

## Research paper

## A comparative study of methods for determining carbonate content in marine and terrestrial sediments

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## ABSTRACT

Carbonate can be produced in a variety of environments on the Earth's surface, such as shallow seas and deep oceans, continental lakes, soils and subsurface aquifers. The carbonate content of sediments is an important proxy in paleoceanography and paleoclimatology and is often used to reconstruct paleoenvironmental evolution of the earth. Many methods have been reported to measure the content of carbonate in sediments, but how those methods perform (e.g. degree of accuracy and precision, error-induced factors, operability, cost and time) remains understudied. Here, we employ three widely-used non-instrumental methods, including acid-base titration, gasometric method, and loss on ignition (LOI) based on muffle combustion, together with X-ray diffraction for mineral phase analysis, to compare the carbonate content data of sediments from deep ocean (water depths from 1218 m to 6147 m) of the western Pacific and Cenozoic sedimentary rocks from the Qaidam basin, northern Tibetan Plateau. The results show that data accuracies of most methods are closely related to mineral compositions in sediments (e.g. carbonate species and clay mineral contents) and analytical operations. Non-instrumental methods generally demonstrate low precisions (avg. RSD of 3.36%) in determining sediments with low carbonate contents (< 20% wt). Among the three approaches, the LOI method performs best with relatively high accuracy (avg. recovery of 99.79%) and precision (avg. RSD of 0.27%) when determining carbonate-rich sediments with simple mineral compositions (e.g. only calcium carbonate). Although dehydroxylation of clay minerals might influence the results, the LOI method has advantages of ease of operation, short time-consuming and convenience for batch determinations. Acid-base titration and gasometric methods indicate moderate precisions (avg. RSD of 1.73% and 2.76%, respectively) and accuracies (108.64% and 101.85%, respectively) with quick measurement, affordable cost and requirement of high-quality manual operation. Additionally, we suggest that the analytical procedures, such as sample size, reaction time, temperature, reagent concentration, weighing error, endpoint judgement of titration can influence the data quality. This study provides significant selecting principles for carbonate determination methods and would be beneficial to carbonate-related study in various aspects of geosciences.

## 1. Introduction

Carbonate can be produced in both marine and terrestrial environments, as a common mineral composition in soils, sediments and rocks. Carbonate minerals in the global ocean, which are mainly involved in shallow carbonate platform sediments and deep ocean biogenic calcareous deposits, are regarded as the most significant inorganic carbon reservoir on the Earth's surface (Schimmel, 1995; Feely et al., 2004; Arrigo, 2007). The species, concentrations, elemental and isotopic compositions of carbonate in sediments and sedimentary rocks can be influenced by a variety of environmental and climatic factors, such as temperature, pH, precipitation, biological productivity,

microbial community and hydrological conditions (Wang, 1999; Morse, 2003; Zeebe et al., 2008; Dupraz et al., 2009; Swart, 2015; Zamanian et al., 2016). Therefore, carbonate-related proxies of sediments or sedimentary rocks are widely used in paleoceanography, paleolimnology, paleoclimatology and paleoenvironmental study (Farrell and Prell, 1989; Ekart et al., 1999; Pälke et al., 2012).

Variations in marine sedimentary carbonate content play a critical role in indicating fluctuations in paleo-ocean carbonate compensation depth (CCD), such as the sharp decrease of CCD during the Paleocene-Eocene Thermal Maximum event in the South Atlantic Ocean (Zachos et al., 2005) and the increase of CCD on the Eocene-Oligocene boundary documented in the tropical Pacific Ocean (Coxall et al., 2005). Due to

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the close relationships with temperature, precipitation, solution acidity and biological activity, carbonate content serves as a crucial proxy in reconstruction of paleoenvironmental and paleoclimatic changes based on paleo-lake sediments and loess-paleosol sequences (e.g. Wang et al., 2005; Hodell et al., 2007; Liu et al., 2008; Marković et al., 2008; Zhu et al., 2008; Jian et al., 2014). The significance of carbonate content also presents in evaluation of the unconventional hydrocarbon resource potentials and associated development. For example, shales with high carbonate content largely contribute to hydraulic fracturing technology during shale gas exploitation process (Chalmers et al., 2012; Furmann et al., 2014; Cao et al., 2016; Yang et al., 2016a; Zhang et al., 2018; Huang et al., 2019).

Reported methods for determination of carbonate content in sediments can be divided into five types due to the following rationales. First, based on the reaction between carbonate and hydrochloric acid (Lamas et al., 2005), carbonate content can be calculated by determining the consumed HCl through an acid-base titration method (Yang et al., 2016b). Weight difference before and after acid treatment is considered to be the dissolved carbonate in application of the min-using method (Burbank et al., 2013). The released CO<sub>2</sub> from reaction can be measured titrimetrically by coulometers, gravimetrically by the gravimetric method, volumetrically by the gasometric method and calcimeters, or manometrically by the “Karbonat Bombe”, vacuum-gasometric system and rapid quantitative analysis methods (Müller and Gastner, 1971; Huffman, 1977; Jones and Kaiteris, 1983; Yuan and Liu, 1997; Trapp et al., 1998; Formolo et al., 2004; Yu, 2007; Kennedy and Woods, 2013; Higuchi et al., 2014; Ren et al., 2014; Du et al., 2018). Second, values of carbonate content in sediments can be evaluated by measuring the concentrations of Ca<sup>2+</sup> and Mg<sup>2+</sup> using an inductively coupled plasma-atomic emission spectrometry (ICP-AES). In addition, EDTA (ethylene diamine tetraacetic acid) titration can be used to measure calcium carbonate-rich sediments by detecting only Ca<sup>2+</sup> (Choi et al., 2017). Third, the inorganic carbon in sediments is measured by an elemental analyzer and converted to carbonate content (Li et al., 2020). Fourth, the direct measurements of carbonates are conducted through the weight loss of decomposition under high temperature conditions by the thermogravimetric analysis (TGA) and loss on ignition (LOI) methods (Dean, 1974; Choi et al., 2017; Tenkouano et al., 2019). Lastly, based on the correlations between carbonate content and physical parameters of sediments (Weber, 1998; Huang et al., 2019) or mineral phase spectra, plenty of instrumental methods have been developed to rapidly and nondestructively determine carbonate content for sediments. For instance, fourier transform infrared spectroscopy (FTIR) and diffuse reflectance infrared fourier transform spectroscopy (DRIFTS), (Pérez-Ponce et al., 1998; Reig et al., 2002; Vagenas et al., 2003; Tatzber et al., 2006; Ge et al., 2009; Rosén et al., 2010; Liu et al., 2013; Veerasingam and Venkatachalapathy, 2014), as well as CO laser infrared photoacoustic spectroscopy (IRPAS) (Dóka et al., 1998), X-ray diffraction (XRD) (Roselle, 1982) and optical lightness (Balsam et al., 1999).

