minerals

MDPI

Article

The Measurement Reliability of δ^{13}C of Dissolved Organic Carbon: A Validation for Speleothem Samples

Gang Xue [1,2,*], Yanjun Cai [3,*], Peng Cheng [1], Le Ma [1], Xing Cheng [4], Shouyi Huang [3] and Yanbin Lu [1]

1 State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China
2 State Key Laboratory of Continental Dynamics, Department of Geology, Northwest University, Xi'an 710069, China
3 Institute of Global Environmental Change, Xi'an Jiaotong University, Xi'an 710054, China
4 Shaanxi Experimental Center of Geological Survey, Shaanxi Institute of Geological Survey, Xi'an 710054, China
* Correspondence: xuegang@nwu.edu.cn (G.X.); yanjun_cai@xjtu.edu.cn (Y.C.)

Abstract: The carbon isotopic composition of dissolved organic carbon ($\delta^{13}C_{DOC}$) in speleothems, based on high-precision U-Th ages, has great potential to reconstruct past ecology, microbial activity, and carbon cycling. Identifying the reliability of the pretreatment and measurement of speleothem $\delta^{13}C_{DOC}$ is therefore essential to putting it into practice. Actually, we have previously verified the reliability of the method for speleothem $\delta^{13}C_{DOC}$ measurements. However, it was only based on the final $\delta^{13}C_{DOC}$ values of homogeneous speleothem powder and is unable to evaluate the effects of different experimental conditions and the impacts of adding acid on $\delta^{13}C_{DOC}$ if using speleothem as the study samples. In this study, we used an organic reagent (potassium sorbate) as the study sample and designed a conditional experiment that simulates the protocols for speleothem $\delta^{13}C_{DOC}$ analysis and presented the resulting data to inspect the effects of the experimental processes on the analysis of $\delta^{13}C_{DOC}$. The results show that the standard deviation of duplicate samples is 0.1‰, which is close to that of the previous work for organic reagents and water samples, and the results were not affected by different experimental conditions and operation steps (such as adding orthophosphoric acid, digestion time, and storage duration of resulting CO_2 in storage vessels), suggesting that this method is robust to detect the speleothem $\delta^{13}C_{DOC}$. Considering the range and standard deviation of results, we proposed that the $\delta^{13}C_{DOC}$ record could be used in various studies when the amplitudes of the $\delta^{13}C_{DOC}$ record are larger than 0.1‰, especially greater than 0.4‰.

Keywords: speleothems; dissolved organic carbon; δ^{13}C; conditional experiment

check for updates

Citation: Xue, G.; Cai, Y.; Cheng, P.; Ma, L.; Cheng, X.; Huang, S.; Lu, Y. The Measurement Reliability of δ^{13}C of Dissolved Organic Carbon: A Validation for Speleothem Samples. *Minerals* **2024**, *14*, 454. https://doi.org/10.3390/min14050454

Academic Editor: Dan Asael

Received: 1 March 2024
Revised: 22 April 2024
Accepted: 24 April 2024
Published: 25 April 2024

Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Investigating the dynamics of organic carbon in the earth's surface system under the natural climate background is of great significance to understanding carbon cycling and ecosystem evolution. Therefore, developing techniques to extract related information about organic carbon cycling dynamics from geological archives is essential. Up to now, multiple organic components in various geological archives have been used as proxies to trace ecological evolution and associated climate changes in paleoclimatic studies [1]. Amongst sorts of proxies, stable carbon isotopic composition of organic substances has been one of the most important roles in reconstructing vegetation variations and climate changes [2,3].

Speleothems are secondary carbonate; their δ^{18}O records have attracted the attention of scientists in the field of reconstructing paleoclimate changes [4,5], mainly because of the highly accurate U-Th ages [4,6]. As an opportunity to introduce organic matter research into the speleothem precise chronology frame, it would be significant to better inspect the ecology and environment information during the past [7–11]. The largest amount of organic components in speleothem, dissolved organic carbon (DOC), a labile component that turns over fast in soils [12], mainly originates from plant and microbial contributions in the overlying system [11,13]. Based on the radiocarbon ages of DOC in speleothems, scientists have reconstructed the soil turnover time during the Holocene [11]. Therefore, developing a method to extract DOC and measure its $\delta^{13}C$ ($\delta^{13}C_{DOC}$) in speleothem has the potential to inspect the ecology, microbial activity, and carbon cycling variations in karst regions [9,11,13].

