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Supplemental Material

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SUPPLEMENTAL MATERIAL FOR

Finding a VOICE In the Southern Hemisphere: A New Record of Global Organic Carbon?

Weger, Ralf J., Eberli, Gregor P., Rodriguez Blanco, Leticia, Tenaglia, Maximillian, Swart, Peter K.

CONTENTS

Chronostratigraphic Overview

The Mendoza Group was deposited during Late Jurassic – Early Cretaceous age (Leanza and Hugo, 1977; Aguirre-Urreta and Rawson, 1997; Aguirre-Urreta et al., 2005). However, there are a variety of arguments and differences in the interpretation of ammonite zone boundaries and their placement in absolute time that produces different age models. Below we delineate in detail how these interpretations and our resulting age model align with the currently accepted ages.

Ammonite biozones in the Vaca Muerta Formation had been studied and defined even prior to Weaver (1931). Since then, numerous revisions and refinements have been completed (among many others, Leanza, 1945; Leanza and Leanza, 1973; Leanza and HA, 1981; Leanza, 1996; Parent, 2006; Parent et al., 2011; Parent et al., 2015; Vennari, 2016; Parent et al., 2017). Leanza et al. (2020a) and Leanza et al. (2020b) provide an extensive summary contrasting the current state of the Andean ammonite zonation in comparison to the standard Tethyan realm (Sub-Mediterranean) (Leanza et al., 2020a) and in reference to Paleomagnetic Polarity Chrons (Leanza et al., 2020b). Comparing those two different versions with information from the latest Geologic Time Scale (Gale et al., 2020; Hesselbo et al., 2020) reveals that the exact positioning of Andean Ammonite Biozones in absolute time remains a topic of discussion (Fig. S1). According to Parent et al. (2015), the ammonite zones of the oldest sediments at the base of the Vaca Muerta Formation are *Picunleufense (α and β)* which are contemporaneous with the *Hybonoticeras hybonotum* in the Tethyan realm (Sub-Mediterranean) standard and directly overlain by *Pseudolissoceras Zitteli*. Vennari (2016) does not include those biozones in her biostratigraphic chart of the lower Tithonian, but her oldest biozone is *Virgatosphinctes andesensis* which includes the *Picunleufense* (α and β) and is directly below *P. Zitteli*. In this study we follow Vennari and place the base of the Vaca Muerta Formation in the low portion of the V. *andesensis* Zone (into *Picunleufense* according to Parent et al. (2015)). The

Tithonian-Berriassian boundary (143.1 myrs) is placed by Gale et al. (2020) within the lower half of the *Berriasella jacobi* ammonite zone in the Tethyan realm (Sub-Mediterranean). This placement is fairly consistent with both Leanza et al. (2020a) and Leanza et al. (2020b) who correlate the lower half of the *B. jacobi* ammonite zone in the Tethyan realm as time equivalent to the lower most portion of the *Substeueroceras koeneni* ammonite zone in the Andean but placements of Tithonian – Berriasian boundary by others are widely different. Riccardi (2015) as well as (Salazar et al., 2020, an example from chile, only a few hundred km to the NE), place the Tithonian – Berriasian boundary at or near the top of the *C. alternans* zone which they correlate to the lower part of the *B. jacobi* zone in the Tethyan realm (Sub-Mediterranean province). Parent et al. (2015) positions the Tithonian – Berriasian boundary at the top of the *S. koeneni* zone (the base of the *Argentiniceras nodeliferum* zone), correlating it to the upper part of the *B. jacobi* zone in the Tethyan realm, making the entire *S. koeneni* ammonite zone approximately 1 my older. Finally, Kietzmann et al. (2018) position of the Tithonian – Berriasian boundary based on ammonite zone duration into the lower half of the *S. koeneni* zone.The transition from the Berriasian to the Valanginian stage is placed by most researcher, except for Riccardi (2015), at the top of the *Spiticeras damesi* zone (base of the *Neocomites wichmanni* zone) in the Andean and correlated to the top of the *Tirnovella alpillensis* zone (base of the *"Thurmanniceras" pertransiens* zone) from the standard Tethyan realm (Sub-Mediterranean province) (Leanza et al., 2020a).

