Reviewer #1

L50: Sr/Ca has been widely shown to have significant vital effects impacting its accuracy (DeCarlo et al. 2016, Paleoceanography)

We thank the reviewer for highlighting the importance of “vital effects” on coral Sr/Ca thermometry. As described in DeCarlo et al. (2016) and previous works such as Sinclair and Risk (2006), coral trace element “vital effects” include Rayleigh fractionation within the semi-isolated calcifying fluid. In the revised manuscript, we have rewritten the Introduction (around Line 50) to state that the fluid composition is not only altered by selective ion uptake but also Rayleigh fractionation. We have also cited DeCarlo et al. (2016) and Sinclair and Risk (2006) in the Introduction.

L120/130: Please report the long-term reproducibility (2sd) for Sr and Ba isotopes, as is done for C and Ca isotopes.

We now have revised the text in Section 2.2 to report the "long-term reproducibility" for both Sr and Ba isotopes. The long-term reproducibility is 0.02‰ (2SD) for δ88Sr and 0.03‰ (2SD) for δ138Ba based on repeated measurements of the coral reference material JCp-1.

Fig 3: Please report 2SD shading on δ13C. Typo in caption: (e) currently reads δ138/134Ca.

We have updated Figure 3 to include the shaded band representing the 2SD analytical uncertainty for the δ13C record. We have corrected the typo in the caption for panel (e).

L225: The findings of Gussone and others (2003) are misstated: rather than an increase in temperature leading to higher δ44Ca values, an increase in temperature pushes the selection preference of 42Ca over 44Ca (fractionation factor) toward unity, such that δ44Ca in the theoretical solid are indistinguishable from δ44Ca in the fluid.

We appreciate the reviewer’s attention to details and apologise for the inaccurate description of the finding by Gussone et al. (2003). We agree that inorganic aragonite precipitation at higher temperatures results in solid δ44Ca values that are closer to the fluid composition, thereby reducing the isotopic discrimination between 42Ca and 44Ca. We have revised the manuscript to accurately reflect the thermodynamic isotope fractionation described by Gussone et al. (2003).

L235: In terms of calcium ion dehydration prior to passage through a channel, I appreciate that the work of Hoffman and others (2012) shows that water-ion exchange reactions are temperature dependent, such that the resultant magnitude of kinetic isotope fractionation is affected. That said the manuscript uses this mechanism to suggest that the fractionation factor (αCa) is likely changing, although no calculation of αCa is presented. With only the δ44Ca values, as presented in Fig 4a, it's difficult to follow how this mechanistic interpretation relates to the data. Notably, the findings of the cited work by Mejía an others (2018) suggested that decreasing temperatures lead to modelled increases in the magnitude of αCa, allowing more selective uptake of the light isotope.

Aside from this point, it would be helpful to clarify why the corals studied by Böhm and others (2006) or Inoue and others (2015) would not also be susceptible to more selective uptake of light Ca through the same dehydration mechanism invoked for the corals measured within this study. In Inoue and others (2015), one out of three coral colonies showed a decrease in δ44Ca with increasing temperature.

It would be helpful to show δ13C v. SST and δ13C v. δ44Ca to clarify the suggested connection between SST, photosynthetic activity/δ13C, and the resultant indirect relationship between δ44Ca and SST.

We thank the reviewer for this insightful comment regarding the mechanisms of Ca isotope fractionation. We agree that according to the thermodynamics of ion desolvation described in Hofmann et al. (2012), higher temperatures likely weaken the hydration shell around Ca ions and lower the energy barrier for ion desolvation. Theoretically, this thermodynamic effect should reduce the magnitude of isotope fractionation (i.e. higher δ44Ca) at higher temperatures, which is the opposite of our observation.

As the reviewer notes, the CaSri-Co model (Mejia et al., 2018) also identifies calcification/transport rate as a critical driver of Ca isotope fractionation. Their model indicates that an increase in the rate of Ca uptake enhances the kinetic isotope effect, resulting in lower δ44Ca values (Mejia et al., 2018). While we did not calculate a specific fractionation factor (αCa) due to the lack of direct measurements of the calcifying fluid's isotopic composition, we propose that high SST likely stimulates metabolic activity (supported by higher δ13C), leading to a faster Ca transport. This metabolically driven increase in ion flux results in stronger kinetic preference for light Ca isotopes.

Regarding the contrast with previous studies (Böhm et al., 2006; Inoue et al., 2015), the discrepancy may result from the complexity of coral physiological processes. Different coral species and even individual colonies can exhibit distinct metabolic responses to the complex interplay of various environmental factors. As a result, the apparent temperature dependence of Ca isotope fractionation can vary different between studies depending on the specific environmental condition and physiological state. Our study focuses on a single *Porites* colony within a relatively warm environment (above 24 °C).