Considering the content of organic carbon preserved in speleothems is low, a method for tracing organic carbon is necessary. Excitingly, a study conducted by Lang et al. [14] showed that the analysis of $\delta^{13}C_{DOC}$ for the trace carbon in water samples is reliable. Based on this work, our previous work modified the method for analyzing carbonate samples, and the results showed that the $\delta^{13}C_{DOC}$ values of homogeneous speleothem carbonate powers are consistent with each other within errors of 0.2‰ [15]. However, it was only verified based on the final resulting $\delta^{13}C_{DOC}$ values using the same protocol for each sample, but the effects of different experiment conditions during each step on the results are still unknown. Therefore, what experimental conditions are implemented on speleothems that are influential on reliability need to be further inspected.

In this study, we used potassium sorbate as the study sample, going through all the experimental processes that follow the method for speleothem samples reported previously [15] and setting up different experiment conditions to finally check the reliability of pretreatment and measurement for speleothem $\delta^{13}C_{DOC}$. This study aims to comprehensively evaluate whether our method can provide a new window for the analysis of $\delta^{13}C$ of dissolved organic matter in various carbonate samples.

2. Materials and Methods

The valid method for the analysis of $\delta^{13}C_{DOC}$ has been reported by Lang et al. [14]. Based on the various organic reagents and water samples, they clarified the reliability of the method and proved that the method is effective for the stable isotope analysis of trace DOC (μg C) as well [14]. However, for speleothem $\delta^{13}C_{DOC}$ analysis [15], the experimental steps are partly different from those of organic reagents and water samples [14]. To inspect the validity and reliability of that modified method for speleothem $\delta^{13}C_{DOC}$, the conditional experiment needs to be further conducted.

Unfortunately, it is unable to evaluate the impacts of adding acid to $\delta^{13}C_{DOC}$ if using speleothem as the study sample (because carbonate must be dissolved using phosphoric acid). Alternatively, organic reagents were used as the study samples in this study. Potassium sorbate is a type of potassium salt of sorbic acid [16]. Its chemical formula is $C_6H_7KO_2$, and it is generally used as a food preservative. Considering its high water solubility, good thermal stability, and non-toxicity [17], we hence used it as the study sample.

As such, different experimental conditions were conducted on potassium sorbate samples, and the experimental processes simulated the protocols for $\delta^{13}C_{DOC}$ analysis of speleothems. The main differences from the previous methods [9,14] are as follows: (1) The study samples were treated with orthophosphoric acid to simulate the process of removing carbonate. (2) This modified method is a line-off operation; the collected CO_2 was stored in storage vessels. (3) The experiment was not conducted entirely in one single vial.

To circumvent the contribution of exogenous contaminants to the experimental results, all the glassware for the experiment was cleaned with Milli-Q water (TOC < 3 ppb) and subsequently pre-combusted in a muffle furnace at 450 °C for 4 h, then wrapped in aluminum foil. In addition, Milli-Q water is also used to prepare the chemical reagent and dissolve the potassium sorbate in this study; it was filtered by the water purification system (Millipore, Billerica, MA, USA), and the continuous automatic monitoring of the instrument shows TOC < 3 ppb.

The mass of each potassium sorbate sample is randomly selected because it is difficult for the balance to accurately obtain trace masses of samples on the one hand, and on the other hand, organic matter is unevenly distributed in stalagmites. This random selection simulates the sampling of speleothem samples. After that, the duplicated samples (potassium sorbate) were put into 40 mL borosilicate vials and dissolved in Milli-Q water.

