Evolving Earth 1 (2023) 100016

Contents lists available at ScienceDirect

Evolving Earth

journal homepage: www.sciencedirect.com/journal/evolving-earth

Is there a link between carbon isotopes and sea level in epicontinental carbonate settings?

Page C. Quinton [*], Michael C. Rygel

State University of New York, College at Potsdam, Department of Earth and Environmental Sciences, 44 Pierrepont Ave., Potsdam, NY, 13676, USA

A B S T R A C T

A presumed link between carbon isotopic trends and sea level change features prominently in many studies of epicontinental carbonates. In these shallow marine environments, a combination of basin restriction, burial/oxidation of organic carbon, proximity to terrestrial carbon sources, carbonate mineralogy, and/or meteoric influence can result in $\delta^{13}C_{carb}$ records that are distinct from that of the open ocean. Because many of these processes are linked to sea level change, it has been argued that sea level might exert a significant and systematic control on the $\delta^{13}C_{carb}$ records from epicontinental settings. Multiple studies have attempted to document sea level's influence on carbon isotopic trends, but they do so with only limited constraints on sea level change and without objective evaluations of interpreted trends and relationships. We argue that the complex and complicated set of processes influencing carbon isotopic values in epicontinental settings requires a systematic approach to truly address the question of sea level's influence on $\delta^{13}C_{carb}$. Only by integrating carbon isotopic records with a detailed sedimentological and sequence stratigraphic framework can we properly track changes in depositional environments and reconstruct the transgressive-regressive history of the rocks. Trends and relationships in these robust datasets can be evaluated with rank correlation tests specifically designed and empirically tested to deal with noisy datasets. In short, we map a possible path forward for systematic testing of the relationship between sea level and $\delta^{13}C_{carb}$.

1. Introduction: the carbon isotopic proxy

Carbon isotopic excursions have become an important chemostratigraphic, paleoclimatic, and paleoredox tool in recent decades, so much so that we've developed an impressive collection of acronyms to name them (SPICE, GICE, HICE, TICE, etc.). Global excursions are particularly important because they reflect a significant perturbation to the global carbon cycle and potentially indicate a change in atmospheric carbon dioxide levels. Generally, positive carbon isotopic excursions are generated when organic carbon, which tends to be enriched in ^{12}C, is transferred from surface reservoirs (e.g., ocean and atmosphere) to sediment and eventually sedimentary rock. The preferential removal of ^{12}C is recorded as an increase in the $\delta^{13}C_{carb}$ (the ratio of ^{13}C–^{12}C) values of coeval marine carbonates. Burial of organic carbon also results in the removal of carbon dioxide from the atmosphere. Thus, positive carbon isotopic excursions can be interpreted to reflect a decrease in atmospheric carbon dioxide levels. This relationship is the basis of the carbon isotopic proxy in paleoclimatic studies.

While the application of the carbon isotopic proxy to paleoclimatic questions has been successful at constraining fluxes in the global carbon cycle (Cramer and Jarvis, 2020), processes in shallow marine carbonate settings can complicate our interpretation of the geochemical record. Although influenced by global ocean chemistry, carbon isotopic values from carbonates formed in shallow or restricted marine environments may show a significant departure from the global signal via a complex set of local and regional processes. Modern studies of shallow marine environments have demonstrated that these processes can result in as much as a 4‰ offset in $\delta^{13}C_{DIC}$ values (carbon isotopic value of dissolved inorganic carbon) relative to the open ocean (Patterson and Walter, 1994). The relationship between the $\delta^{13}C_{carb}$ trends of shallow marine environments and global ocean chemistry is further complicated because changes in sea level (whether they be eustatic or relative) can directly and/or indirectly influence many of the processes controlling carbon isotopic values. Correlation between relative sea level and carbon isotopic trends documented in recent shallow marine settings (Swart and Eberli, 2005; Swart, 2008) and carbonates from epicontinental seas (Jenkyns, 1996; Immenhauser et al., 2003; Fanton and Holmden, 2007) is argued to be a consequence of the control that sea level can exert on carbon isotopic values. However, there are also cases where carbon isotopic patterns show no relationship with sea level change (Husinec and Bergström, 2015; Quinton et al., 2023).