Improvements on the above methods have also been reported to increase measurement accuracy. For example, the automatic potentiometric titrator can eliminate the potential errors caused by misjudging the endpoint of titration (Sun et al., 2012). Large uncertainties induced by the dissolution of non-carbonate phases of Mg<sup>2+</sup> and Ca<sup>2+</sup> can be inhibited under careful selection of the leaching solution when using an ICP-AES method (Barber, 1974; Robinson, 1980; Song et al., 1998; Qiao et al., 2006). The LOI method has advantages in batch determinations of sediment samples at low cost. However, results by the LOI method are susceptible to various factors such as ignition temperature, exposure time, sample size and crucible positions in the muffle furnace (Heiri et al., 2001; Zhang and Mu, 2007; Wang et al., 2011). Most instrumental methods require calibration, such as multifarious spectroscopy methods (Dóka et al., 1998; Bruckman and Wriessnig, 2013), even the highly-accurate and widely-used coulometers (Mörth and Backman, 2011). Carbonate measurements related studies in recent years highly

depend on automated analytical instruments (high expense and long time consumption when measuring massive samples) but overlook the non-instrumental methods. Furthermore, high-efficiency and more-applicable determination methods for different types of sediments (e.g. marine and terrestrial sediments, one-kind carbonate and multiple carbonate compositions, low and high carbonate content sediments, small and large numbers of samples) remain poorly known.

This study employs several non-instrumental methods (acid-base titration, the gasometric method, and the loss on ignition method) together with X-ray diffraction to measure carbonate contents of marine and terrestrial sediment samples. The purposes are 1) to summarize and compare the advantages and disadvantages of these methods, 2) to offer appropriate suggestions for each approach and 3) to figure out suitable determination methods for marine and terrestrial sediments.

## 2. Samples

The analyzed samples include 20 deep ocean sediment samples and 9 terrestrial sedimentary rock samples. The seafloor sediment samples were retrieved using a box sampler and collected from the tropical western Pacific Ocean (7–13 °N, 140–148 °E), mainly distributing in the southern sector of the Mariana Trench with water depths of 1–6 km (Fig. 1). Marine samples are multicomponent mixed sediments, including predominant foraminiferal sands and clays with subordinate silts and sands (Table A. 2). Terrestrial samples, mainly mudstones and marlstones, were collected from two Cenozoic outcrop sections in the northeastern Qaidam basin, NW China (Fig. 2). The Qaidam basin sits 2.7–3.0 km above sea level and covers an area of 120,000 km<sup>2</sup> (Jian et al., 2018). The Cenozoic sedimentary strata in the Qaidam basin are composed of continental sedimentary facies with widely distributed lake, fluvial and delta sediments from the Eocene Xia Ganchaigou Formation to the Miocene Shang Youshashan Formation (Jian et al., 2013). Samples collected from the Huaitoutala section are dominated by meandering and braided river systems and involve channel and overbank deposits (Zhuang et al., 2011), whereas samples from the Dahonggou section consist of lacustrine deposits, alluvial fan deposits and overbank deposits (Lu and Xiong, 2009). For the specific sample settings and information see Figs. 1 and 2.

Marine and terrestrial sediment samples were first dried, and then ground to powder (grain size < 74 μm) for mineralogical identification by XRD analysis. The results of XRD analysis demonstrate quite different mineral compositions of the unknown samples. Marine sediments consist of relatively diverse mineral components which are dominated by quartz, halite and multiple carbonates (i.e. calcite, aragonite, and dolomite) (Fig. 3a), whereas the terrestrial sediments have similar mineral compositions with quartz, plagioclase, calcite and clay minerals (Fig. 3b).

Granodiorite is the most widely distributed rock in crust and usually composed of quartz, plagioclase, orthoclase, amphibole and biotite. Standard material samples (SS) with carbonate contents of 5%, 15%, 30%, 50% and 70% by weight were prepared by using mixtures of pure CaCO<sub>3</sub> (AR, > 99.0%, CAS#471-34-1, Sinopharm Chemical Reagent Co., Ltd (Abbr: SCRC), China) and granodiorite powders. The determination values of carbonate content in the standard and unknown samples are expressed as percentages by weight (% wt) in this study.

## 3. Methodology

### 3.1. Acid-base titration method

Acid-base titration is a conventional method for measuring carbonate contents of sediments. The result precision is closely related to mineralogy, organic matter, sample size, acid concentration, reaction time and operation process (Chave, 1965; Suess, 1970; Telek and Marshall, 1974; Al-Aasm et al., 1990; Caughey et al., 1995; Kassim, 2013). The reaction between carbonate and superfluous hydrochloric