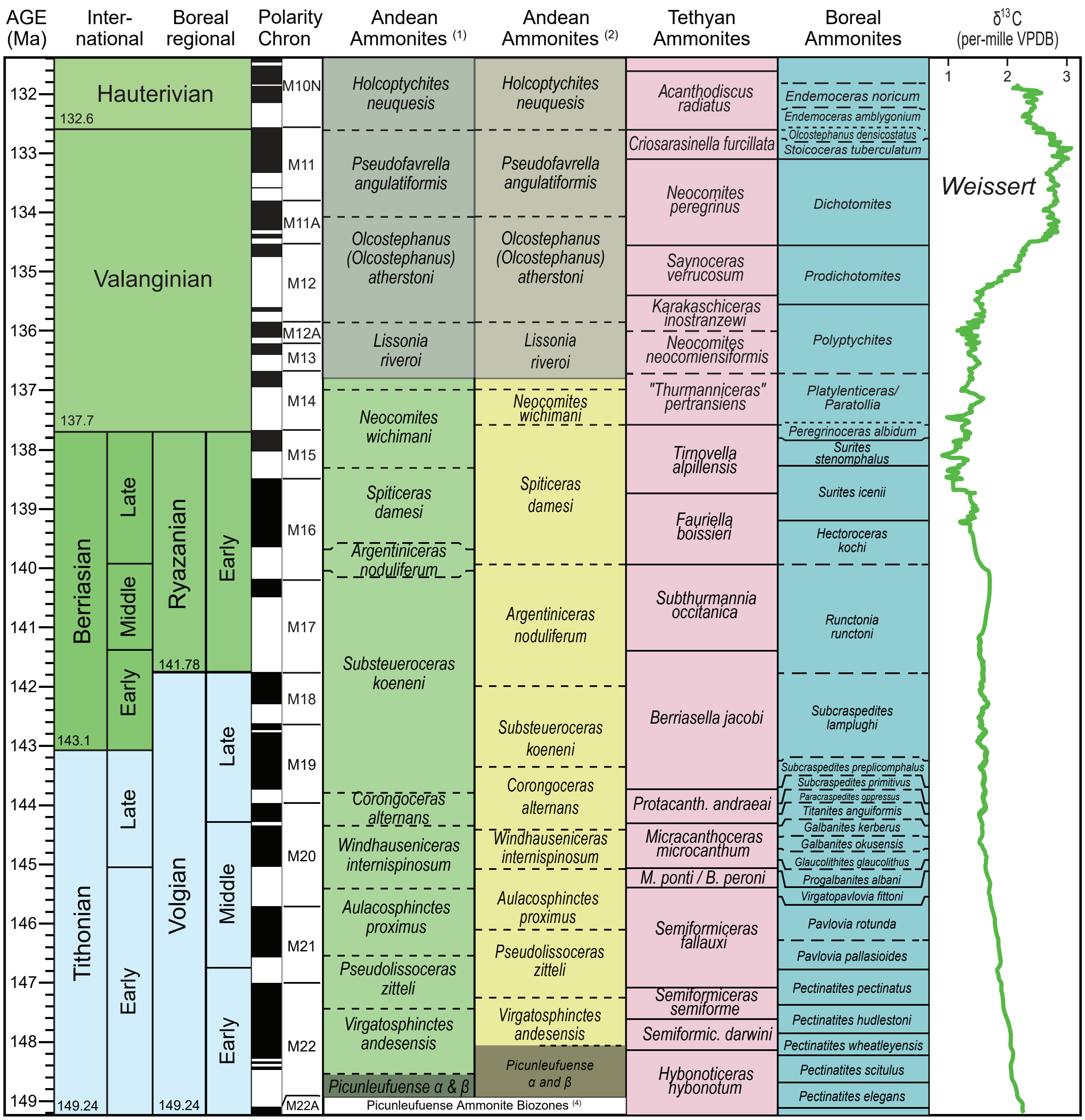
The youngest deposits of the Vaca Muerta-Quintuco system fall into the *Lissonia riveroi* ammonite zone which is thought to be contemporaneous to the ammonite zone above *T. pertransiens* (Parent et al., 2015) or *Neocomites neocomiensiformis* in Mediterranean/Tethyan Standard (Leanza et al., 2020a) of Early Valanginian age.