The possibility that sea level may exert a significant and systematic control on the carbon isotopic values of shallow marine carbonates has important implications for the carbon isotopic proxy, especially given that the primary pre-Mesozoic record for carbon isotopic trends is derived from carbonates formed in epicontinental seas. Herein, we

* Corresponding author.
E-mail address: quintopc@potsdam.edu (P.C. Quinton).

https://doi.org/10.1016/j.eve.2023.100016
Received 4 October 2023; Received in revised form 16 October 2023; Accepted 16 October 2023
Available online 17 October 2023

review the processes that influence $\delta^{13}C_{carb}$ values of shallow water carbonates and how those processes might be influenced by sea level. We focus on three different models from the literature relating sea level to carbon isotopic records, explore complications with these models, and propose tests to quantitatively verify whether $\delta^{13}C_{carb}$ trends are related to sea level in the geologic record.

2. Sea level change and carbon isotopes

The carbon isotopic values of shallow marine carbonates are influenced by a complex set of processes that can generally be placed into four categories: net photosynthesis, terrestrial organic carbon influx, meteoric input and/or diagenesis, and carbonate sedimentation (Fig. 1). These processes can significantly influence the $\delta^{13}C_{carb}$ values of carbonates in epicontinental seas because these settings routinely become restricted from the open ocean, have surface waters that experience non-equilibrium conditions with the atmosphere, and can be greatly influenced by freshwater and terrestrial carbon sources. Because sea level controls many of these processes, it has been argued that sea level change, whether it be eustatic or regional, might result in systematic carbon isotopic patterns in epicontinental settings.

2.1. Carbon cycle model

The connection between sea level and carbon cycling is a recurring theme in the literature (Jenkyns, 1996; Fanton and Holmden, 2007). The core tenet of this model is that sea level controls the net surface area for primary productivity, as well as upwelling of nutrient-rich waters (that can fuel primary productivity) and/or oxygen-poor waters (that can promote the preservation of organic carbon). The net result is that sea level change influences the net burial or oxidation of organic carbon and thus the $\delta^{13}C_{carb}$ value recorded in coeval carbonate deposits. During transgression, increased upwelling of nutrient-rich waters and increased surface area for primary productivity results in increased organic carbon burial. The result is increased $\delta^{13}C_{carb}$ values in coeval carbonate sediments. During regression, primary productivity decreases which causes decreased $\delta^{13}C_{carb}$ values in coeval carbonate deposits. These effects could reflect global or regional processes and can be amplified by proximity to terrestrial carbon sources (typically enriched in ^{12}C) and basin restriction. Regardless, the net result is that transgressions might led to positive excursions in $\delta^{13}C_{carb}$ values. This relationship has been argued for in multiple Paleozoic and Mesozoic basins (Jenkyns, 1996; Fanton and Holmden, 2007; Katz et al., 2007).

2.2. Meteoric water model

Sea level and meteoric influence are linked because sea level controls proximity to shoreline and the geographic extent of subaerial exposure. During sea level lows, penetration of meteoric fluids (potentially enriched in respired ^{12}C) can lead to alteration of carbon isotopic values in existing carbonates. The result is that carbon isotopic are altered beneath sequence boundaries and other exposure surfaces. The effects of this model, described by Allan and Matthews (1982), are avoided in geochemical studies by looking for signs of meteoric alteration. However, sea level and its control on meteoric fluids can potentially have a more active role in the generation of carbon isotopic trends.