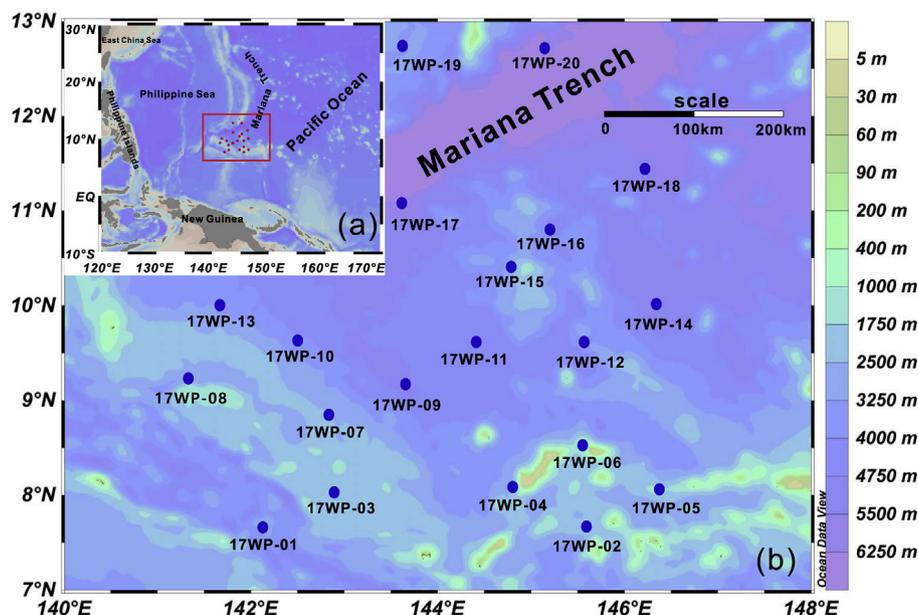


Fig. 1. Marine sediment sample locations. Most samples are located in southern Mariana Trench with different water depths.

acid is conducted first to avoid the inefficient dissolution, followed by back titration to the residual acid with standard sodium hydroxide solution. The consumed base reflects the proportion of carbonate in sediment (Grimaldi et al., 1966; Wang et al., 2006). The specific operation process is written below.

The first step was to prepare a 0.1 mol/L NaOH solution and

calibrated it with 1.5 g potassium acid phthalate (KHP) powders (AR, > 99.8%, CAS#877-24-7, SCRC, China) for three repeats until the solution appeared and stayed reddish for half a minute. The exact concentration of standard NaOH solution was calculated as follows

$$C_{NaOH} = m / (M_{KHP} \times V / 1000) \quad (1)$$

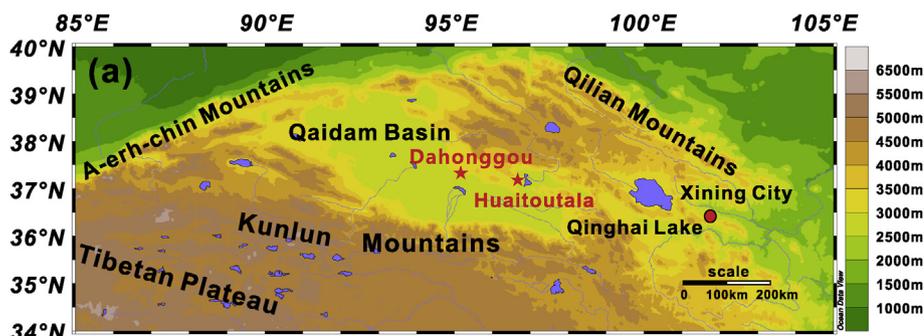
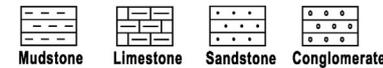


Fig. 2. (a) The location of the analyzed terrestrial sediments. (b) and (c) Lithological descriptions of the Dahonggou and Huaitoutala sections. The sampling locations (the red asterisks) are located in the Qaidam Basin, Qinghai province, NW China, at an altitude of about 3000 m. E<sub>3</sub> is the abbreviation of the Xia Ganchaigou formation, N<sub>1</sub>, N<sub>2</sub><sup>1</sup> and N<sub>2</sub><sup>2</sup> represent Shang Ganchaigou formation, Xia Youshashan formation and Shang Youshashan formation, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Age (Ma)	Epoch	Formation	Lithology	Age (Ma)	Epoch	Formation	Thickness	Lithology
8	Middle-Late Miocene	N <sub>2</sub> <sup>2</sup>	[Lithology symbols]	8.1	Middle-Late Miocene	N <sub>2</sub> <sup>2</sup>	2400	[Lithology symbols]
15				Early Miocene			N <sub>2</sub> <sup>1</sup>	
22	Oligocene	N <sub>1</sub>	2000					
35.5			Late Eocene					
				1600				
			1400					
			1200					
			1000					
			800					
			600					
			400					
			200					
			0					



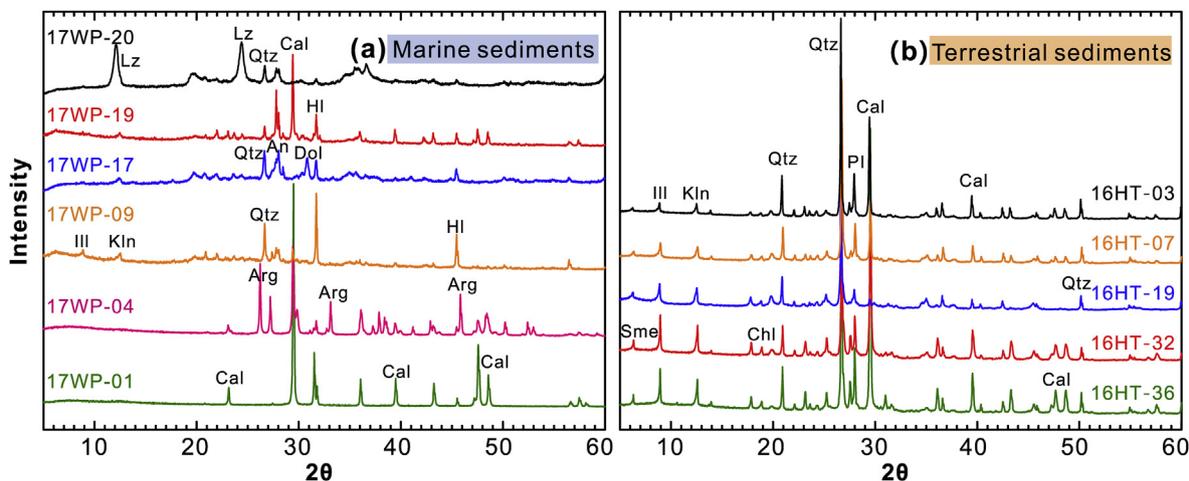


Fig. 3. XRD analysis results of selected marine (a) and terrestrial (b) samples. Qtz: quartz, Pl: plagioclase, An: anorthite, Cal: calcite, Arg: aragonite, Dol: dolomite, Lz: lizardite, HI: halite, Sme: smectite, Ill: illite, Kln: kaolinite, Chl: chlorite.