We hypothesise that in this warm environmental settings, high SST likely stimulates metabolic activity, which induces a stronger rate-driven Ca isotope fractionation. This interpretation is consistent with the specific findings of Inoue et al. (2015) for “Colony A”, which showed a breakdown of the positive trend and a shift towards lighter δ44Ca values specifically at temperatures above 24 °C. Similarly, the data in Böhm et al. 2006 reveal that the positive correlation appears to be less defined at the higher temperature range.

Finally, we have added a new figure to the revised manuscript. The figure shows a significant (*p* < 0.001) positive correlation between skeletal δ13C and SST, which confirms that temperature is a driver of metabolic rates in SCS coral samples. In addition, the plot of δ13C vs δ44Ca reveals a significant (*p* = 0.009) negative correlation, supporting our hypothesis that periods of enhanced metabolic activity are linked to stronger light isotope selectivity.

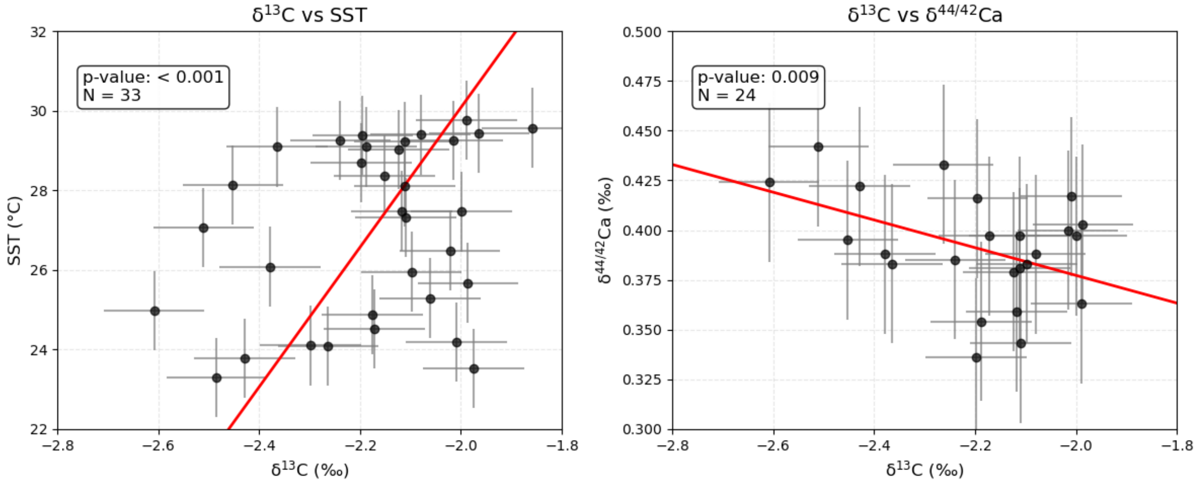

Figure R1: York regression analysis of the relationships between (a) skeletal δ13C vs. SST and (b) skeletal δ13C vs. δ44Ca.

L260: While the work of Müller and others (2018) finds a negative correlation between δ88Sr and temperature, they are clear than this is opposite the common trend seen between δ44Ca and temperature. It would be helpful for the reader to contextualize this point by Müller as it relates to the interpretation of Shannon (1976), which suggests that both Sr and Ca are transported and fractionated via a similar biologically-mediated pathway and is used to explain the similarity between changes in δ88Sr and δ44Ca observed in this study.

We thank the reviewer for this helpful suggestion. We recognize that Müller et al. (2018) found a negative temperature dependence for δ88Sr, which is in contrast to the positive correlation observed for δ44Ca. We clarify that while previous studies reported different fractionation behaviours for Sr and Ca, our coral record show coherent negative temperature dependencies for both δ44Ca and δ88Sr. We interpret this consistency as evidence that the rapid metabolic flux of ions at high SST imposes a significant kinetic control on isotope fractionations of both systems within annual growth bands of a single coral skeleton. This interpretation is further supported by the similarity in effective ionic radii (Shannon, 1976), which suggests that Sr and Ca share the same transmembrane pathways and thus respond similarly to the rate-driven kinetic fractionation.

L285: How was the magnitude of Ba isotope fractionation calculated?

The magnitude of Ba isotope fractionation was calculated as the difference between the isotopic composition of the coral skeleton and the ambient seawater. Since we did not observe significant variations in the seawater Ba isotope composition in our study site (Discussion 4.1), we used the regionally mean seawater value of δ138Ba = 0.63‰ (Cao et al., 2020) to calculate the fractionation factor for each sub-sample.