The topic of absolute ages is even more complex and more controversial, and still a topic of discussion. Radio-isotopic dates from outcrop sections near the top of the Tithonian that provide an age of 140 Ma for the Tithonian – Berriassian boundary have been presented by Aguirre-Urreta et al. (2019). In conjunction with other dates obtained in the Neuquen Basin (Aguirre-Urreta et al., 2015; Naipauer et al., 2015; Horton et al., 2016; Aguirre-Urreta et al., 2017) and in other places around the world (Bralower, 1990; Muttoni et al., 2018). Aguirre-Urreta et al. (2019) made a convincing case that proposed an overall 5 Myr shift for the entire age range. In 2020 a new and revised Geologic Time Scale was published (Gradstein et al., 2020) in which the ages of the bases for Tithonian, Berriasian, and Valanginian have been changed. Nevertheless, the IUGS Stratigraphic chart (Cohen et al., 2013; updated) retains the previously accepted dates. For consistency and to facilitate comparison to other published records of carbon isotope values we use the age model provided by the Cramer and Jarvis (2020) in the Geologic Time Scale 2020. In their age model, the base of the Tithonian is determined to be 149.24 Ma old, the J/K boundary is positioned at 143.1 Ma, and the base of the Valanginian is set to be 137.7 Ma (Fig. S1). Because the focus here is the comparison of new $\delta^{13}C$ values measured in organic material with previously published records in other parts of the world, we follow the conventions summarized by (Leanza et al., 2020a) and use Andean Ammonite Zonation described by Vennari (2016) and those by (Kietzmann et al., 2018) relative to their corresponding magnetostratigraphic polarity Chrons as shown by Kietzmann et al. (2018); (2021) using the absolute ages of these Chrons provided by Ogg (2020) (Fig. S1).

Lateral Variations of Isotopic Values

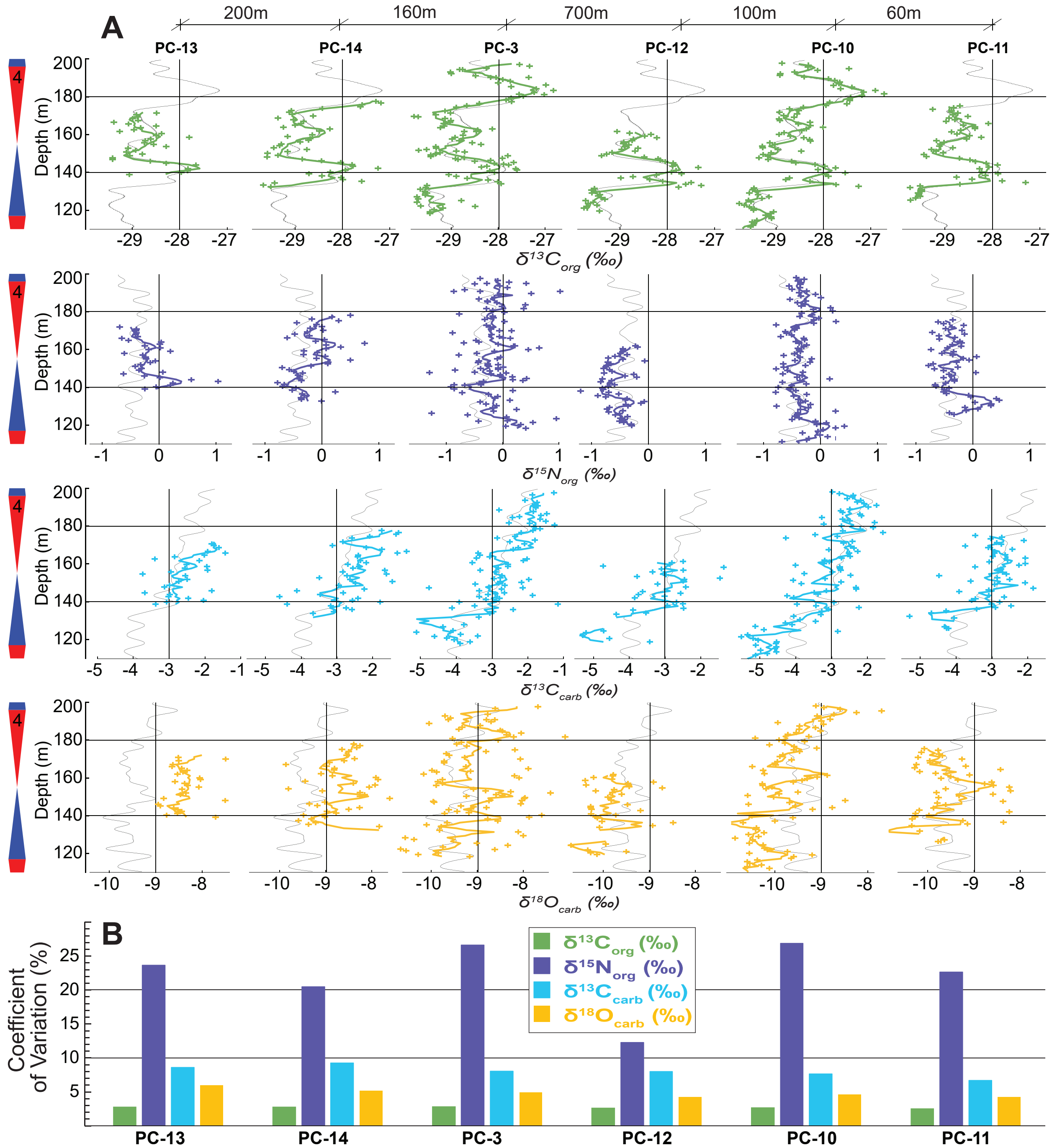
The large quantity and the stratigraphic distribution of the geochemical samples measured in this study provide a unique opportunity to analyse their variability both vertically as well as horizontally. One way in which we quantify this variability, we compared 145 one-meter-thick intervals for which five or more samples have been analysed (Fig. S2). The sample measurements of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ show strong variation away from the underlying trend of the entire dataset while the values of $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ are more focussed around the low frequency portion of the entire dataset. Quantitatively, the Coefficient of Variation (CV) calculated for different sections and the entire dataset reveal that $\delta^{13}C_{org}$ shows overall the least variability (Fig. S2 B). Consequently, $\delta^{13}C_{org}$ is most suitable for the correlation between sections at varying locations. The $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ show much higher laterally variability and require more samples at individual stratigraphic locations before stable values suitable for correlation are obtained. Yet, the variation of the other isotopes is deemed low enough to justify a combining all sections into a single data set (Fig. 6 in main paper). The distribution of all isotopic values and their statistical parameters are shown in for of Box plots (Fig. S3).