Sea level can influence the degree of basin restriction and therefore the ratio of meteoric fluids to sea water. During sea level lows, basin restriction can create an isotopically evolved fluid (typically low carbon isotopic values due to increased meteoric influence). As sea level rises, increased circulation and/or shifting shoreline position leads to decreased meteoric influence and higher $\delta^{13}C_{carb}$ values in coeval carbonate sediments. The result is that transgressions could lead to positive excursions in $\delta^{13}C_{carb}$ values. Such a model was proposed by Immenhauser et al. (2003) based on data from the Late Carboniferous. If a common phenomenon, such an active role for meteoric fluids would be

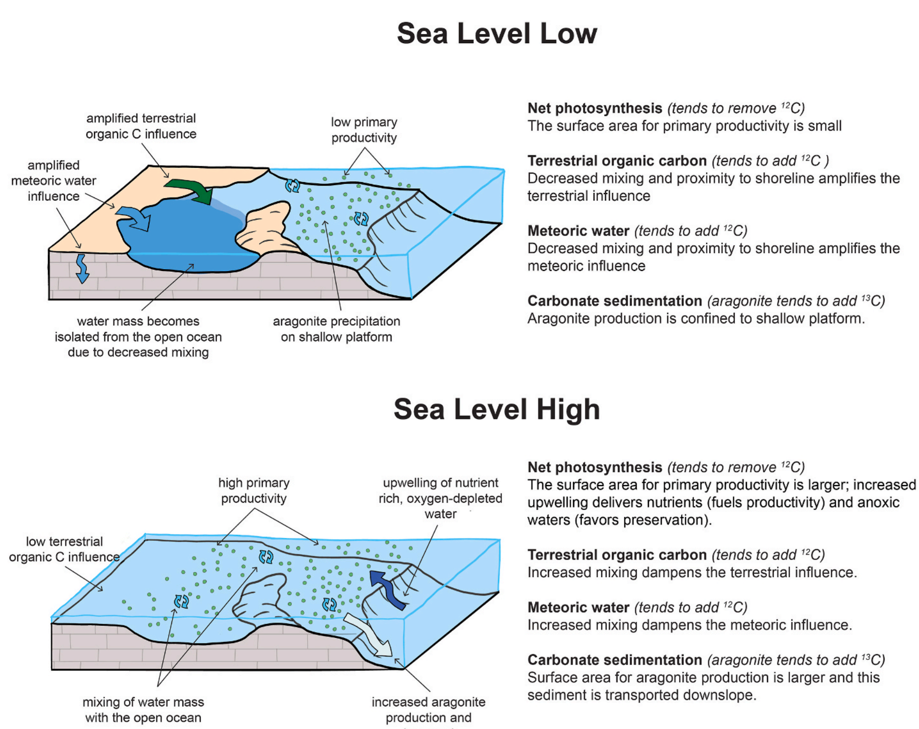

Fig. 1. Schematic diagram outlining some of the common processes that can influence carbon isotopic values in epicontinental settings. To illustrate how those processes vary with sea level, the two endmember states of sea level change (sea level low and sea level high) are shown. These are the processes typically invoked in models arguing for a systematic relationship between sea level and $\delta^{13}C_{carb}$ trends. For a full summary of the processes influencing $\delta^{13}C_{carb}$ trends see Ahm and Husson (2022).

problematic for paleoclimatic and chemostratigraphic studies because the meteoric influence cannot be avoided simply by avoiding meteoric cement.

2.3. Carbonate sedimentation model

Sea level controls the production, export, mixing, and type of carbonate sediments. These processes are linked to carbon isotopic trends because the sediments are the records of those trends, and the type of carbonate controls the value recorded. Aragonite tends to form in the shallowest water settings and typically has carbon isotopic values 2–3‰ higher than the low magnesium calcite (LMC) that forms on the flanks of the carbonate banks (Swart and Eberli, 2005). Based on these relationships and observations from the Great Bahama Banks, Swart (2008) argued that sea level change would result in positive carbon isotopic excursions that get preserved even after the aragonite is recrystallized to LMC after burial. In this scenario, as sea level rises, aragonite production increases and carbon isotopic values increase. Those sediments are mixed and moved downslope resulting in increasing carbon isotopic values in those settings. The result is a series of progressively younger positive carbon isotope excursions along a transect of the basin.