where  $m$  is the mass of KHP (g);  $M_{KHP} = 204.22$ ;  $V$  is the consumed volume of NaOH solution (ml). The pH of solution was used as criterion in determination of titration endpoint to eliminate the interference of sediment color. Each 0.1 g powder sample was weighed and mixed with ultrapure water to measure the pH value. Then 20 ml 0.1 mol/L HCl was added to react sufficiently with each sample for 48 h. The residual acid was titrated by standard NaOH solution until the pH meter (SX-620, Sanxin, China) (inserted into solution) showed values consistent with the previous data, implying the arrival of titration endpoint. Blank samples were treated with the same procedures. Carbonate in sediment was given as

$$W_{CaCO_3} = (V_0 - V_1) \times C_{NaOH} \times F / m \times 100 \quad (2)$$

where  $W_{CaCO_3}$  represents carbonate content (% wt);  $C_{NaOH}$  is the concentration of standard NaOH solution (mol/L);  $V_0$  and  $V_1$  are the consumed NaOH solution in blank and formal experiments, respectively (ml);  $m$  is sample mass (g);  $F = 0.05004$  (Yang et al., 2016b).

It is necessary to allow sufficient reaction time of HCl and carbonate to reach equilibrium. Thus, a series of reaction time, including 3 h, 6 h, 18 h, 25 h, 30 h, 40 h and 48 h, was set in pre-experiment to figure out the best. A standard sample (70%SS), which was mixed by 70% pure  $CaCO_3$  and 30% granodiorite powders, was utilized to monitor the operation process.

### 3.2. Loss on ignition method

Loss on ignition (LOI) method is widely conducted in the determination of carbonate and organic matter contents of various sediments via calculating weight loss of the sample before and after ignition (Davies, 1974; Dean, 1974; Froelich, 1980; Ben-Dor and Banin, 1989; Cambardella et al., 2001; Heiri et al., 2001; Bisutti et al., 2004; Boyle et al., 2004; Wang et al., 2011). The procedure of the LOI method in this study was divided into two parts, i.e., removing organic carbon under 550 °C for 2 h and subsequently decomposing carbonate minerals under 900 °C for 6 h. The detailed procedure is described as follows, given by Heiri et al. (2001).

Crucibles were first put in a muffle furnace (SX2-4-10, Nantong Hunan, China) at 600 °C for 30 min, followed by cooling in a desiccator for 20 min until constant weight was reached, and weighed as  $M_0$  (ca. 10 g for each crucible) with a 0.1 mg analytical balance (ESJ182-4, Longteng, China). After drying in an oven (DHG-9140A, Jinghong, China) overnight (105 °C, 12 h), the powder samples (each for 3 g) were added to crucibles and cooled in the desiccator for 20 min. The co-weight of the matching crucible and sample was weighed as  $M_{105}$ . Samples and crucibles were burnt in the muffle furnace to get rid of

organic matter at 550 °C for 2 h and to decompose carbonate at 900 °C for 6 h. Cooling in the desiccator and weighing are required after each combustion ( $M_{550}$  and  $M_{900}$ ). Consequently, the carbonate content  $W_{CaCO_3}$  (% wt) was calculated as

$$W_{CaCO_3} = (M_{550} - M_{900}) / (M_{105} - M_0) \times 100 \times 2.27 \quad (3)$$

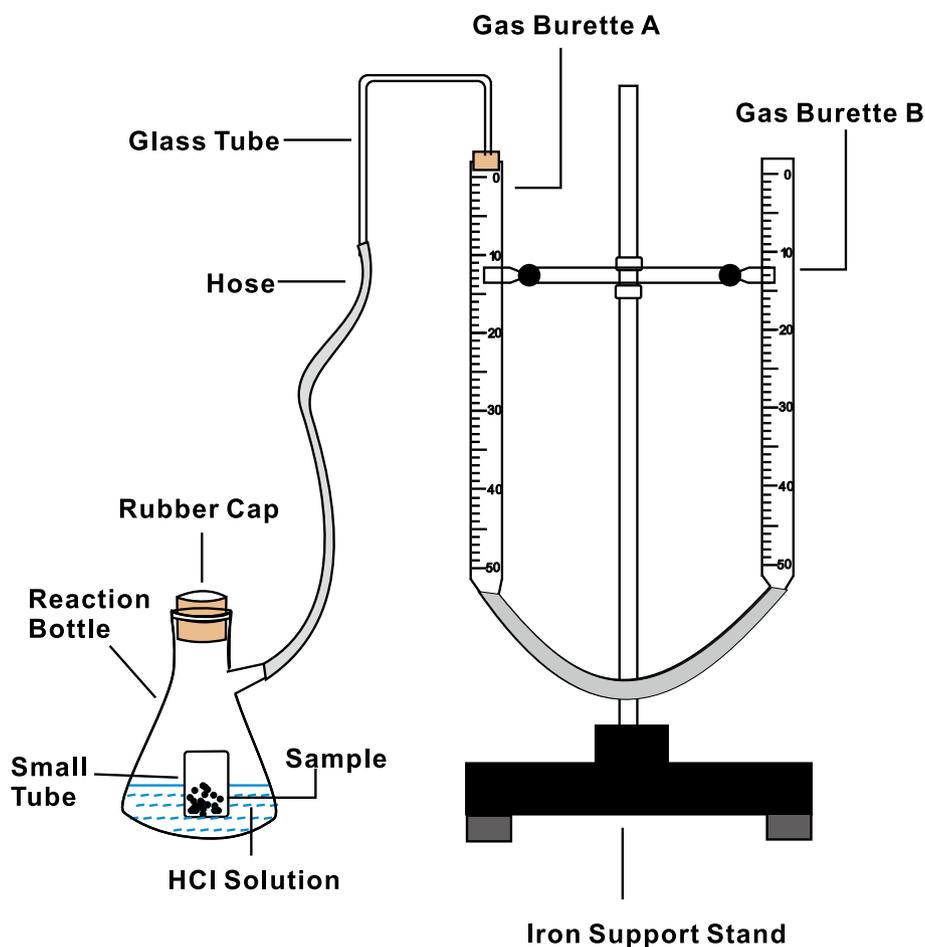
where  $M_0$  is the net weight of crucible,  $M_{105}$ ,  $M_{550}$  and  $M_{900}$  are the co-weight of sample and crucible before combustion, after combustion at 550 °C and 900 °C, respectively (Dean, 1974; Heiri et al., 2001; Zhang and Mu, 2007).

