vs (A) CaCO₃ abundance, (B) Mg/Ca (mol/mol), (C) Sr/Ca (nmol/ μ mol), (D) Mn/Sr (mol/mol), and (E) δ^{18} O in bulk carbonate samples from ODP Hole 866A at Resolution Guyot.



Figure S2 Cross-plots of various parameters measured for bulk carbonate samples from ODP Hole 866A at Resolution Guyot. R^2 and *p*-value are from the SMA regression model. (A) δ^{13} C vs δ^{18} O, (B) $\delta^{44/40}$ Ca vs $\delta^{88/86}$ Sr, (C) δ^{13} C vs $\delta^{44/40}$ Ca, (D) 87 Sr/ 86 Sr vs $\delta^{88/86}$ Sr, (E) δ^{13} C vs $\delta^{88/86}$ Sr, and (F) $\delta^{44/40}$ Ca vs 87 Sr/ 86 Sr.



Figure S3 Cross-plots of isotope ratios and selected lithological proxies in bulk carbonate samples from the ODP Hole 866A at Resolution Guyot. R^2 and p-value are from the SMA regression model. (A) $\delta^{44/40}$ Ca vs CaCO₃, (B) $\delta^{88/86}$ Sr vs CaCO₃, (C) 87 Sr/ 86 Sr vs CaCO₃, (D) $\delta^{44/40}$ Ca vs Mg/Ca, (E) $\delta^{88/86}$ Sr vs Mg/Ca, (F) 87 Sr/ 86 Sr vs Mg/Ca, (G) $\delta^{44/40}$ Ca vs Sr/Ca, (H) $\delta^{88/86}$ Sr vs Ca/Sr, (I) 87 Sr/ 86 Sr vs Sr/Ca, (J) $\delta^{44/40}$ Ca vs Mn/Sr, (K) $\delta^{88/86}$ Sr vs Mn/Sr, (M) $\delta^{44/40}$ Ca vs δ^{18} O, (N) $\delta^{88/86}$ Sr vs δ^{18} O, and (O) 87 Sr/ 86 Sr vs δ^{18} O.



Figure S4 $\delta^{44/40}$ Ca values from Hole 866A of ODP Leg143 at Resolution Guyot, mid-Pacific Ocean. A) $\delta^{44/40}$ Ca values from this study with error bars of ±0.05‰. Crosses represent duplicate measurements. B) $\delta^{44/40}$ Ca values from Blättler et al. (2011) with error bars of ±0.12‰. Blättler et al. (2011) measured $\delta^{44/42}$ Ca relative to NIST-915a. The data and corresponding error bars of ±0.06‰ were converted using the equation: $\delta^{44/40}$ Ca_{SW} = $\delta^{44/42}$ Ca_{915a}/0.488 - 1.86, where 0.488 assumes mass fractionation follows a kinetic law and 1.86 is the value the Northwestern Laboratory measures for 915a relative to seawater (e.g., Du Vivier et al., 2015).



Figure S5 ⁸⁷Sr/⁸⁶Sr records of porewater (Paull et al., 1995) and bulk carbonate (This study; Paull et al., 1995).



Figure S6 Sensitivity test for $\delta^{88/86}$ Sr response to early diagenetic 87 Sr/ 86 Sr shifts. A) 87 Sr/ 86 Sr_{carb_initial} values set to the range of ratios measured for the present dataset and all other parameters set to modern values. B) 87 Sr/ 86 Sr_{carb_initial} set to the average for the present dataset, 87 Sr/ 86 Sr_{fluid} allowed to range from 0.7082 to 0.7092, and the remaining two parameters set to modern values.