We use the Coefficient of Variation (CV) and the range of multiple measurements taken from distinct stratigraphic intervals to assess the lateral variability of isotope data between measured sections that cover the same strata (Fig. S2 and Fig. 5 in main paper). For small interval analysis we limit the analysis to the range of measured values due to the small sample number per interval (5-8). The application of CV in variability quantification is common in reliability theory and risk assessment (Southard, 2018). Given the challenges that arise during statistical evaluation of small sub-samples we will use a definition of the CV as the reciprocal of Signal to Noise Ratio (SNR) (Bushberg and Boone, 2011). The high frequency variations of our measurements that contain the proximity (or near time) variability information. In other words, SNR is simply the comparison of one specific frequency band (e.g. that expected to be predominantly Noise) to another (e.g. that expected to contain relevant data) we define a trend to high frequency data ratio (THFR), a SNR method equivalent, as the $\log_{10}$ of the Root-Mean-Square (RMS) of the low frequency component (the long-term trend) of our data divided by the RMS of our data's high frequency component.



Modified from: GTS-2020 (Gaie et al., 2020 and Hesselbo et al., 2020)

Figure S1: Late Jurassic to Early Cretaceous integrated time scale modified from Gale et al. (2020) and the other guy Hesselbo et al. (2020). Summary of numerical ages of epoch/series and age/stage boundaries with selected ammonite zones for the Tethyan and Sub-Boreal realm. Magnetostratigraphic correlations to the marine magnetic anomaly M-sequence and to Tethyan and Boreal ammonite zones provided by Hesselbo et al. (2020). Andean Ammonite Biozones (1) are positioned relative to their paleomagnetic polarity timescale as presented by Leanza et al. (2020a) and Kietzmann et al. (2018). Andean Ammonite Biozones (2) are positioned relative to Ammonite Biozone locations relative to Tethyan realm as presented by Leanza et al. (2020b) and Vennari and Pujana (2017). Valanginien Andean Ammonite Biozones are as presented by Aguirre-Urreta et al. (2008) and Aguirre-Urreta et al. (2019). Biozones Picunleufuense α and β proposed by Parent et al. (2015) are positioned as suggested by Vennari (2016) at the very base of the Tithonian, below Ammonite Biozone Virgatosphinctes andesensis. (M. ponti = Micracanthoceras ponti; B. peroni = Burckhardticeras peroni).