The accuracy of carbonate content measured by the LOI method is closely related to sample size. A standard material sample (50%SS) and two unknown samples (17WP-17, 17WP-03) with different carbonate contents were selected for pre-experiment to determine the appropriate size (0.1 g, 0.3 g, 0.5 g, 1 g, 3 g, 5 g) for the LOI method.

### 3.3. Gasometric method

The gasometric method is supported by various apparatuses with a consistent principle to convert the volume of  $CO_2$  released from the reaction between carbonate and HCl into carbonate content (Dreimanis, 1962; Jones and Kaiteris, 1983; Huang et al., 2007; Fagerlund et al., 2010; Ren et al., 2014). Temperature and pressure (T-P) conditions, predominantly by temperature, have a great impact on the precision of gasometric method mainly by influencing the specific gravity of  $CO_2$  (Ren et al., 2014). Therefore, the gasometric operation is ordinarily conducted under consistent T-P conditions to avoid the interference of external environments. Calculation and standard curve are two common solutions for converting  $CO_2$  to  $CaCO_3$ . The former requires each measurement of atmospheric pressure, operating temperature and  $V_{CO_2}$  to calculate carbonate content. The latter is a linear curve calibrated with pure  $CaCO_3$  in specific T-P conditions, and help to convert results of the experiments treated in the same condition.

The device used in this study mainly consists of a gas generator and a collector, as well as hoses for connection (Fig. 4). It is vital to ensure the airtightness of the device in advance. The mixed solution of 0.5 mol/L  $H_2SO_4$  and Methyl red (AR, CAS#493-52-7, SCRC, China) was put into burette B and entered burette A through a hose to form the collector for measuring  $V_{CO_2}$ . After balancing and recording the liquid level of burette A and B, powder sample was put in a small test tube placed in the bottom of reaction bottle that has been added 20 ml 1 mol/L HCl. The small tube was tilted to trigger the reaction of sample and HCl until reaching equilibrium. Burette A and B were adjusted in the same liquid level by up and down and recorded the level value of burette A. The value difference of burette A before and after reaction



**Fig. 4.** The device design for the gasometric method. The gas generator consists of a reaction bottle and a small test tube containing samples. Hoses and modified burettes were used to transport and to measure the released  $\text{CO}_2$ , respectively.

represents the volume of released  $\text{CO}_2$ .

Various sizes of pure  $\text{CaCO}_3$  from 0.01 g to 0.08 g at 0.005 intervals were adopted to determine the specific volume of released  $\text{CO}_2$  at 24 °C to fit a standard curve prior to the unknown experiments (Yu, 2007). The experiments of unknown samples were conducted in the same conditions and the raw data of  $V_{\text{CO}_2}$  were converted to equivalent  $\text{CaCO}_3$  contents by the standard curve. Besides, five replicate experiments were conducted by using separately 0.01 g, 0.04 g and 0.07 g pure  $\text{CaCO}_3$  powders in order to decide the proper sample size.

### 3.4. X-ray diffraction method

X-ray diffraction (XRD) has been developed as an effective qualitative analysis method for identification of mineral species in sediments and has also been applied in the quantification of carbonate for peak intensity of a single mineral is proportional to the relative mineral content (Roselle, 1982; Kontoyannis and Vagenas, 2000; Al-Jaroudi et al., 2007; Titschack et al., 2009). Note that unknown sample XRD analysis is generally considered to be semi-quantitative due to poor detections for low-abundance minerals (i.e. Alemu et al., 2011; Chen et al., 2011; De Meneses et al., 2013; Caniço et al., 2015; Ribeiro et al., 2017; Al Moajil et al., 2019; Moreira et al., 2019). Thus, XRD analysis in this study was used for qualitative analysis. The mineral species were determined by a Rigaku Ultima IV X-ray diffractometer at Xiamen University and followed the analytical procedures given by Jian et al. (2019). Each powdered sample was continuously scanned under 40 kV, 30 mA,  $2\theta$  range of 5–60° and scanning speed 4°/min.