Figure S7 Stratigraphic correlation of various geochemical proxy data for the entire study interval. Fig. 3 in the main text shows the OAE 1a interval.

| Depth (mbsf) | δ ¹³ C (VPDB, ‰) | δ ¹⁸ O (VPDB, ‰) | δ ^{44/40} Ca (SW, ‰) | δ ^{44/40} Ca (SW, ‰) Duplicate | δ ^{88/86} Sr (NIST987, ‰) | δ ^{88/86} Sr (NIST987, ‰) Duplicate |
|-----------------|--------------------------------|--------------------------------|----------------------------------|---|---------------------------------------|--|
| 203.40 | 2.72 | -1.61 | -0.74 | | 0.37 | |
| 261.33 | 1.34 | -3.24 | -0.80 | | 0.32 | 0.33 |
| 309.25 | 2.77 | -1.12 | -0.77 | | 0.32 | |
| 367.34 | 2.7 | -2.36 | -0.76 | | 0.31 | |
| 405.83 | 2.68 | -1.8 | -0.77 | | 0.32 | |
| 483.15 | 1.28 | -3.41 | -1.00 | -0.99 | 0.29 | 0.28 |
| 521.4 | 2.6 | -1.82 | -0.87 | | 0.27 | |
| 550.52 | 2.9 | -2.68 | | | 0.29 | |
| 571.15 | 2.04 | -2.21 | -1.04 | -1.01 | 0.26 | |
| 589.87 | 2.76 | -1.96 | -0.88 | | | |
| 618.34 | 4 | -1.7 | -0.94 | -0.91 | 0.30 | |
| 648.40 | 4.2 | -1.38 | -1.00 | | 0.27 | 0.28 |
| 666.82 | 5.12 | -1.6 | -1.16 | -1.13 | 0.27 | |
| 686.30 | 3.7 | -2.67 | -1.09 | | 0.26 | |
| 696.8 | 3.92 | -2.37 | -1.06 | | 0.25 | |
| 725.1 | 3.68 | -2.4 | -1.03 | | 0.26 | |
| 744.15 | 3.8 | -2.08 | -0.99 | | 0.27 | 0.27 |
| 763.2 | 4.65 | -1.98 | -0.89 | -0.86 | 0.32 | |
| 772.65 | 4.32 | -2.43 | -0.89 | | 0.30 | |
| 794.45 | 2 | -1.72 | -0.88 | -0.87 | 0.33 | |
| 821.6 | -0.64 | -1.3 | -0.91 | | 0.28 | 0.29 |
| 850.81 | 0.52 | -2.3 | -0.95 | | 0.29 | |
| 868.9 | 2.22 | -2.31 | -1.06 | | 0.27 | |
| 878.8 | 2.17 | -2.86 | -1.07 | -1.04 | 0.28 | 0.29 |
| 888.17 | 2.3 | -2.4 | -0.96 | | 0.29 | |
| 907.85 | 2.54 | -2.87 | -0.95 | -0.95 | 0.29 | |
| 924 | 0.31 | -2.54 | -0.88 | | 0.32 | |
| 943.13 | 1.33 | -2.51 | -1.02 | | 0.30 | |
| 972.33 | 2.4 | -2.25 | -0.96 | | 0.29 | |
| 1010.93 | 2.53 | -1.81 | -0.91 | -0.88 | 0.30 | |
| 1058.20 | 1.5 | -2.59 | | | 0.33 | 0.32 |
| 1107.2 | 2.65 | -2.27 | -0.93 | | 0.29 | |
| 1193.75 | 1.49 | -2.84 | -0.91 | -0.90 | 0.30 | |

Table S1 Elemental, C, O, Ca, and Sr isotope geochemistry of carbonate samples from Hole 866A, ODP Leg 143, Resolution Guyot, mid-Pacific

Table S1 Continued.