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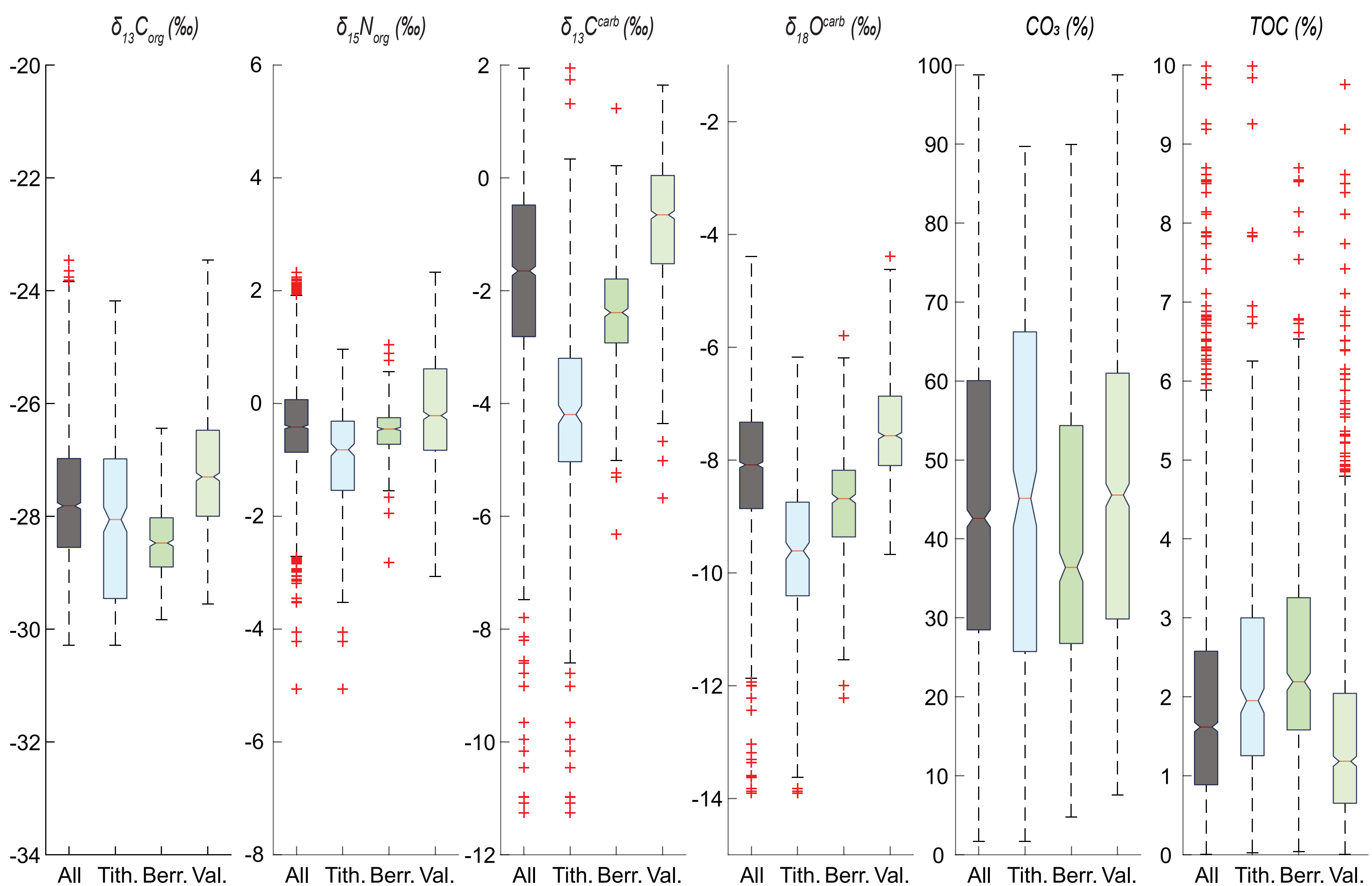

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