3. Is it really that simple?

The three models for the relationship between sea level and $\delta^{13}C_{carb}$ values argue for a systematic relationship based on a subset of potential processes influencing carbon isotopic values and do so based on generalized relationships between these processes and sea level. Very few studies of the ancient record attempt to establish the relationship between sea level and carbon isotopes by interpreting carbon isotopic patterns against a detailed sequence stratigraphic framework (some exceptions include Fanton and Holmden, 2007; Katz et al., 2007; Swart and Eberli, 2005; Husinec and Bergström, 2015; Quinton et al., 2021, 2023). Instead, many argue for the relationship based on regional to global relative sea level curves. Correlations between carbon isotopic trends and sea level can exist only in the eye of the interpreter, and very few studies attempt to constrain the relationship quantitatively (Quinton et al., 2021, 2023). This begs the question: does sea level change really influence the carbon isotopic trends of epicontinental carbonates in a systematic, repeatable, and resolvable way or are there too many complicating factors at play?

One important potential complication to models relating sea level change and $\delta^{13}C_{carb}$ trends is that they tend to oversimplify the complex processes influencing carbon isotopic values in shallow marine carbonates (Table 1). For example, rising sea level has been linked to the upwelling of nutrient rich water, driving an increase in net primary productivity and the burial of organic matter. However, exposure and weathering of rocks on land during a fall in sea level might just as easily accomplish a similar result by increasing nutrient supply via fluvial input (Oehlert et al., 2019). Thus, it is conceivable that increased $\delta^{13}C_{carb}$ values due to nutrient fueled primary productivity could occur during both sea level rise and fall. It becomes difficult to establish a relationship between sea level and carbon isotopic trends if the end member states of sea level change (high and low) influence the carbon isotopic values in the same way and/or if its influence is dependent on other external factors.

Input of terrestrial organic matter has an equally complex relationship with sea level change. Although sea level change can influence the proximity of shoreline and basin restriction and therefore the influx of terrestrial carbon sources, how those carbon sources impact the $\delta^{13}C_{carb}$ values is complex and variable. The source and type of organic matter contributing carbon to the dissolved inorganic carbon (DIC) of a water mass can greatly influence the $\delta^{13}C_{DIC}$. In the modern, terrestrial organic carbon with an average value of −27‰ tends to be more enriched in ^{12}C than marine organic carbon (which ranges from −18‰ to −22‰). Remineralization of terrestrial organic carbon in modern nearshore settings can result in lower $\delta^{13}C_{DIC}$ (Patterson and Walter, 1994; Ahm and Husson, 2022). However, the average carbon isotopic composition of marine and terrestrial organic matter has changed over time. In the Silurian and Devonian, average terrestrial organic carbon had $\delta^{13}C$ values of approximately −26‰ and was more enriched in ^{12}C than marine organic carbon (Peters-Kottig et al., 2006). However, in the Mississippian through Permian, average terrestrial organic carbon $\delta^{13}C$ values were between −22‰ and −23‰ and were less enriched in ^{12}C than marine organic carbon (Peters-Kottig et al., 2006). Consequently, changes in the relative proportion of terrestrial versus marine organic matter remineralization would have had varying effects on the $\delta^{13}C_{carb}$ values in epicontinental settings through time.

There are many other processes that can influence $\delta^{13}C_{carb}$ trends in shallow water settings that are either independent of, or only loosely connected to, changes in sea level. The influx of terrestrial material (whether it be organic carbon or meteoric water) and its influence on $\delta^{13}C_{carb}$ values in epicontinental settings is controlled by climate, fluvial processes, and regional geology in addition to proximity to shoreline and basin restriction (Ahm and Husson, 2022). Regional precipitation patterns control the amount of surface runoff and how long that water interacts with the rocks exposed at the surface. A shallow marine setting adjacent to an arid regional climatic regime might be expected to have less influence from meteoric water. Alternatively, a shallow marine setting adjacent to an area that experiences strongly seasonal and/or

Table 1
Summary of the common processes influencing carbon isotopic values of shallow marine carbonates along with complicating factors. Sources are [1] Ahm and Husson (2022), [2] Oehlert et al. (2019), [3] Patterson and Walter (1994), [4] Peters-Kottig et al. (2006), [5] Swart (2008), [6] Geyman and Maloof (2021).

