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ARTICLE TYPE

Determination of carbon and oxygen isotopes of matrix complicated geological samples: comparison of different analytical methods

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Several automated on-line carbonate reaction devices coupled with isotope ratio mass spectrometers (IRMS) have been frequently used to determine the isotopic compositions of the carbon and oxygen in carbonates due to their high efficiency and small sample size. However, although the $\delta^{13}C$ and $\delta^{18}O$ values were measured with good precision with each device whether the measured data remains consistent between among these different analyzsis methods remains unknown. We report a systematic comparison for the $\delta^{13}C$ and $\delta^{18}O$ values in the matrices of complicated geological samples measured using a Kiel IV and a GasBench II, as well as through dual-inlet isotope ratio mass spectrometry (DI-IRMS). Large variations were observed between the measured $\delta^{13}C$ and $\delta^{18}O$ values for some loess and lake sediments, with maximum differences of -0.4‰-+0.3‰ for $\delta^{13}C$ and -0.5‰-+0.6‰ for $\delta^{18}O$ relative to the mean values of the three methods. Moreover, the $\delta^{13}C$ values obtained using the Kiel IV-IRMS method are generally lower than those using the other two methods were, while the $\delta^{18}O$ values measured by the Kiel IV-IRMS method are obviously higher than those obtained through DI-IRMS. These results might have been due to the different effects of the organic matter in samples analyzed through different methods. However, vacuum roasting could not eliminate this effect and instead increased the variability of $\delta^{13}C$ and $\delta^{18}O$ values in some samples. The usefulness of the Kiel IV was limited to the analysis of samples containing small -amounts of carbonate due to this pronounced effect. In contrast, GasBench II might produce data more reliably for these types of samples. Consequently, caution must be exercised when selecting a method for analyzing samples with complicated matrices to minimize any potential error.

Introduction

The stable compositions of the carbon and oxygen isotopes in carbonate minerals have been used as proxy indicators in geosciences, including palaeoceanography and terrestrial palaeoclimate studies.[1-5] These isotopes are typically measured through a technique involving the following: phosphoric acid is used to digest the solid carbonate material, releasing water and CO_2 the gas is subsequently purified for measurements at m/z 44-46 through isotope ratio mass spectrometry.[6,7] Several measuring methods have been developed based on this protocol for broad use in the research community.[8-14] The conventional method utilizes an off-line reaction between carbonate and phosphoric acid at 25°C overnight and subsequent cryogenic purification combined with a dual-inlet measurement using an isotope ratio mass spectrometer.[8] As technology has developed, some automated on-line carbonate reaction devices have been designed and linked to isotope ratio mass spectrometers. The most commonly used instruments are a Kiel carbonate device coupled with an isotope ratio mass spectrometer (Kiel-IRMS)[9-11] and a GasBench gas preparation device coupled with an isotope ratio mass spectrometer (GasBench-IRMS).[12-14] These automated devices usually adopt a different method for gas preparation, i.e., reactions at a higher temperature (70°C) over a shorter time (<10min or 1 hr). These changes have largely increased the efficiency and throughput of those instruments. However, how the changes influence the measured $\delta^{13}C$ and $\delta^{18}O$ values remains unclear, particularly for some geological samples with complicated matrices. Therefore, the three methods must be compared, and the consistency of the $\delta^{13}C$ and $\delta^{18}O$ values measured using those methods must be systematically examined.

The geological samples usually contain a measurable amount of organic materials. Some volatile organic molecular fragments were treated as though their similar molecular weights were similar to that of carbon dioxide and were thought to interfere

with carbon and oxygen analyses.[15] Moreover, some researchers believed that reacting organic matter with phosphoric acid could liberate carbon dioxide which has a different isotopic composition from that produced from the calcium carbonate.[8] To eliminate the influence of organic matter, some pre-treatments, such as roasting the samples under vacuum or digesting them using bleach (or hydrogen peroxide) were employed to remove labile organic matters before analyzing carbon and oxygen isotopes. To date, many works discussed the effect of pre-treatment on the isotopic composition of the biogenic and inorganic carbonates.[15-19] However, no agreement was reached so far. Although some researchers thought that the pre-treatment was problematic because it increased the variability of isotope values in treated samples,[17-19] this type of pre-treatment still used before conducting isotope analyses of impure carbonates.