Furthermore, the potassium sorbate solutions were treated with or without a 3 mL, 3 mol/L orthophosphoric acid solution, which was made from a diluted 12 mol/L orthophosphoric acid solution (99%, Merck, Darmstadt, Germany) in Milli-Q water, and then they were placed for 0, 48, and 72 h at room temperature. Subsequently, they were transferred to custom-made reactors, which are glass tubes with a 30 cm length (upper 20 cm with a 6 mm width and lower 10 cm with a 2 cm width) using plastic droppers that were pre-cleaned by the sterilization process under vacuum conditions. Moreover, 3 mL of supersaturated potassium persulfate oxidizing solution (100 mL of water + 4 g of $K_2S_2O_8$ (Sigma-Aldrich, Merck, Darmstadt, Germany, 99.99%) + 20 µL of H_3PO_4) as an oxidant was then added to potassium sorbate solutions [14]. Following that, the custom-made reactors were equipped with a vacuum line to remove the CO_2 for 20 min or longer until the vacuum values were lower than 1.0×10^{-3} mbar and kept stable, and subsequently, the reactors were sealed with a torch. Then, the reactors were placed in a bath heated at 99 °C for 1–2 h to oxidize the samples (DOC) to CO_2. At last, the reactors were equipped with the vacuum line again, liquid nitrogen and alcohol traps were used to remove H_2O and other gases, and the purified CO_2 gas was cryogenically transported to a storage vessel for measurement of carbon isotope composition.

The $\delta^{13}C$ of CO_2 produced from potassium sorbate samples was detected by using an Isoprime100 gas source stable isotope ratio mass spectrometer (IRMS) equipped with a MultiPrep system at the Institute of Earth Environment, Chinese Academy of Sciences. Specifically, the storage vessel was first connected to the dual system of Isoprime100, and high-purity nitrogen flushed the gas flow line and was subsequently treated with vacuum. After the vacuum value was lower than 7.0×10^{-3} mbar, CO_2 was released into the dual system. After that, the instrument automatically ran and detected the isotopic composition. The inter-laboratory carbonate standard TB1 was used to monitor the stability of the instrument and calibrate the $\delta^{13}C$ of the potassium sorbate. The $\delta^{13}C$ values reported here are relative to the Vienna PeeDee Belemnite (VPDB) standard. The results of TB1 show that the precisions of the $\delta^{13}C$ analyses are better than 0.12‰ (2σ).

3. Results

3.1. The Fidelity of $\delta^{13}C_{DOC}$

Twenty duplicated samples were pretreated under different experimental conditions (Table 1 and Figure 1). On 20 March, samples 1, 2, and 3 were placed for 72 h with no orthophosphoric acid solution. On 13 June, samples 4, 5, 6, 7, and 8 were added orthophosphoric acid solution and placed for 0 h; samples 9, 10, 11, and 12 were added orthophosphoric acid solution and placed for 48 h. On 21 June, samples 13 and 14 were added orthophosphoric acid solution and placed for 0 h; samples 15, 16, and 17 were added orthophosphoric acid solution and placed for 48 h; and samples 18, 19, and 20 were placed for 48 h with no orthophosphoric acid solution.

The results show that the $\delta^{13}C$ of duplicate potassium sorbate samples varies between −26.8‰ and −26.4‰ with a range of 0.4‰, showing good repeatability within detecting uncertainties (Figure 1). By calculating them, the average value is −26.6‰ and the standard deviation is approximate 0.1‰ which is close to that of previous work for organic reagent and water samples analysis [14], suggesting that the modified method (simulate protocols for $\delta^{13}C_{DOC}$ of speleothem) is reliable for analyzing $\delta^{13}C_{DOC}$ of speleothem and other carbonate samples. In reverse, given the stability of $\delta^{13}C$ of duplicated potassium sorbate samples, it can be the external standard sample to detect the reliability of experimental processes, the state of the instrument, and calibrate the $\delta^{13}C_{DOC}$ of the speleothem.

Table 1. The details of duplicated samples.