Summary of processes influencing the carbon isotopic values of shallow marine carbonates				
Processes influencing $\delta^{13}C$ of carbonates	**Primary productivity & burial of organics**	**Terrestrial organics**	**Meteoric influence**	**Carbonate mineralogy & sedimentation**
	Organic material is enriched in ^{12}C relative to the oceans and atmosphere[1]	Modern terrestrial organics tend to be enriched in ^{12}C relative to marine organic carbon[2,3]	Meteoric water can be enriched in ^{12}C because via respired carbon[1]	Shallow water aragonite is enriched in ^{13}C relative to deeper water calcite[5]
Increased (↑) $\delta^{13}C$ of carbonates (simple model)	↑ primary productivity and burial	↓ terrestrial organics	↓ meteoric influence	↑ aragonite or ↓ calcite
Decreased (↓) $\delta^{13}C$ of carbonates (simple model)	↓ primary productivity and burial	↑ terrestrial organics	↑ meteoric influence	↓ aragonite or ↑ calcite
Complications	A variety of different processes can influence primary productivity and the burial of organics; there are also complications associated with the relative abundance of marine versus organic carbon (next column)[2]	The carbon isotopic value of terrestrial organics has changed through time; in the Late Paleozoic, terrestrial organic carbon may have been depleted in ^{12}C relative to marine organic carbon and the relationship describe above would have been reversed[4]	Climate, fluvial processes, and regional geology can have a profound effect on the carbon isotopic signature of meteoric waters[1]	Carbonate components can have carbon isotopic differences caused by vital effects, non-equilibrium precipitation, and differences in the fractionation[6]

flashy rainfall might experience significant influence from meteoric water but since that runoff doesn't spend much time interacting with terrestrial carbon sources (e.g., organic carbon or exposed rocks) its carbon isotopic composition might more closely match that of atmospheric CO_2. Changes in the paleogeographic position of rivers along the shoreline (and the meteoric water they carry) could also conceivably influence the $\delta^{13}C_{carb}$ values of a shallow marine setting. Shoals, reefs, or other positive topographic features that reduce mixing can also locally influence the $\delta^{13}C_{carb}$ values of these shallow marine settings. Lastly, the nature and extent of the rocks that the meteoric fluids interact with will influence how that water effects the $\delta^{13}C_{carb}$ values (exposed carbonates are expected to contribute more ^{13}C while organic rich rocks will contribute more ^{12}C).

Data collection and the nature of the carbonate record might also complicate our attempts to test for a systematic relationship between carbon isotopic trends and sea level in ancient epicontinental settings. Ideally, the goal is to generate a carbon isotopic curve that reflects average trends in the $\delta^{13}C$ value of the DIC in that shallow marine setting. But there are plenty of sources of noise that might interfere with that goal, including nondeposition, erosion, or differences in allochem type. Carbonate mud has been established as the component most likely to record the $\delta^{13}C_{DIC}$ value of the ocean at the time of precipitation (Geyman et al., 2022) and, due to its lower permeability, the least likely to be altered (Hayes et al., 1989). A combination of vital effects, non-equilibrium precipitation, and differences in the fractionation factor of other allochem types can result in significant departure from the $\delta^{13}C$ value of the water they precipitate from (Swart, 2008; Geyman and Maloof, 2021). While carbonate mud represents the ideal record of $\delta^{13}C_{DIC}$ values, not all of it can be treated equally. Automicrite that precipitates in pore space can be greatly influenced by the anoxic remineralization of organic carbon with resulting $\delta^{13}C_{carb}$ values greatly enriched in ^{13}C (Ahm and Husson, 2022). Because it would be very challenging to construct a carbon isotopic record of shallow marine settings solely from carbonate mud, it's likely that differences in allochem type contribute to variation in $\delta^{13}C_{carb}$ values from epicontinental settings. The dominant type of allochem commonly varies with environment and environments shift with changes in sea level; as such it is possible that this variable can contribute to a relationship between sea level and carbon isotopic trends. But it is just as likely that it could introduce noise into the system that could obscure a relationship between sea level and carbon isotopes.