In this paper, we measured the $\delta^{13}C$ and $\delta^{18}O$ values of a set of geological samples using three methods, to examine the consistency of the measured isotopic values. Concurrently, some samples were roasted under vacuum to remove any labile organic matter before the isotopic analysis. We will also discuss the effects of the organic matter on the measured $\delta^{13}C$ and $\delta^{18}O$ values.

Materials and methods

The samples analyzed in this study include soil carbonate nodules, loess samples, lake sediments and marl, these samples were ground into 200 mesh fractions and homogenized thoroughly using a mortar and pestle. The carbonate nodules were taken from paleosol horizons of S0, S1 and S2, spanning Holocene, last interglacial and interglacial time respectively, from a profile in Yangling county, Shannxi Province, China (YAL-S0-C, YAL-S1-B, YAL-S2-2B), a paleosol horizon of S15 from the Chashmanigar loess-soil sequence in southern Tajikistan (TJK-S15)[20] and paleosol horizons during the Eocene from the Lingcha profile in the Hengyang basin, Hunan Province, China (HD02-1, HD02-2, HD02-3 and HDPE-205);[21] the loess samples were taken from loess horizons of L1 and L3 (LT-L1 and LT-L3, spanning the late Pleistocene) in the Lingtai loess-soil sequence[22], surface soil layers at sites along a south-north transect on the Chinese Loess Plateau (LP-3, LP-5, LP-7, LP-13 and LP-17), Longyangxia in Gonghe county, Qinghai Province, China (LYX-201) and the Tenggeli desert in Western Inner Mongolia, China (TGL). The lake sediments were taken from sediment cores collected from Daihai Lake in Liangcheng county, Inner Mongolia, north-central China (DH-281, DH-491, DH-495, DH-537, DH-539 and DH-541)[23] and Xingyun Lake, which lies 1723m above the mean sea level in Jiangchuan county, Yunnan province, southwest China (XY-06, XY-130, XY-186, XY-293, XY-349 and XY-425); the marl samples were taken from the Meishan section during the latest Permian in Zhejiang province, south China (B32-3, B34-17, B34-18, B34-21, B34-27, B34-36, B34-37 and B34-38).[24] These samples were chosen because they are representative geological samples formed in various depositional environments (e.g., wind-blown, lake and marine deposits), and these samples span a long geological period from

the Holocene to the latest Permian. Moreover, these samples contain variable amounts of carbonate, organic matter and silicate detritus. Table S1† shows that the carbonate nodules have relatively high carbonate contents (28-86%), low organic matter contents and low to medium amounts of silicate detritus. In contrast, the loess samples contain relatively low amounts of carbonate (2-13%), low organic carbon contents (0.2-2%) and high amounts of silicate detritus. The lake sediments are characterized by low to medium carbonate content (5-44%), relatively high organic carbon contents (1-7%) and medium to high amounts of silicate detritus. The marl samples possess low to medium carbonate contents (6-69%), low organic carbon contents (0.1-1.2%) and medium to high amounts of silicate detritus. In this study, 8-12 samples of each type were studied to ensure that the statistical results were reliable.

To investigate the effects of the labile organic matter in the samples when analyzing the carbon and oxygen isotopes of the carbonates, we vacuum roasted some samples. These samples were roasted at 200˚C under vacuum in a drying oven (Model No. 1425-2, Sheldon Manufacturing Inc.) for 2 hr. The carbon and oxygen isotope values of the treated and untreated samples were measured using two on-line methods and one off-line method. The on-line measurements were performed using a Kiel IV carbonate device (Thermo Fisher Scientific) and a GasBench II gas preparation device (Thermo Fisher Scientific). The carbonates in the samples were treated with phosphoric acid at 70˚C while using both devices. The reaction time was 10 min for the Kiel IV and 1 hr for the GasBench II. The carbon and oxygen isotope ratios of the CO_2 were measured using a MAT-253 isotope ratio mass spectrometer (Thermo Finnigan). For the GasBench II, the produced CO_2 first passed through a chromatograph (GC) column to remove any contaminant gases before injection into the mass spectrometer. The precision for the carbon and oxygen isotope measurements exceeded 0.06‰ and 0.1‰ (1σ), respectively. The accuracy and precision were routinely checked by running a carbonate standard, which was IVA-CO-1 ($\delta^{13}C_{VPDB}$=+2.21‰, $\delta^{18}O_{VPDB}$=-1.90‰), and this standard was repeatedly calibrated using an international standard, which was NBS 19, after every six sample measurements. The off-line measurements involved a carbonate digestion in McCrea-type reaction vessels[6] followed by measurements in dual-inlet mode using the same MAT-253 isotope ratio mass spectrometer (DI-IRMS). All of the carbon and oxygen isotope values are reported in parts per mil (‰) relative to V-PDB.