Sample Code	$\delta^{13}C_{DOC}$ (‰)	Gas Pressure	Yield	Mass of Carbon (μg)	Remarks
1	−26.4	3.7	118.1	41.4	no acid, and the reaction time is 72 h (20 March 2019)
2	−26.6	5.2	164.5	58.5	
3	−26.5	4.6	146.3	51.2	
4	−26.7	15.3	143.7	171.6	with acid, and the reaction time is 0 h (13 June 2020)
5	−26.7	10.8	94.6	122.0	
6	−26.7	3.3	104.9	37.1	
7	−26.6	9.9	173.6	111.5	
8	−26.7	8.7	198	97.7	
9	−26.5	12.5	171.1	140.3	with acid, and the reaction time is 48 h (13 June 2020)
10	−26.6	8.7	120.2	97.4	
11	−26.5	11.1	107.3	124.7	
12	−26.6	0.5	13.7	5.1	
13	−26.5	6.1	195.4	68.9	with acid, and the reaction time is 0 h (21 June 2020)
14	−26.6	8.4	266.2	94.1	
15	−26.5	6.0	190.5	67.2	with acid, and the reaction time is 48 h (21 June 2020)
16	−26.6	6.5	205.5	73.0	
17	−26.8	5.8	185	65.3	
18	−26.7	7.6	243.5	86.0	no acid, and the reaction time is 48 h (21 June 2020)
19	−26.6	5.7	180.2	63.7	
20	−26.7	5.4	169	60.2	
Average	−26.6				
SD (1σ)	0.1				

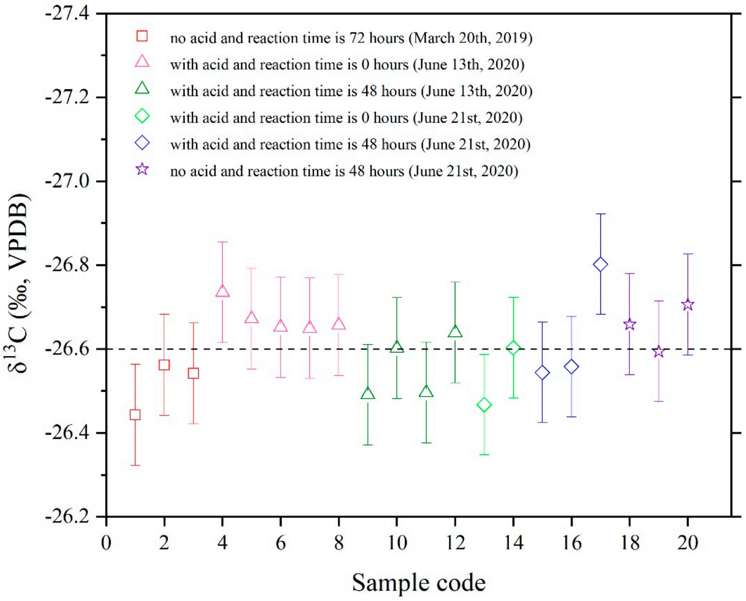

Figure 1. The $\delta^{13}C$ of duplicate potassium sorbate samples.

3.2. The $\delta^{13}C_{DOC}$ Values and Different Experimental Conditions

To verify the effects of the addition of acid on the $\delta^{13}C_{DOC}$ of the study samples, it was tested by adding 3 mL of orthophosphoric acid solution into the parts of the study samples. The results show that the $\delta^{13}C_{DOC}$ values of those samples added 3 mL orthophosphoric acid with an average value of −26.6‰ are equivalent to those of samples without orthophosphoric acid solution (Figure 2), indicating the effects of adding acid can be neglected. It also rules out the possibility of contamination from DOC in orthophosphoric acid, which potentially alters the carbon isotopic compositions of study samples. Further, given that digesting speleothem carbonate by using orthophosphoric acid is a priority step before oxidizing DOC in speleothem, the same results from this conditional experiment suggest that the digestion reaction itself would not affect the $\delta^{13}C_{DOC}$ of the study samples.

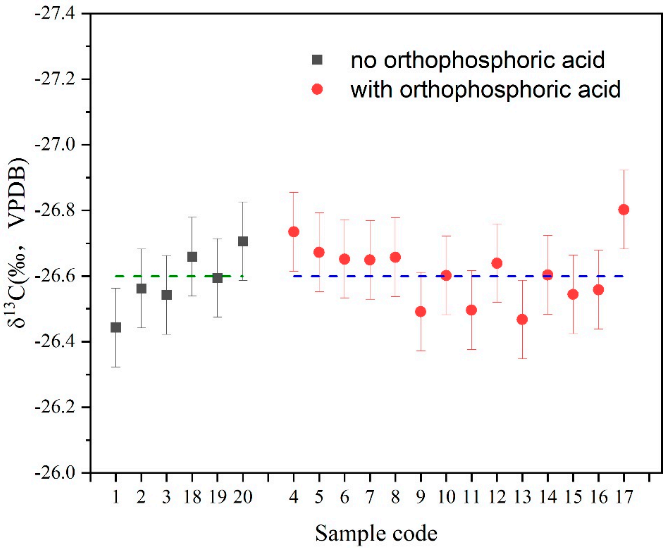

Figure 2. The $\delta^{13}C_{DOC}$ results from a comparison between samples with and without orthophosphoric acid. The green and blue dashed lines represent the average values of without and with orthophosphoric acid, respectively.