## 4. Results and discussion

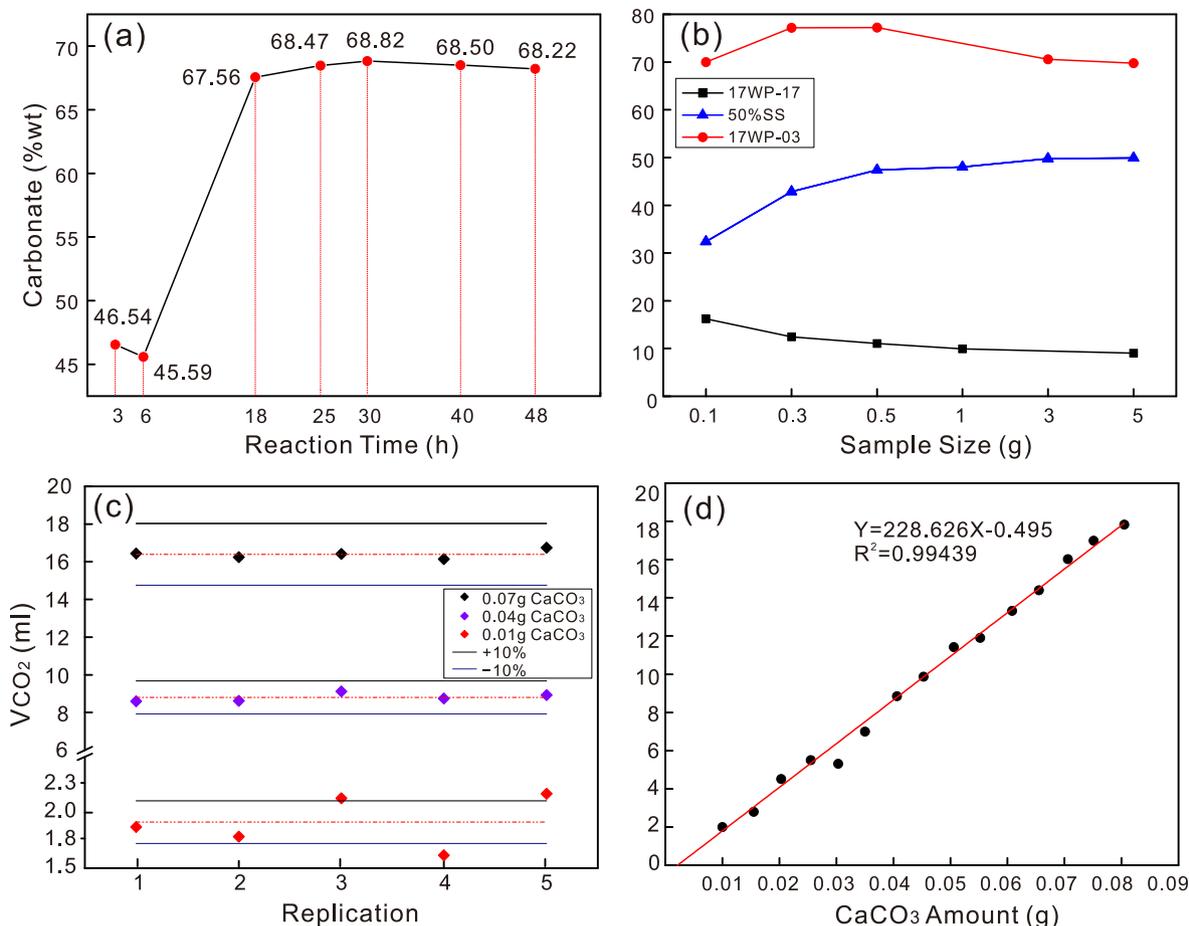
### 4.1. Pre-experiments

#### 4.1.1. The acid-base titration experiments

Reaction time plays an important role in accurate determination of sediment carbonate content by the acid-base titration method. The experimental results of reaction time test show that the measured values of carbonate content increase with time before 25 h. It means that the reaction time of 20 ml 0.1 mol/L HCl and 0.1 g 70%SS should exceed 25 h at ambient temperatures to ensure the sufficient dissolution of carbonate (Fig. 5a). Additionally, the same carbonate content values were obtained from 25 h to 48 h experiments by using standard materials with 70% carbonate. Hence, considering the potential presence of carbonate-dominated unknown samples (> 70% wt), the reaction time of titration experiments in this study was fixed to be 48 h.

#### 4.1.2. The loss on ignition experiments

The unknown samples 17WP-03 and 17WP-17 as well as standard materials with 50% carbonate (50%SS) were used to determine the optimal sample size for the LOI method. Results indicate that LOI analyses on samples with low amounts (e.g. 0.1 g, 0.3 g, 0.5 g) have significantly larger errors than that of high-amounts samples (Fig. 5b). The measured values of all samples are varied but tend to be similarly steady with the increasing sample sizes. The results of standard materials (50%SS) with sample sizes of 3 g and 5 g have < 0.21% wt bias. Besides, ignition temperature and exposure time used in this study were also proven to meet the test requirement by the accurate determination of 50%SS. We suggest that 3 g is the appropriate amount for each



**Fig. 5.** Results of the pre-experiments for exploring best operation conditions for the acid-base titration, LOI and gasometric methods. Here, we mainly concern reaction time in the acid-base titration method (a), sample sizes in the LOI method (b), relationship between replicating errors and CaCO<sub>3</sub> amounts (c) and standard curve in the gasometric method (d). In (c), samples with low, moderate and high CaCO<sub>3</sub> amounts are represented by colored rhomboids and distributed in three layers due to the different CO<sub>2</sub> output. The red line in each layer represents the mean value of five replicates. Black and blue lines indicate relative error ranges of 10% above and below the mean values, respectively. The standard curve (d) is obtained by linear regression of the data from the reaction of pure calcium carbonate and hydrochloric acid at 24 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

unknown sample and the combustion conditions was set as 550 °C, 2 h and 900 °C, 6 h.

#### 4.1.3. The gasometric experiments

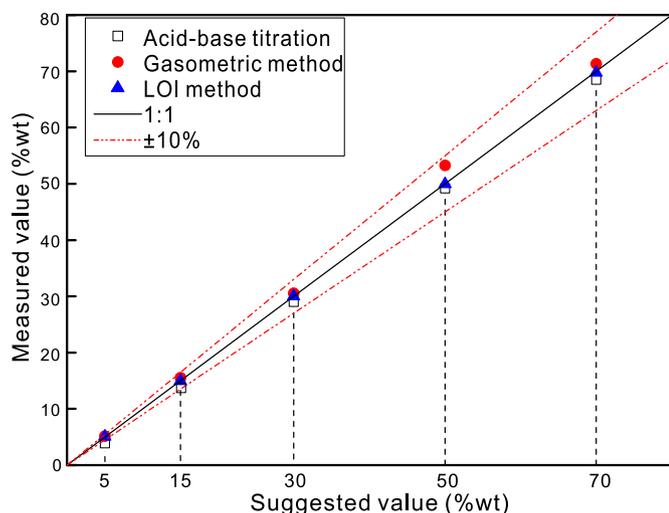
The detection limit (including maximum and minimum) of CO<sub>2</sub> volume of the gasometric device was detected to be 2–19 ml by determined with 0.01–0.08 g CaCO<sub>3</sub>. Lower or higher CO<sub>2</sub> emissions out this range were not accepted due to non-negligible operational errors during balance of liquid levels and visual judgement of volume change. The replicated experiments with different amounts of CaCO<sub>3</sub> (Fig. 5c and 0.01 g, 0.04 g, 0.07 g) indicate that utilizing large amount of CaCO<sub>3</sub> have higher precision (RSD of 1.40%) than that of middle (RSD of 2.50%) and small (RSD of 12.20%) quantities (for terminology RSD see 4.2.1). Therefore, the sizes of unknown samples should change flexibly with carbonate contents to achieve high-precision data, and thus it is suggested to use approximately 0.07g CaCO<sub>3</sub> for reaction. Here, we set 1 g, 0.2 g and 0.1 g as the sizes of samples with < 10% wt, about 40% wt and > 70% wt carbonate contents, respectively (ps: unknown samples were first tested by acid-base titration). To simplify measurement process and data calculation, an effective standard curve (Fig. 5d, R<sup>2</sup> = 0.994) was established with pure CaCO<sub>3</sub> at 24 °C to assist with parameters conversion.