Results and discussion

The $\delta^{13}C$ and $\delta^{18}O$ values for the geological samples, measured using the Kiel IV-IRMS, GasBench II-IRMS and DI-IRMS methods, are listed in Table S2†. Most of the samples were measured three times using the Kiel IV-IRMS and GasBench II-IRMS methods to produce the mean values. However, the samples were measured only once using DI-IRMS because this method requires relatively large sample sizes. The standard deviations for the highest $\delta^{13}C$ and $\delta^{18}O$ values measured using the Kiel IV-IRMS method exceed 0.06‰ and 0.12‰,

respectively. In contrast, the standard deviations for the $\delta^{13}C$ and $\delta^{18}O$ values measured using the GasBench II-IRMS method fall mostly within 0.09‰ and 0.15‰, respectively. The relatively large standard deviations observed with both methods stem occur
5 with the loess and lake sediments samples.

To clearly show the subtle differences in the measured $\delta^{13}C$ and $\delta^{18}O$ values, we normalized the data by subtracting the average $\delta^{13}C$ and $\delta^{18}O$ values of one sample, which was measured using the three methods, from the $\delta^{13}C$ and $\delta^{18}O$ values
10 of the same sample after each method. The resulting $\Delta^{13}C$ and $\Delta^{18}O$ values represent the ranges of the deviation from the average $\delta^{13}C$ and $\delta^{18}O$ measured using each method. As shown in Fig. 1, the $\Delta^{13}C$ and $\Delta^{18}O$ values of the carbonate nodules, the lake sediments in Daihai and the marls are mostly below ±0.1‰
15 and ±0.2‰, respectively, for all three methods. In contrast, the $\Delta^{13}C$ and $\Delta^{18}O$ values of the loess samples display relatively large variations: $\Delta^{13}C$ varies from -0.41‰ to +0.29‰ (Fig. 1a) and $\Delta^{18}O$ varies from -0.50‰ to +0.58‰ (Fig. 1b). A large variation is also observed in $\Delta^{18}O$ values of the sediments from
20 Xingyun Lake ($\Delta^{18}O$ range: -0.44‰-+0.43‰), but the $\Delta^{13}C$ values of the samples exhibit little variation except for sample XY-130 whose $\Delta^{13}C$ varies from -0.23‰ to +0.14‰. In general, most of the $\Delta^{13}C$ and $\Delta^{18}O$ values of the loess samples and the lake sediment from Xingyun Lake remain within ±0.2‰ and
25 ±0.4‰, respectively. The larger deviation for the $\Delta^{13}C$ and $\Delta^{18}O$ values from Xingyun Lake relative to those of Daihai Lake may occur due to the relatively high amount of organic matter in these sediments (Table S1†).
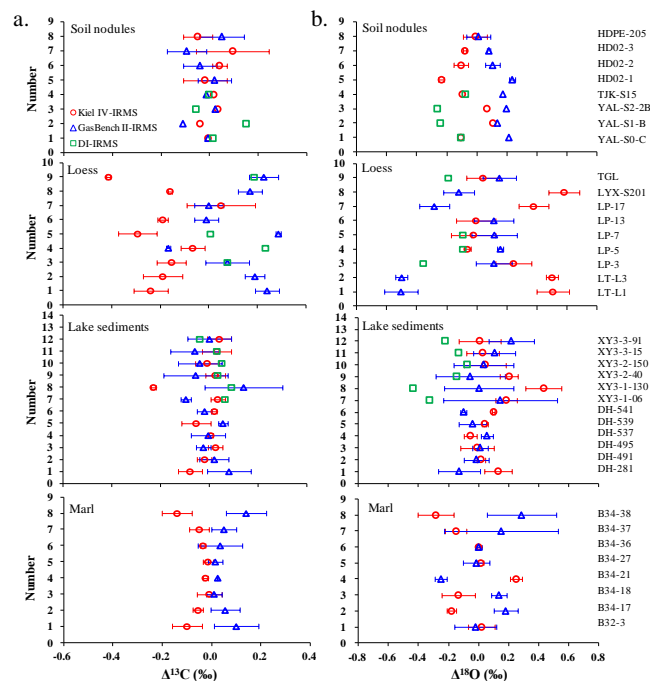