Overall, there are a complex set of factors that complicate the carbon isotopic trends recorded in epicontinental settings. These complicating factors might not be directly or completely influenced by sea level change. Even in a scenario where sea level change is influencing $\delta^{13}C_{carb}$ trends, complicating factors might obscure the signal. Given all of that, is there a way to test for a systematic relationship between sea level change and carbon isotopes in epicontinental settings despite these complicating factors?

4. A way forward

We propose a method to quantitively test for a relationship between sea level change and $\delta^{13}C_{carb}$ values. First, all carbon isotopic data must be integrated with a detailed sedimentological and sequence stratigraphic framework to track changes in depositional environments and reconstruct the transgressive-regressive history of the rocks. In the simplest case, the transgressive systems tract (TST) represents an interval of time when the creation of accommodation outpaces sediment accumulation (relative sea-level rise) and the highstand systems tract (HST) represents an interval of time when sediment accumulation exceeds the generation of accommodation (relative sea level fall). Correlation tests widely available in statistical packages like IBM SPSS (e.g., Pearson Correlation or Spearman Rank Correlation) can be used to test for correlation between $\delta^{13}C_{carb}$ trends and the sequence stratigraphic framework by focusing on trends in systems tracts within a given sequence (a sea level cycle). If carbon isotopic trends are correlated with sea level change, then we expect to see a strong statistically significant correlation between carbon isotopic values and meterage in the transgressive systems tract (TST) followed by a strong statistically significant correlation in the opposite direction between carbon isotopic values and meterage in the highstand systems tract (HST). While these traditional correlation tests will generally be enough to establish a relationship between sea level and carbon isotopes, they can result in a type 2 statistical error (that is they report a *p*-value that suggests there is no statistically significant correlation, when in fact there is) when dealing with noisy data. This is problematic given all the complicating factors discussed in section 3 that can potentially influence carbon isotopic values in epicontinental settings.

To test for correlation between sea level and carbon isotopes, we propose the use of correlation tests designed for noisy datasets. The Gaussian Rank Correlation test developed by Boudt et al. (2012) has been empirically tested and compared to traditional tests like the Spearman Rank Correlation test (Bodenhofer et al., 2013). Bodenhofer et al. (2013) demonstrated that the novel Gaussian Rank Correlation test is more successful at identifying correlations in noisy datasets than the traditional tests. It should be noted that the Gaussian Rank Correlation test achieves this success without sacrificing performance at avoiding type 1 errors (wrongly attributing statistical significance when there is none). In Fig. 2 we demonstrate the difference in performance between the Gaussian Rank Correlation test and the traditional Spearman Rank Correlation test for an Ordovician $\delta^{13}C_{carb}$ dataset from Quinton et al. (2021). By artificially introducing a realistic level of noise into that dataset, the Spearman Rank Correlation test fails while the Gaussian Rank Correlation test still identifies the statistically significant correlation. The one drawback is that the Gaussian Rank Correlation test cannot easily be performed in widely accessible statistical analysis packages like IBM SPSS. But it has been implemented in R (Bodenhofer et al., 2013) and with a baseline level of coding knowledge the test can be performed on Excel datasets (directions for performing the analysis are provided in the supplemental materials).

5. Conclusions

The possibility that sea level change in epicontinental settings might result in systematic patterns in $\delta^{13}C_{carb}$ trends, not necessarily connected to global changes in the carbon cycle, needs to be systematically tested. Not only does the possibility of such a relationship have important implications for the use of these records in paleoclimatic and paleoredox applications, but there might also be important information to be learned about regional and local environmental processes operating in a basin.

To test for a relationship between sea level and carbon isotopic trends, we propose the application of a unique statistical correlation method that can deal with noisy datasets. But for these analyses to be conducted, carbon isotopic datasets must be paired with:

- Detailed measured sections to which the carbon isotopic values can be directly tied. These kinds of primary datasets are not as commonly supplied in publications as they should be. With most journals offering online supplementary materials, this is easily remedied.
- Detailed facies analysis and sequence stratigraphic framework for the sections from which the carbon isotopic data is generated in order to tie trends to the transgressive-regressive history recorded by the strata.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Page Quinton reports financial support was provided by National Science Foundation.