On account of speleothem, carbonate subsamples need to be completely digested, and hence, enough reaction time is essential. Generally, according to different concentrations of DOC in various speleothems, 100–500 mg of carbonate should be prepared so that enough gas CO_2 reaches the limitation for detecting $\delta^{13}C_{DOC}$ [9,15]. Previous tests suggested a digestion time of 48 h is generally enough [15], therefore we set 0, 48 h, and 72 h (digestion time occasionally may exceed 48 h) to inspect whether the digestion time affects the $\delta^{13}C_{DOC}$ of study samples.

The results show that there is a good consistency between 0, 48, and 72 h (Figure 3), indicating that digestion time does not obviously affect the $\delta^{13}C_{DOC}$, and the solution still preserves the imprint of the original materials.

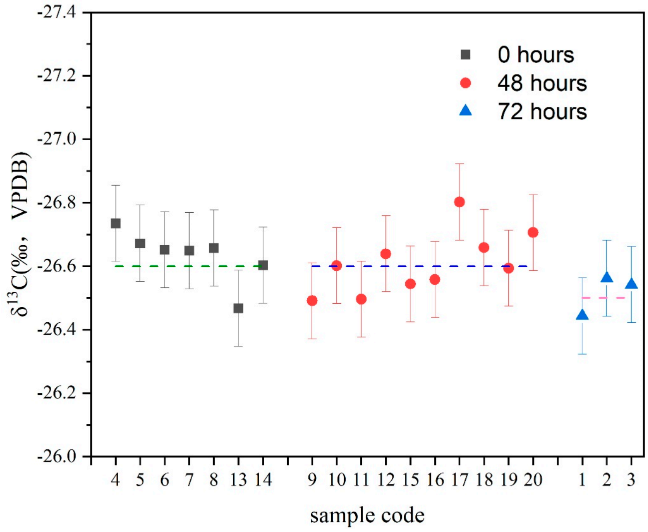

Figure 3. The $\delta^{13}C_{DOC}$ results of different digestion durations. The green, blue, and pink dashed lines represent the average values of different durations respectively.

4. Discussion

4.1. The Possibilities of Contamination

Exogenous carbon contamination is the culprit behind the unreliable data; hence, clarifying the possibilities of contamination is essential. Blank bears the brunt and needs to be checked, and each step needs to be judged on whether the contaminations appear. The above results have shown that there is no deviation of $\delta^{13}C_{DOC}$ during the digestion process and under the different reaction times, indicating the organic contamination carbon can be neglected or the content of contamination is not enough to affect the $\delta^{13}C_{DOC}$ of the study samples.

In addition, it is well known that samples with a higher content of carbon are less susceptible to their carbon isotope composition from exogenous contamination because, even if there is contamination, its proportion is relatively low. The opposite is true for samples with low carbon content. Specifically, if there is contamination with carbon, the final $\delta^{13}C_{DOC}$ could increase or decrease with the decrease in carbon mass in the study samples. To further clarify the possibilities of contamination, we therefore compared the mass of carbon in different samples and their $\delta^{13}C_{DOC}$. The comparison shows that there is no correlation between the amount of carbon and $\delta^{13}C_{DOC}$ (Figure 4), further indicating that the carbon isotopic compositions of DOC in speleothem are not affected by contamination.