Fig. 1 A plot showing (a) differences in $\delta^{13}C$ values ($\Delta^{13}C$) and (b)
30 differences in $\delta^{18}O$ values ($\Delta^{18}O$) for matrix complicated geological samples measured using Kiel IV, GasBench II and dual inlet IRMS.

On the other hand, we also make a statistic study for the $\Delta^{13}C$ and $\Delta^{18}O$ values measured using those three methods (Fig. S1†).
35 One striking feature is that the $\Delta^{13}C$ values for Kiel IV-IRMS seem to be generally lower than the values obtained using the GasBench II-IRMS and DI-IRMS methods. For example, most of the $\Delta^{13}C$ values obtained using the Kiel IV-IRMS method are below 0 with a mean value of -0.06‰. However, most of the
40 $\Delta^{13}C$ values obtained using the GasBench II-IRMS and the DI-IRMS methods exceed 0 and have mean values of 0.03‰ and 0.06‰, respectively (Fig. S1a†). For $\Delta^{18}O$, the Kiel IV-IRMS method tends to yield higher values than the DI-IRMS method. For instance, the Kiel IV-IRMS method results in the most values
45 above or near 0 and a mean value of 0.06‰, while the DI-IRMS method results in only values below 0 and a mean value of -0.20‰. In contrast, the GasBench II-IRMS method yields both negative and positive $\Delta^{18}O$ values, generating a mean of 0.03‰ (Fig. S1b†). These patterns are obvious in the loess samples and
50 lake sediments. However, the discussed differences should either not occur or at least be less pronounced for the pure carbonate samples containing small amounts of organic matter, such as speleothems, as indicated in carbonate nodules.
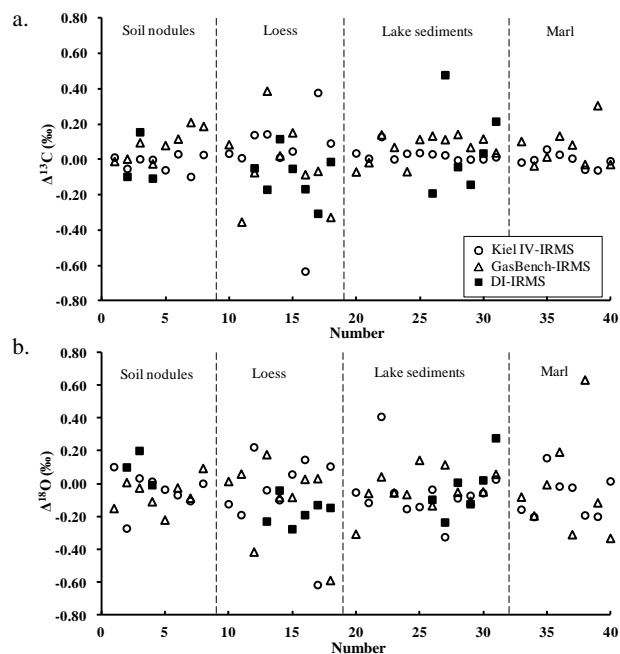

Fig. 2 Changes in $\delta^{13}C$ and $\delta^{18}O$ values after vacuum roasting. (a)
55 $\Delta^{13}C$ and (b) $\Delta^{18}O$ represent the differences in $\delta^{13}C$ and $\delta^{18}O$ values of treated samples from those of untreated ones, respectively.