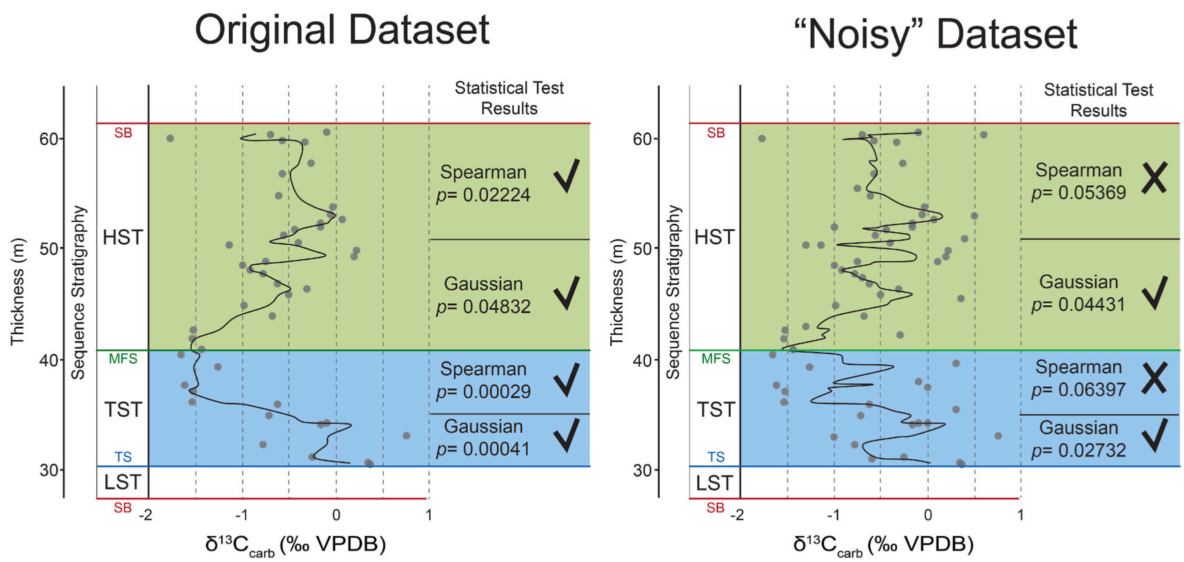

Fig. 2. Comparison of the Spearman Rank Correlation (standard) test and the Gaussian Rank Correlation (designed for noisy data) test performance on a Late Ordovician dataset from Quinton et al. (2021). A standard *p*-value of <0.05 is set for statistically significant correlation. For the original dataset, both tests report statistically significant correlations for the TST (transgressive systems tract) and the HST (highstand systems tract). This finding supports the claim that carbon isotopic trends are correlated with sea level change. To create a hypothetical "noisy" dataset, 19 $\delta^{13}C_{carb}$ values were added to the original dataset. To make the artificial noise realistic, all added values fall within the standard deviation of the real data for each systems tract. For the "noisy" dataset, only the Gaussian Rank Correlation test returned a p-value indicating statistical significance. Note that this example is just for demonstration purposes, refer to Bodenhofer et al. (2013) for a comprehensive comparison of rank correlation test performance. Acronyms for the sequence stratigraphic framework are: LST - lowstand systems tract, TS - transgressive surface, MFS - maximum flooding surface, and SB - sequence boundary.

Data availability

Data will be made available on request.

Acknowledgements

Comments by Howard Falcon-Lang (editor) and J. Fred Read greatly improved this manuscript. We thank Thomas Algeo for his helpful suggestion (on earlier publications) that we explore quantitative methods for testing the relationship between carbon isotopes and sequence stratigraphic framework. Additionally, we thank Robert Gastaldo for his insightful comments on the first draft of a proposal that first articulated some of the ideas in this paper. This project was funded by NSF EAR 2042276 to Quinton and Rygel.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eve.2023.100016.

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