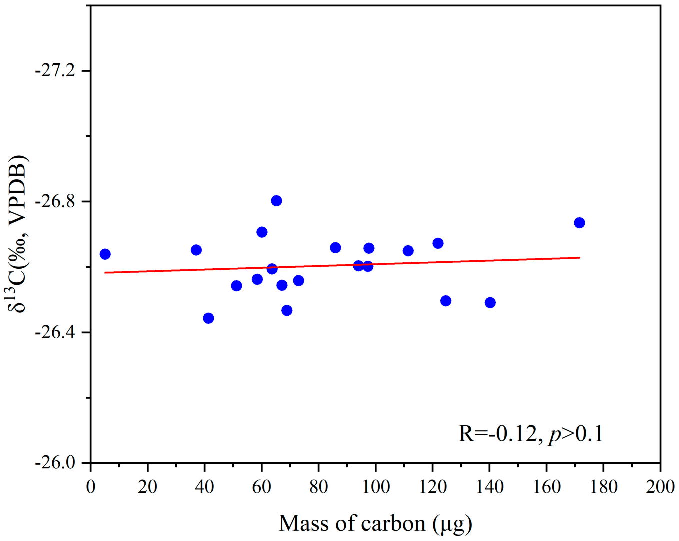

Figure 4. The versus between the mass of carbon and $\delta^{13}C_{DOC}$.

Moreover, at the gap between pretreatments and measurements, the oxidized gas CO_2 needs to be stored in a glass collector for several hours to 2 days for measurements. The leakproofness of those collectors is also an important factor in ensuring the fidelity of the $\delta^{13}C_{DOC}$ of study samples. During the pretreatment, the oxidized amount of CO_2 can be measured by a pressure transmitter in an offline vacuum system. Similarly, the yield of CO_2 could also be detected by the MultiPrep system of the Isoprime100 gas source stable isotope ratio mass spectrometer. Therefore, judging the consistency between the values from the pressure transmitter in an off-line vacuum system and the yields from a stable isotope ratio mass spectrometer can clarify the leakproofness of the collector. We then compared both, and the results show that they can correspond to each other one by one and show a significant positive correlation. Notably, there are some exceptions where the correlation is not ideal. This is because the amounts of CO_2 oxidized from some samples are relatively large; hence, they need to be released from the glass vessel under equilibrium conditions by using the vacuum line, and these values are marked by dotted rectangular boxes (Figure 5).

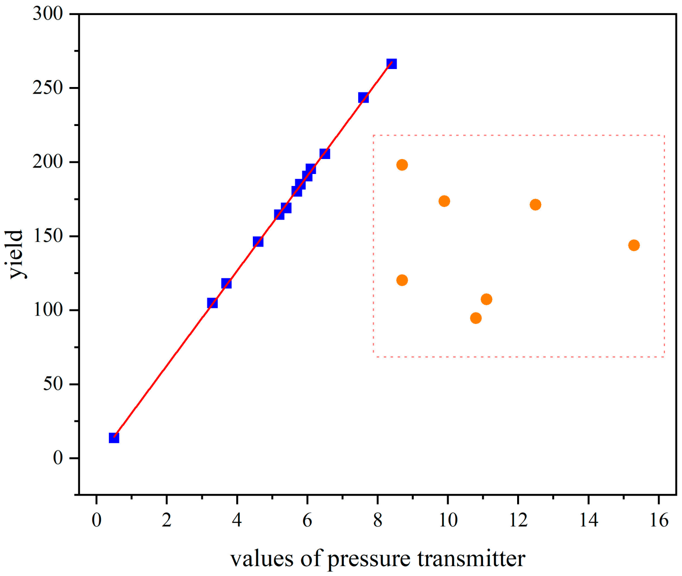

Figure 5. The versus between the values of pressure transmitter and yield of CO_2. The CO_2 from those samples (yellow circles) was released from the storage vessel in advance under equilibrium conditions before analysis.

As a result, the $\delta^{13}C_{DOC}$ of the duplicated samples was not significantly affected by different experimental conditions and pretreatment processes, indicating that for the stable isotopic composition of speleothem DOC, the possibility of contamination from the experimental process can be neglected.