#### 4.2. Comparison of the performance of the acid-base titration, gasometric and LOI methods

##### 4.2.1. Standard materials and replications

The performance of three methods in single measurement with the prepared standards are distinct. The measured values of carbonate in standard materials by the LOI method highly coincide with the suggested values (Fig. 6) with a relative error (RE) < 1.40%, whereas the carbonate contents measured by the gasometric and titration methods are slightly higher or lower than the standards, respectively. The measured values of carbonate-rich samples (i.e. 30%SS, 70%SS, with RE of ca. 1.85%) by the gasometric method agree best with the suggested values. Additionally, acid-base titration test of carbonate-rich standards including 30%SS, 50%SS and 70%SS produces ca. 2.96% RE, demonstrating more accurate measurements in comparison with carbonate-poor samples of 5%SS and 15%SS (with RE > 10%). The comparison of results of the standard materials indicates that the LOI method has steadily accurate performance in measurements of samples with different carbonate contents, whereas the gasometric and acid-base titration methods are more effective for measuring moderately-highly carbonate-rich samples.

Precisions and accuracies of the results were determined with five standard materials and one unknown sample for multiple replicates analysis as presented in Table 1. The precision is represented as the relative standard deviation (RSD) by using the standard deviation of the



**Fig. 6.** Results of standard materials determined by the acid-base titration, gasometric and LOI methods. Points on the black line mean that the measured carbonate content values are consistent with the suggested values and those on red lines indicate a 10% relative error. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

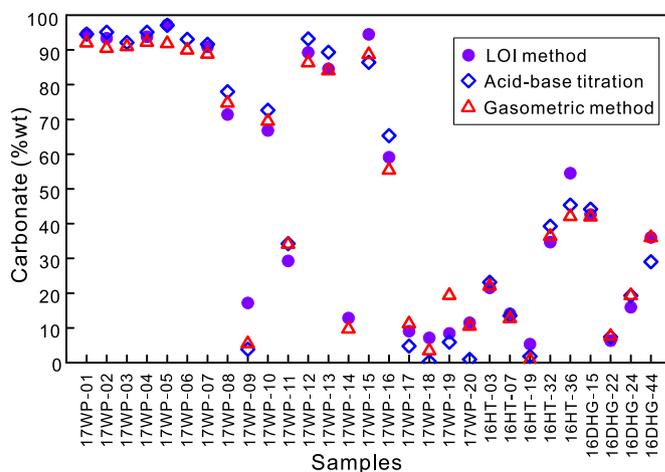
measured carbonate contents from the replicate experiments divided by the mean values. Lower RSD values indicate higher precisions. The recovery, as an indicator of accuracy, is calculated as the mean measured values of carbonate content divided by the standard values and is expressed as percentage. High recovery values, which are close to 100%, demonstrate very high accuracies (Rodriguez et al., 2016).

The statistical analysis displays that the measured values of samples with < 15% carbonate by the acid-base titration and LOI methods have evidently higher RSD values (3.60%, 3.79%) than other samples containing 30%, 50% and 70% carbonate. Otherwise, RSD of the gasometric results are almost invariable (2.68%, 2.80%, 2.71%) with carbonate contents. The reasonable explanation to the changeless RSD values by the gasometric method is that each sample size is distinguished according to the carbonate content. The precisions for high carbonate content standards (i.e. 30%SS, 50%SS and 70%SS) measuring can be ranked from the highest to the lowest in the order of LOI, acid-base titration and gasometric methods. However, the recoveries of acid-base titration (e.g. 121.60%, 95.67%) show great deviation of the measured and standard values in comparison with those of LOI (ca. 99.79%) and gasometric (ca. 102.43%) methods. The contradictory high precision and low accuracy of acid-base titration results (Table 1; Fig. 6) were probably caused by systematically operational errors, for instance, the inaccurate concentration of standard NaOH solution and/or the calibration error of pH meter. In summary, we suggest that the LOI, gasometric and acid-base titration methods show good precision and accuracy, moderate precision and accuracy, and good precision but poor accuracy, respectively.

**Table 1**

The precision and accuracy of determination results of samples with different carbonate contents.

Method	Acid-base titration			The gasometric method			The LOI method		
	17WP-14	30%SS	70%SS	5%SS	30%SS	70%SS	15%SS	50%SS	70%SS
Sample	17WP-14	30%SS	70%SS	5%SS	30%SS	70%SS	15%SS	50%SS	70%SS
Replication	5	5	5	7	6	6	3	3	3
Mean, % wt	9.65	36.48	66.97	5.18	30.55	71.31	14.97	49.94	69.78
SD, %	0.35	0.71	1.01	0.14	0.86	1.93	0.57	0.14	0.18
RSD, %	3.60	1.95	1.50	2.68	2.80	2.71	3.79	0.28	0.26
Recovery, %	–	121.60	95.67	103.60	101.83	101.87	99.80	99.88	99.69