| ⁸⁷ Sr/ ⁸⁶ Sr | ⁸⁷ Sr/ ⁸⁶ Sr Duplicate | Ca (µmol/g) | Na (µmol/g) | Mg (µmol/g) | Sr (nmol/g) | Mn (nmol/g) |
|------------------------------------|---|----------------|----------------|----------------|----------------|----------------|
| 0.70744 | | 9841 | 36 | 124 | 2328 | 582 |
| 0.70740 | | 9847 | 35 | 134 | 2362 | 692 |
| 0.70742 | | 9544 | 36 | 124 | 2066 | 564 |
| 0.70733 | 0.70733 | 9681 | 31 | 129 | 2328 | 692 |
| 0.70733 | | 9656 | 44 | 118 | 2077 | 983 |
| 0.70727 | 0.70727 | 9848 | 64 | 173 | 2667 | 710 |
| 0.70730 | | 8559 | 73 | 138 | 2905 | 746 |
| 0.70733 | | 9170 | 108 | 159 | 3012 | 783 |
| 0.70732 | | 9315 | 100 | 181 | 3609 | 837 |
| 0.70733 | | 9859 | 57 | 175 | 2943 | 564 |
| 0.70736 | | 9443 | 63 | 188 | 3297 | 764 |
| 0.70735 | | 9452 | 61 | 199 | 3770 | 1656 |
| 0.70736 | 0.70735 | 9882 | 69 | 163 | 4314 | 783 |
| 0.70736 | | 9859 | 65 | 159 | 4394 | 673 |
| 0.70736 | | 9602 | 51 | 179 | 4580 | 710 |
| 0.70740 | | 9911 | 47 | 169 | 3938 | 764 |
| 0.70741 | | 9719 | 45 | 156 | 4314 | 710 |
| 0.70741 | | 9574 | 54 | 146 | 4212 | 564 |
| 0.70749 | | 9151 | 49 | 151 | 3045 | 582 |
| 0.70750 | | 9339 | 54 | 147 | 4085 | 673 |
| 0.70748 | 0.70748 | 9274 | 98 | 196 | 4607 | 1129 |
| 0.70751 | | 9239 | 89 | 234 | 4924 | 710 |
| 0.70747 | | 9606 | 70 | 236 | 4599 | 601 |
| 0.70747 | | 9631 | 67 | 191 | 4499 | 710 |
| 0.70749 | | 9887 | 30 | 176 | 4147 | 564 |
| 0.70747 | | 9878 | 24 | 246 | 3553 | 710 |
| 0.70751 | | 9564 | 87 | 249 | 4463 | 983 |
| 0.70750 | 0.70750 | 9493 | 88 | 261 | 5126 | 637 |
| 0.70751 | | 9643 | 66 | 357 | 3041 | 655 |
| 0.70750 | | 9518 | 39 | 240 | 4211 | 764 |
| 0.70751 | | 9640 | 59 | 376 | 2571 | 637 |
| 0.70748 | | 9557 | 63 | 655 | 3804 | 528 |
| 0.70748 | | 8454 | 24 | 513 | 4305 | 582 |

| | Dataset | Slope | Intercept | R^2 | <i>p</i> -value | Reference |
|--|-----------------------|----------------------|-------------|-------|-----------------------|----------------------|
| δ ^{44/40} Ca vs [Sr] (Fig. 2A) | OAE 1a carbonate | -0.00091 ±0.00018 | -0.64±0.06 | 0.47 | 2.1×10 ⁻⁵ | This study |
| | Inorganic calcite | -0.00094 ±0.00005 | -0.85±0.05 | 0.91 | 2.2×10 ⁻¹⁶ | Tang et al. (2008) |
| | Silurian carbonate | -0.00097 ±0.00017 | -0.92±0.09 | 0.53 | 1.1×10 ⁻⁶ | Farkaš et al. (2016) |
| | P-Tr carbonate | -0.00025 ±0.00003 | -1.21±0.02 | 0.35 | 3.1×10 ⁻⁵ | Wang et al. (2019) |
| δ ^{44/40} Ca vs δ ^{88/86} Sr (Fig. 2B) | OAE 1a carbonate | 0.194 ±0.027 | 0.475±0.025 | 0.66 | 7.7×10 ⁻⁸ | This study |
| | Inorganic calcite | 0.185 ±0.019 | 0.286±0.033 | 0.96 | 6.0×10 ⁻⁴ | Böhm et al. (2012) |
| | P-Tr carbonate | 0.131 ±0.082 | 0.560±0.109 | 0.07 | 0.12 | Wang et al. (2019) |

Table S2 Slopes, intercepts, coefficients of determination, and p-values of datasets examined in Fig. 2

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