The changes in the $\delta^{13}C$ and $\delta^{18}O$ values of the geological samples after vacuum roasting for 2 h are shown in Fig. 2. The
60 $\delta^{13}C$ and $\delta^{18}O$ values of the roasted samples were measured using three methods: Kiel IV-IRMS, GasBench II-IRMS and DI-IRMS. We used the $\Delta^{13}C$ and $\Delta^{18}O$ values to characterize, respectively the differences in the $\delta^{13}C$ and $\delta^{18}O$ values of the thermally treated samples from those of untreated samples. In general, the
65 $\Delta^{13}C$ and $\Delta^{18}O$ values determined using the three methods were scattered, respectively within ±0.1‰ and ±0.2‰ for most of the

geological samples except for some loess samples and individual samples of lake sediments and marls. For example, the $\Delta^{13}C$ and $\Delta^{18}O$ determined using Kiel IV-IRMS for the loess samples varied from -0.64‰ to 0.38‰ (mean value: -0.01‰) and from -0.62‰ to 0.22‰ (mean value: -0.06‰), respectively. In contrast, the ranges for the $\Delta^{13}C$ and $\Delta^{18}O$ values determined using the GasBench II-IRMS with the loess samples ranges from -0.35‰-0.39‰ (mean value: -0.03‰) and from -0.59‰-0.18‰ (mean value: -0.10‰), respectively. Meanwhile, the isotope shifts do not occur in constant direction for carbon and oxygen after the thermal treatment.
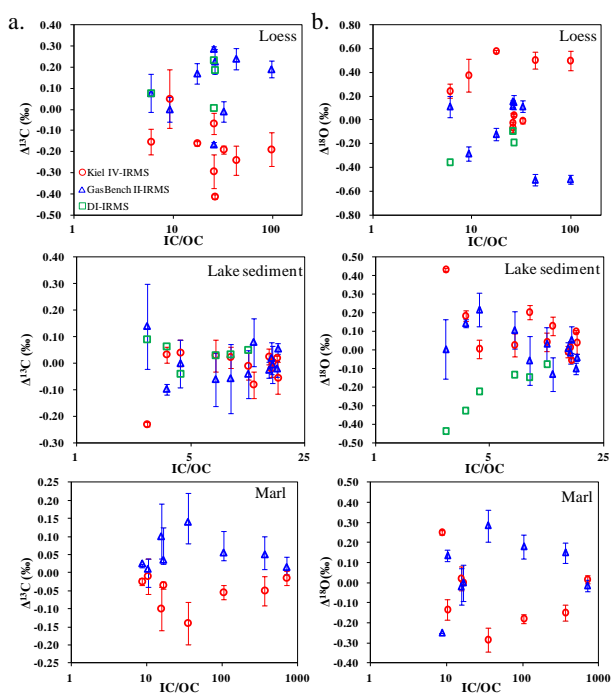

Fig. 3 Changes in $\Delta^{13}C$ and $\Delta^{18}O$ values of loess, lake sediment and marl along with the ratio between carbonate (IC) and organic carbon (OC) content.