Figure 4: It is noted in the test that the correlations between SST and δ44Ca (and δ88Sr) are statistically significant. What type of statistical method was used? In particular, was a Deming type regression used, as is needed for data with uncertainty in both the x and y variables? I ask partially because when browsing the supplementary data, simple linear regressions (2-tailed paired t-test) show statistically significant correlation between δ138Ba and SST. Throughout the text, please clarify the statistical methods used.

We thank the reviewer for the constructive suggestion regarding the statistical method. We have re-analysed all correlations using the York regression method (York et al., 2004) to account for uncertainties in both X and Y variables. We assigned a conservative uncertainty of ±0.5 °C (1SD, Rayner et al., 2003) to the HadISST data, alongside the long-term analytical precisions (2SD) for our isotope measurements (± 0.04‰ for δ44Ca, ± 0.02‰ for δ88Sr, and ± 0.03‰ for δ138Ba). The results confirm that both δ44Ca and δ88Sr exhibit statistically significant negative correlations with SST (p = 0.002 for δ44Ca and $p < 0.001$ for δ88Sr). The York regression yields a p-value of 0.536 for the δ138Ba-SST correlation, suggesting that there is no statistically significant temperature dependence for Ba isotope fractionation. We have revised the manuscript to show these statistical methods and results.

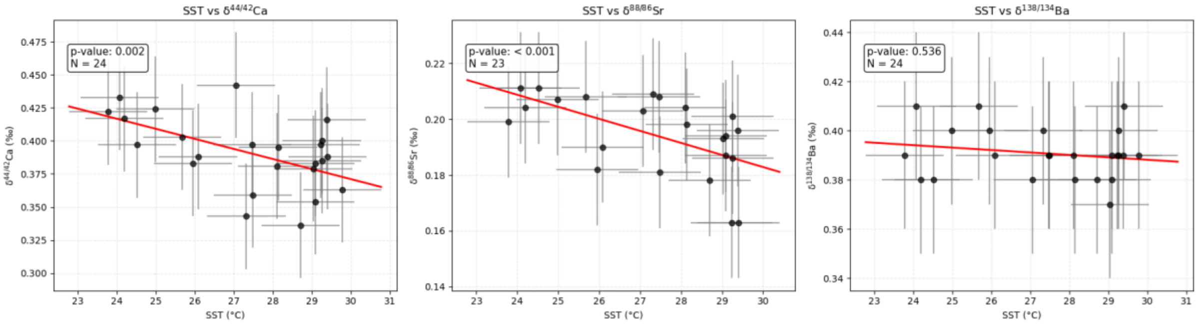

Figure R2: York regression analysis of the relationships between (a) skeletal δ44Ca vs. SST (b) skeletal δ88Sr vs. SST and (c) skeletal δ138Ba vs. SST.

L320: The author’s mention that “temperature-sensitive partitioning of Sr and Ca into coral aragonite is likely the primary driver of seasonal variations in skeletal Sr/Ca records”, however the analysis throughout the text discusses mechanistic drivers of these signatures as related to ion transport into the extracellular calcifying fluid. Can you clarify what is meant?

We clarify that while the rate of ion transport exerts a strong kinetic control on the isotope fractionations of δ88Sr and δ44Ca, it does not necessarily change the elemental Sr/Ca ratio of the calcifying fluid. Although metabolic rates fluctuate seasonally and change ion fluxes of both Ca and Sr, the Sr/Ca ratio within the fluid remains relatively comparable to that of seawater. This stability in the fluid Sr/Ca ratio, despite variations in absolute ion concentrations, implies that skeletal Sr/Ca is primarily controlled by temperature-dependent partitioning during aragonite precipitation.

Reviewer #2

I find the manuscript interesting but I am not totally convinced by the explanations given by the authors, or at least, it needs more discussion.

L34: There are many more studies dealing with this subject. Please acknowledge this.

We thank the reviewer for pointing this out. We have expanded the citations (Cohen & McConnaughey, 2003; Allemand et la., 2004; Al-Horani et al., 2003; Gagnon et al., 2012; Tambutte et al., 2011) in the introduction to provide a more comprehensive overview of this topic.

L63: Sr/Ca is also largely dependent of the growth rate (eg deVilliers et al 1994). Is it comprised in the uptake dynamics?

We clarify that the growth rate effect on Sr/Ca, as described by de Villiers et al. (1994), is generally interpreted as a kinetic effect occurring during the precipitation of aragonite crystals. In our study, uptake dynamics refer to the active transport of ions from seawater into the extracellular calcifying fluid. While high transport rates are necessary to support high skeletal growth rates, the specific mechanism by which growth rate alters skeletal Sr/Ca is different. The former relates to the supply of ions to the fluid, whereas the latter relates to the partitioning of ions from the fluid into the solid crystals. We have clarified this point in the revised manuscript.