4.2. The Implications of This Method for Speleothem $\delta^{13}C_{DOC}$ Measurement

The discussion above, at least, indicates the pretreatment and measurement for $\delta^{13}C_{DOC}$ analysis of the organic reagent are reliable. The processes, including adding acid, reaction time, and storage time (the collected CO_2 in the storage vessel), have no significant impacts on the results of $\delta^{13}C_{DOC}$ of the study samples (not carbonate). However, some points still need to be noticed. Firstly, the results show the storage time of CO_2 in glass vessels hardly affects the results of $\delta^{13}C_{DOC}$, and the storage time generally is only less than 2 days. Although a previous study shows that storage times of up to three weeks do not result in significant changes in the amount and isotopic value of carbon measured [14], we still recommend measuring the isotopic composition as soon as possible. Secondly, try to select samples with high concentrations of dissolved organic matter in any case, because higher concentrations can significantly offset the impact of potential contamination of organic carbon, although we did not find the risk of contamination of carbon in the samples with low carbon concentrations. Notably, the standard deviation and range of organic reagents (potassium sorbate) are 0.1‰ and 0.4‰, respectively; thus, when the amplitude of speleothem $\delta^{13}C_{DOC}$ variations exceeds 0.4‰, they could represent more reliable signals for discussing the changes and their implications, at least above 0.2‰ (2 times standard deviations). Last but not least, this study makes up for the deficiencies of the previous study on $\delta^{13}C_{DOC}$ of speleothem carbonate and checks the impacts of adding acid, reaction time, and potential contamination on the $\delta^{13}C_{DOC}$ results.

5. Conclusions

This study verifies that a modified method is reliable to analyze speleothem $\delta^{13}C_{DOC}$. The experimental processes did not significantly affect the stable carbon isotopic composition of the dissolved organic carbon in the study samples. In this work, the standard deviation of duplicate organic reagents (potassium sorbate) is 0.1‰, which is close to that of the previous work for organic reagents and water samples. This suggests that not only the $\delta^{13}C_{DOC}$ of duplicate potassium sorbate is stable, but it also indicates that the potassium sorbate can be the standard sample to detect the state of the instrument and calibrate the $\delta^{13}C_{DOC}$ of the speleothem samples. Notably, the results also imply some points that need to be considered when speleothem samples are treated. Specifically, try to select the samples with high concentrations of dissolved organic carbon for the analysis of $\delta^{13}C_{DOC}$. At the same time, to avoid any deviation from the experimental results, it is best to measure the resulting CO_2 as soon as possible. Importantly, it should be ensured that, when the amplitudes of the $\delta^{13}C_{DOC}$ record are larger than 0.1‰, especially greater than 0.4‰, the $\delta^{13}C_{DOC}$ record could be more convincingly discussed for the various topics on which scientists are focused.

Author Contributions: Conceptualization, G.X.; methodology, G.X., Y.C., P.C. and L.M.; validation, G.X., Y.C. and P.C.; formal analysis, G.X. and L.M.; data curation, G.X. and L.M.; writing—original draft preparation, G.X.; writing—review and editing, G.X., Y.C., P.C., S.H. and X.C.; supervision, Y.C. and P.C.; project administration, Y.L.; funding acquisition, G.X., Y.C. and Y.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Natural Science Foundation of China grants (42102231 to G.X.), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB 40010203 to Y.C.), and the Opening Fund of the State Key Laboratory of Loess and Quaternary Geology (SKLLQG2115 and SKLLQG1723 to G.X.).