Our results show that the $\Delta^{13}C$ and $\Delta^{18}O$ values of the geological samples determined using the three different methods are mostly smaller than ±0.1‰ and ±0.2‰, respectively. Therefore, the Kiel IV-IRMS, GasBench II-IRMS and DI-IRMS methods can generate comparable $\delta^{13}C$ and $\delta^{18}O$ values for most samples within the precision range. However, the $\Delta^{13}C$ and $\Delta^{18}O$ values of some loess samples and some sediment samples from Xingyun Lake displayed relatively large variation. Because some previous studies revealed that the organic matter in the samples may influence the $\delta^{13}C$ and $\delta^{18}O$ values of the carbonates,[8,15] we examined the relationship of the $\Delta^{13}C$ and $\Delta^{18}O$ values with the organic carbon (OC) contents of the loess samples, the sediment from Xingyun Lake and marl, respectively. The results show that the $\Delta^{13}C$ and $\Delta^{18}O$ values measured using the three techniques do not display large deviations from the mean values as the OC contents increase in the loess samples and the lake sediment (Fig. S2†). Conversely, the $\Delta^{13}C$ and $\Delta^{18}O$ values for samples with relatively low OC contents vary greatly. To explain this phenomenon, we plotted the $\Delta^{13}C$ and $\Delta^{18}O$ values against the carbonate percentages of those samples. The results show that the magnitude of the deviations in $\Delta^{13}C$ and $\Delta^{18}O$ generally decreases as the carbonate percentages increase (Fig. S3†). The large deviations we observed mainly occur when the samples have relatively low carbonate percentages, which were particularly prominent in the $\Delta^{18}O$ values. Therefore, the deviation of the $\Delta^{13}C$ and $\Delta^{18}O$ values may be attributed to the net effect of the OC and carbonate contained in the samples. This connection is obvious after plotting the $\Delta^{13}C$ and $\Delta^{18}O$ values vs. the ratio between carbonate and OC (IC/OC) (Fig. 3). The magnitude of the deviation in the $\Delta^{13}C$ and $\Delta^{18}O$ values of the loess, lake sediment and marl samples increase overall as IC/OC decreases. Specifically, the organic matter strongly affects the $\delta^{13}C$ and $\delta^{18}O$ values in samples with low carbonate contents. In a previous study, Oehlerich *et al.*[25] found that the total-inorganic-carbon to total-organic-carbon ratio (TIC/TOC) of ≥0.3 was the threshold for obtaining reliable measurements of the isotope composition of calcium carbonate. However, we observed higher IC/OC threshold ratios for the - geological samples with complicated matrices. Specifically, the IC/OC threshold ratios are >5 for the lake sediment, >100 for the marl samples and generally >30 for the loess (but with some outliers) when assuming the margin of error is 0.1‰ and 0.2‰ for $\Delta^{13}C$ and $\Delta^{18}O$, respectively (Fig. 3). This apparent discrepancy between the threshold ratio reported by Oehlerich *et al.*[25] and ours may be attributed to the different materials used during the study; Oehlerich *et al.*[25] only analyzed artificial mixtures of a carbonate standard (calcite) with various organic compounds. We also noticed that the threshold ratios varied for different geological samples, which may be attributed to the different types of organic matter in those samples. This relationship deserves further study.

Furthermore, our results show that the Kiel IV-IRMS method tends to produce lower $\delta^{13}C$ values than the other two methods (Fig. S1a†). The differences in the $\Delta^{13}C$ values for the three techniques may be attributed to the effects of the labile organic matter on the $\delta^{13}C$ measurement. Previous studies have proposed two types of effect: (1) the contaminants (e.g., C_2H_5OH, CS, BCl, NO_2, N_2O) liberated from the organic matter may increase the measured $\delta^{13}C$ and $\delta^{18}O$ values of the carbonates the weak 45 and 46 ion beams can be amplified;[26,27] (2) the reaction of organic matter with phosphoric acid could liberate CO_2 with a different isotopic composition from that produced from the carbonates.[8] Midwood and Boutton[28] also noticed losses in the acid soluble organic matter and soil N after acid after treating soil samples with acid, although they thought that these changes had no discernible effect on the $\delta^{13}C$ of the soil organic matter. For the Kiel IV-IRMS method, the samples reacted with phosphoric acid under vacuum and at 70˚C. The high reaction temperature and vacuum volatize or oxidize the organic compounds after the phosphoric acid digestion. In contrast, the other two techniques only involve vacuum (for DI-IRMS) or high temperatures (for GasBench II-IRMS). Therefore, the GasBench II-IRMS and DI-IRMS are less affected by the organic matter in the samples. Theorganic matter may produce two different results: shifting $\delta^{13}C$ toward less negative values through the first effect mentioned above or shifting $\delta^{13}C$ toward more negative values

through a second effect because the organic matter usually exhibits values that are more negative than the carbonates. Based on our data, net negative shift in the $\delta^{13}C$ values was observed for the Kiel IV-IRMS data relative to the GasBench II-IRMS and DI-IRMS data. Therefore, the oxidation of organic matter is the major factor influencing the $\delta^{13}C$ analysis of the carbonates in the impure samples when using Kiel IV-IRMS. In addition, the $\delta^{13}C$ values measured using the Kiel IV-IRMS method became more negative when the carbonate content decreased (Fig. S3†). This relationship confirms that the organic matter strongly affects samples containing small amounts of carbonates.