Methods

L87: could you specify the entire name of the species?

We have specified the full scientific name of the coral species as *Porites lutea* in the revised manuscript.

More information in the methods is needed.

L89: what were the weights of the subsamples?

Subsamples of approximately 0.5 mg were used in this study. This information has been added to the revised manuscript.

L95: Size of the analysed samples?

Typically, 0.5 mL of the sample solution with a Ca concentration of 20 ppm was used for trace element analyses, corresponding to a mass of 10 ug Ca per analysis.

L106: what is the in-house standard? Value? Why d18O data is not presented in the manuscript, as it is generally measured with d13C?

The in-house standard used in our laboratory is “Std Bremen” which was made from a German limestone. It has been calibrated against NBS-19 and yields a long-term mean δ13C value of –2.93 ± 0.10‰ (2SD). We have updated the Methods section to add this specific information in the revised manuscript.

We focused on δ13C because it serves as a direct proxy for coral metabolic activity, which is central to our discussion on metabolically driven ion transport dynamics. To maintain a focused discussion on the biological mechanisms of ion uptake, we chose not to include the δ18O records in this manuscript.

Ca, Ba and Sr isotopes: size of the samples analysed?

The analysed sample sizes used for chemical purification and isotope analyses are 50 ug for Ca, 250 ng for Sr, and 50 ng for Ba. We have added these aliquot specifications to the respective method section in the revised manuscript.

L122: what is the accepted value?

The accepted value for the coral JCp-1 standard is 0.195 ± 0.008 (2SE, Krabbenhoft et al., 2009) relative to the NBS 987 standard. We have included this value in the revised manuscript to ensure data quality.

Figure2: please add the error bars in a corner of the graphs.

We have added error bars representing the average long-term analytical precision (2SD) for each proxy in the corner of the respective panels.

L231-236: Why this mechanism is not apparent for the other studies? The explanations are not clear for me and I do not really understand why this mechanism expresses for some corals and not for some others.

We thank the reviewer for highlighting this comparison. As detailed in our response to Reviewer 1 (the comment on L235), we propose that the observed negative δ44Ca-SST correlation is mainly driven by metabolically stimulated active transport rates and associated strong kinetic fractionation.

I have the same remark for the explanations of Sr isotopes.

We thank the reviewer for this remark. As detailed in our response to Reviewer 1 (the comment on L260), we interpret the coherent negative temperature dependence of both δ88Sr and δ44Ca as evidence of a shared active transport pathway. This coupling is facilitated by their similar effective ionic radii of Sr and Ca (Shannon, 1976). In the revised manuscript, we have clarified that this synchronised kinetic fractionation is driven by the same metabolic mechanism.

L254: delete one "in"

Done.

If the mechanisms are the same for Ca and Sr, why there is no significant relationship between d44/42Ca and d88/86Sr? is it expected even if the mechanisms of their variations are the same?

We appreciate the reviewer’s comment. In the revised manuscript, we have evaluated the relationship between δ44Ca and δ88Sr using York regression analysis to account for analytical uncertainties in both variables (please also see our response to Reviewer 1’s comment on Figure 4). This statistical analysis reveals a significant positive correlation (*p* = 0.001) between δ44Ca and δ88Sr. This positive correlation supports our hypothesis that the temperature-driven upregulation of the Ca channel/pump accelerates the transport of both Ca and Sr ions, resulting in a simultaneous kinetic isotope effect that drives both isotope systems towards light values during periods of enhanced ion uptake.

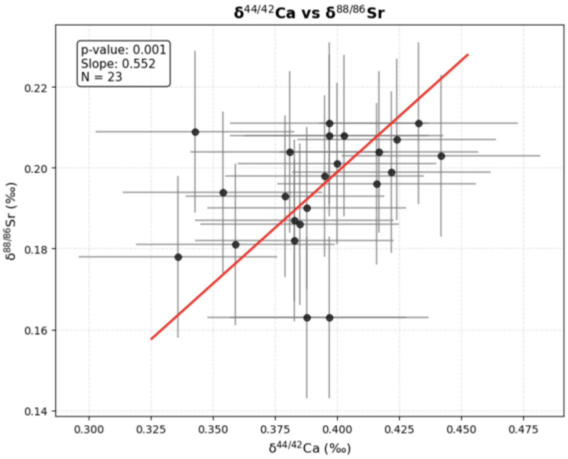

Figure R3: York regression of skeletal δ44Ca vs. δ88Sr.