Data Availability Statement: All data can be found in Table 1.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Meyers, P.A. Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. *Org. Geochem.* **1997**, *27*, 213–250. [CrossRef]
2. Cerling, T.E.; Harris, J.M.; MacFadden, B.J.; Leakey, M.G.; Quade, J.; Eisenmann, V.; Ehleringer, J.R. Global vegetation change through the Miocene/Pliocene boundary. *Nature* **1997**, *389*, 153–158. [CrossRef]
3. Boutton, T.W. Stable carbon isotope ratios of soil organic matter and their use as indicators of vegetation and climate change. In *Mass Spec-Trometry of Soils*; Boutton, T.W., Yamasaki, S., Eds.; Marcel Dekker: New York, NY, USA, 1996; pp. 47–82.
4. Cheng, H.; Edwards, R.L.; Sinha, A.; Spotl, C.; Yi, L.; Chen, S.; Kelly, M.; Kathayat, G.; Wang, X.; Li, X.; et al. The Asian monsoon over the past 640,000 years and ice age terminations. *Nature* **2016**, *534*, 640–646. [CrossRef]
5. Xue, G.; Cai, Y.; Ma, L.; Cheng, X.; Cheng, H.; Edwards, R.L.; Li, D.; Tan, L. A new speleothem record of the penultimate deglacial: Insights into spatial variability and centennial-scale instabilities of East Asian monsoon. *Quat. Sci. Rev.* **2019**, *210*, 113–124. [CrossRef]
6. Bajo, P.; Drysdale, R.N.; Woodhead, J.D.; Hellstrom, J.C.; Hodell, D.; Ferretti, P.; Voelker, A.H.L.; Zanchetta, G.; Rodrigues, T.; Wolff, E.; et al. Persistent influence of obliquity on ice age terminations since the Middle Pleistocene transition. *Science* **2020**, *367*, 1235–1239. [CrossRef] [PubMed]
7. Blyth, A.J.; Hartland, A.; Baker, A. Organic proxies in speleothems a new developments, advantages and limitations. *Quat. Sci. Rev.* **2016**, *149*, 1–17. [CrossRef]
8. Blyth, A.J.; Smith, C.I.; Drysdale, R.N. A new perspective on the $\delta^{13}C$ signal preserved in speleothems using LC-IRMS analysis of bulk organic matter and compound specific stable isotope analysis. *Quat. Sci. Rev.* **2013**, *75*, 143–149. [CrossRef]
9. Lechleitner, F.A.; Lang, S.Q.; Haghipour, N.; McIntyre, C.; Baldini, J.U.; Prufer, K.M.; Eglinton, T.I. Towards Organic Carbon Isotope Records from Stalagmites: Coupled $\delta^{13}C$ and ^{14}C Analysis Using Wet Chemical Oxidation. *Radiocarbon* **2019**, *61*, 749–764. [CrossRef]
10. Wang, C.; Bendle, J.A.; Greene, S.E.; Griffiths, M.L.; Huang, J.; Moossen, H.; Zhang, H.; Ashley, K.; Xie, S. Speleothem biomarker evidence for a negative terrestrial lfeedback on climate during Holocene warm periods. *Earth Planet Sci. Lett.* **2019**, *525*, 115754. [CrossRef]
11. Xue, G.; Cai, Y.; Cheng, P.; Lechleitner, F.A.; Zhang, H.; Zheng, Y.; Wei, Y.; Huang, S.; Yang, L.; Cheng, X.; et al. The climate control of soil organic carbon dynamics inferred from speleothem radiocarbon ages. *Geophys. Res. Lett.* **2023**, *50*, e2022GL101875. [CrossRef]
12. Neff, J.C.; Asner, G.P. Dissolved organic carbon in terrestrial ecosystems: Synthesis and a model. *Ecosystems* **2001**, *4*, 29–48. [CrossRef]
13. Guo, Z.; Wang, Y.; Wan, Z.; Zuo, Y.; He, L.; Li, D.; Yuan, F.; Wang, N.; Liu, J.; Song, Y.; et al. Soil dissolved organic carbon in terrestrial ecosystems: Global budget, spatial distribution and controls. *Glob. Ecol. Biogeogr.* **2020**, *29*, 2159–2175. [CrossRef]
14. Lang, S.Q.; Bernasconi, S.M.; Früh-Green, G.L. Stable isotope analysis of organic carbon in small (µg C) samples and dissolved organic matter using a GasBench preparation device. *Rapid Commun. Mass Spectrom.* **2012**, *26*, 9–16. [CrossRef]

15. Xue, G.; Cai, Y.J.; Cheng, P.; Ma, L.; Cheng, X. Progress and challenge of organic carbon isotope composition research in stalagmite. *J. Earth Environ.* **2019**, *10*, 105–115, (Chinese edition with English abstract).
16. Pylypiw, H.M.; Grether, M.T. Rapid high-performance liquid chromatography method for the analysis of sodium benzoate and potassium sorbate in foods. *J. Chromatogr.* **2000**, *A883*, 299–304. [CrossRef] [PubMed]
17. An, X.C.; Hu, Y.X.; Wang, N.; Zhou, X.Y.; Liu, Z.Y. Continuous juice concentration by integrating forward osmosis with membrane distillation using potassium sorbate preservative as a draw solute. *J. Membr. Sci.* **2019**, *573*, 192–199. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.