Comparatively, the $\delta^{18}O$ analysis of the carbonates is influenced by many factors. In addition to the effect of the organic matter, the oxygen isotope exchange during digestion may also influence the $\delta^{18}O$ value. In a previous study, lower $\delta^{18}O$ values were obtained when using a common acid bath than when using sealed McCrea-type reaction vessels, and this effect was attributed to the oxygen isotope exchange between CO_2 and the phosphate polymers or free water, the dissolution of CO_2 in the acid and the incomplete removal of CO_2 during extraction[29]. In this study, the Kiel IV carbonate device has an extraction process that is nearly identical to the common acid bath method; the CO_2 produced from the carbonate was instantly gathered in a trap using liquid nitrogen. In contrast, the DI-IRMS uses McCrea-type reaction vessels. However, the pattern we observed when comparing the $\delta^{18}O$ values between the Kiel IV-IRMS and DI-IRMS methods (Fig. S1b†) is the reverse of that observed by Swart et al.[29] Therefore, the oxygen isotope exchange between CO_2 and the phosphate polymers or free water does not account for the pattern generated by our data. In this case, the effects that originate from organic matter may be the primary reason for the observed pattern. Although the reaction between organic matter and phosphoric acid would preferentially use ^{16}O in phosphoric acid, the equilibration of the isotopes in the evolved CO_2 and phosphoric acid may compensate for this shift, minimizing the net effect from this reaction. In contrast, the aforementioned first effect may be the primary reason for the variation in the oxygen isotopes. Because the Kiel IV-IRMS method promotes this effect when compared to the other two methods, it tends to produce relatively high $\delta^{18}O$ values. In contrast, the GasBench II-IRMS usually generates $\delta^{18}O$ values between those yielded by the other two methods, particularly for loess and lake sediment (Fig. S1b†). These results may occur because the GC column preinstalled in the GasBench II can separate the contaminants liberated from organic matter from the CO_2, eliminating the first effect. In this case, the GasBench II-IRMS may produce more reliable $\delta^{18}O$ values.

Comparing the data for the treated and untreated samples reveals that vacuum roasting soes not eliminate efficiently the effect of the organic matter on the measured $\delta^{13}C$ and $\delta^{18}O$ values. Instead, this method increased the variability in the $\delta^{13}C$ and $\delta^{18}O$ values from some treated samples (Fig. 2). The same phenomenon has been observed for skeletal and inorganic calcium carbonate in a previous study.[15] Therefore, using these pre-treatment methods with geological samples during the analysis of stable carbon and oxygen isotopes is inappropriate.

Conclusion

This paper systematically compares the analyses of the $\delta^{13}C$ and $\delta^{18}O$ values of geological samples using a Kiel IV-IRMS, a GasBench II-IRMS and a DI-IRMS. Large variations were observed in the measured $\delta^{13}C$ and $\delta^{18}O$ values of samples with complicated matrices, such as the loess and some lake sediment samples, using the three methods. These variations may be attributed to the differential effects of the organic matter with different methods. Moreover, the $\delta^{13}C$ and $\delta^{18}O$ values measured using the Kiel IV-IRMS method obviously deviate from the mean values of the three methods with decreasing carbonate contents; therefore, using this method to analyze the samples containing small amount of carbonate requires caution. Comparatively, the GasBench II-IRMS method may give the most reliable data for these types of samples. Vacuum roasting is an inappropriate treatment method because it increased the variability of the $\delta^{13}C$ and $\delta^{18}O$ values in some treated samples.

References

1. M. J. Leng, N. Roberts, J. M. Reed, J. S. Hilary, *Journal of Paleolimnology,* 1999, **22**, 187-204
2. T. Ishimura, U. Tsunogai, T. Gamo, *Rapid Commun. Mass Spectrom,* 2004, **18**, 2883-2888
3. M. J. Leng, J. D. Marshall, *Quaternary Science Reviews,* 2004, **23**, 811-831
4. B. G. Cai, R. L. Edwards, H. Cheng, M. Tan, X. Wang, T. S. Liu, *Geophysical Research Letters,* 2008, **35**, L02705
5. Y. J. Wang, H. Cheng, R. L. Edwards, X. G. Kong, X. H. Shao, S. T. Chen, J. Y. Wu, X. Y. Jiang, X. F. Wang, Z. S. An, *Nature,* 2008, **451**, 1090-1093
6. J. M. McCrea, *Journal of Chemical Physics,* 1950, **18**, 849-857.
7. T. B. Coplen, C. Kendall, J. Hopple, *Nature,* 1983, **302**, 236-238.
8. S. Epstein, R. Buchsbaum, H. Lowenstam, H. C. Urey, *Geological Society of America Bulletin,* 1953, **64**, 1315-1325.
9. M. Lopez Correa, P. Montagna, B. Vendrell‑Simon, M.McCulloch, M.Taviani. *Deep‑Sea Research II,* 2010, **57**, 471-486.
10. A. Dutton, B. T. Huber, K. C. Lohmann, W.J.Zinsmeister, *Palaios*, 2007, **22**, 642-650.

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11. T. S. Tobin, A. J. Schauer, E. Lewarch, *Rapid Commun. Mass Spectrom,* 2011, **25**, 2149-2152

12. C. Spötl, T. W. Vennemann, *Rapid Commun. Mass Spectro.,* 2003, **17**, 1004-1006

13. J. Fiebig, B. R. Schöne, W. Oschmann, *Rapid Communications in Mass Spectrometry,* 2005, **19**, 2355-2358.

14. D. Paul, G. Skrzypek, *International Journal of Mass Spectrometry,* 2007, **262**, 180-186

15. H. Wierzbowski, *International Journal of Mass Spectrometry,* 2007, **268**, 16-29

16. K. W. Keatings, J. A. Holmes, T. H. E. Heaton, *Chemical Geology,* 2006, **235**, 50-261

17. T. Mcconnaughey, *Geochimica et Cosmochimica Acta,* 1989, **53**, 151-162.

18. M. Boiseau, A. Juillet-Leclerc, *Chemical Geology,* 1997, **143**, 171-180.

19. A. G. Grottoli, L. J. Rodrigues, K. A. Matthews, J. E. Palardy, O.T.Gibb, *Chemical Geology,* 2005, **221**, 225- 242

20. Z. L.Ding, V. Ranov, S. L.Yang, A. Finaev, J. M. Han, G. A. Wang, *Earth and Planetary Science Letters*, 2002, **200**, 387-400.

21. Y. S. Tong, Y. Q. Wang, Q. Li, *Geological Review*, 2006, **52**, 153-162. (In Chinese with English abstract)

22. X. Wang, P. A Peng, Z. L. Ding, *Palaeogeography, Palaeoclimatology, Palaeoecology*, 2005, **223**, 9-19.

23. X. Wang, L. L. Cui, J. L. Xiao, Z. L. Ding, *Chemical Geology*, 2013, **347**, 123-134.

24. S. C. Xie, R. D. Pancost, J. H. Huang, P. B. Wignall, J. X. Yu, X. Y. Tang, L. Chen, X. Y. Huang, X. L. Lai, *Geology*, 2007, **35**, 1083-1086.

25. M. Oehlerich, M. Baumer, A. Lücke, C. Mayr, Rapid Commun. Mass Spectrom., 2013, **27**, 707-712.

26. J. N. Weber, P. Deines, P. H. Weber, P. A. Baker, *Geochim. Cosmochim. Acta,* 1976, **40**, 31-39.

27. S. Epstein, R. Buchsbaum, H. Lowenstam, H. C. Urey, *Geological Society of America Bulletin,* 1951, **62**, 417-426.

28. A. J. Midwood, T. W. Boutton**,** *Soil Biol Biochem***,** 1998**, 30,** 1301**-**1307.

29. P. K. Swart, S. J. Burns, J. J. Leder, *Chemical Geology,* 1991, **86**, 89-96.

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