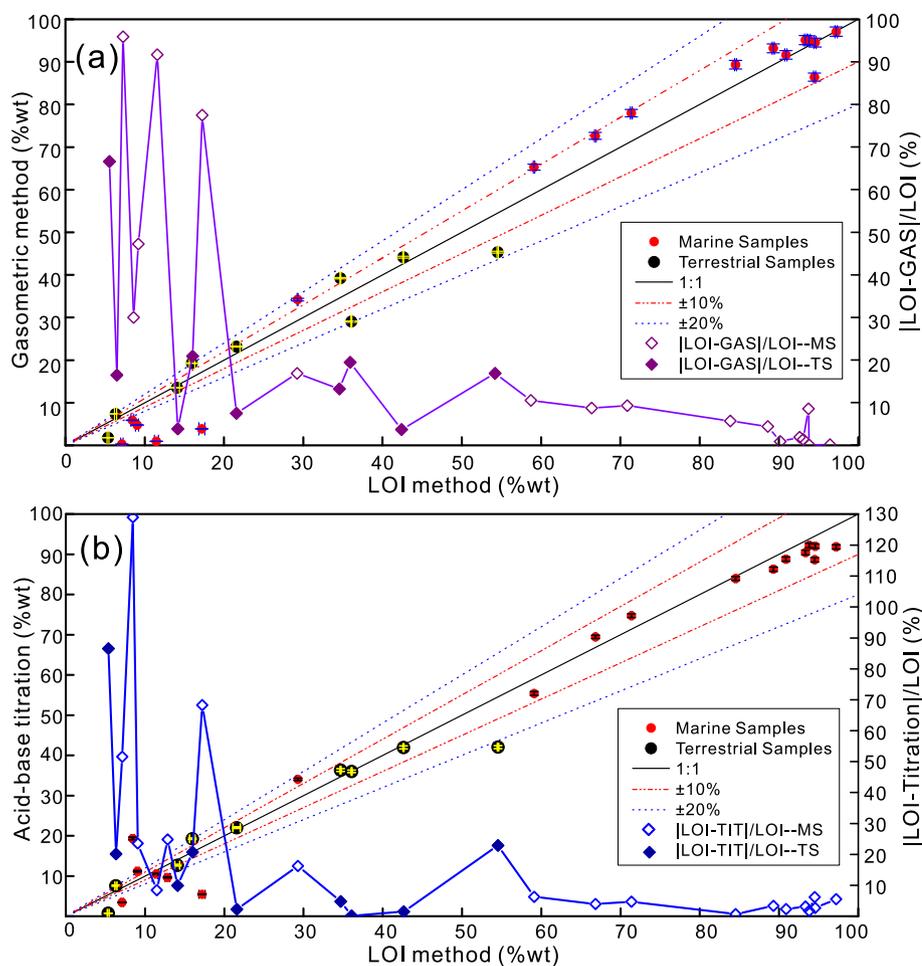
**Fig. 7.** Carbonate content results of the analyzed marine and terrestrial samples measured by the LOI, gasometric and acid-base titration methods. Each sample was detected in three ways, purple circle for the LOI method, blue rhombus for the acid-base titration method and red triangle for the gasometric method. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

**4.2.2. Unknown sediment samples**

As shown in Fig. 7, carbonate contents of the analyzed marine samples vary widely from 0.95% wt to 97.22% wt and display distinct clusters with high values (> 50% wt) and low values (< 20% wt). Marine sediments with overwhelmingly high carbonate contents (> 90% wt) are dominated by foraminifera sands. In contrast, the analyzed terrestrial sediments have less varied carbonate contents, ranging from 0.72% wt to 54.53% wt. Measured values by the gasometric method are generally lower than that of the other two methods for carbonate-rich (> 90% wt) samples. The differences of the measured carbonate values among the three methods are mostly less than 5% wt, apart from several anomalous values (with difference of 6.95–13.33% wt). A comprehensive table of experimental data and an error bar collection of all replications in this study are shown in the appendix (Table A. 3 and Fig. A. 1).

Given the good performance of the LOI method in determination of standards, the unknown sample results by the acid-base titration and gasometric methods are compared separately with that of the LOI method. LOI and gasometric tests on marine and terrestrial samples produce highly similar carbonate content values for carbonate-rich (especially > 90% wt) sediments but show largely inconsistent values for carbonate-poor (< 20% wt) sediments (Fig. 8a). Anomalously low carbonate values were produced for several samples (e.g. 17WP-09, 17WP-17, 17WP-19, 17WP-20 and 16HT-19) by the gasometric method. There is a good correlation between acid-base titration and LOI results except for minor samples (Fig. 8b). The carbonate percentages of samples 17WP-09, 17WP-18, 16HT-19 and 16HT-36 obtained by the LOI method are significantly higher than those based on the acid-base titration method, but sample 17WP-19 is on the contrary (Table A. 3).

Our unpublished geochemical data estimate that sample 17WP-09



**Fig. 8.** The comparison of gasometric method (a) and acid-base titration (b) with LOI method based on marine and terrestrial sediment samples. The black-blue lines mean 0%, 10% and 20% value deviations of two methods. The right vertical coordinate represents the ratio calculated by using the value difference of two methods divided by the measured value of LOI method. Purple (blue) solid and hollow diamonds represent separately terrestrial and marine sediments. The purple (blue) line indicates the trend of the differences in values measured by the two methods go with the carbonate content. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

has < 8% wt carbonate and sample 17WP-20 has very low (< 1.8% wt) carbonate content. This is inconsistent with the results by the LOI method, which indicate > 10% wt carbonate in these two samples (Fig. 7; Table A. 3). This can be explained as follows. The LOI method assumes that all CO<sub>2</sub> is produced by decomposition of carbonate minerals, ignoring dehydroxylation of other mineral components in sediments (Ball, 1964; Mook and Hoskin, 1982; Dankers and Laane, 1983; Frangipane et al., 2009). For example, clay minerals dehydrate the structural water at 400–800 °C resulting in an overestimation of carbonate content during combustion under 550–900 °C (Grim, 1953; Dean, 1974; Kennedy and Woods, 2013). As indicated by Fig. 3, terrestrial samples 16HT-19 and 16HT-36 and marine sample 17WP-09 are rich in clay minerals (51.9%, 26.3% and 19.7%, respectively), and the clay minerals are dominated by illite and kaolinite. In addition, sample 17WP-20 contains abundant lizardite, which is a hydrous layered silicate mineral similar to clay minerals (Caruso and Chernosky, 1979; Mellini and Zanazzi, 1987; Rinaudo et al., 2003). Thus, dehydroxylation of clay minerals in these samples lead to overestimation of carbonate content by the LOI method.

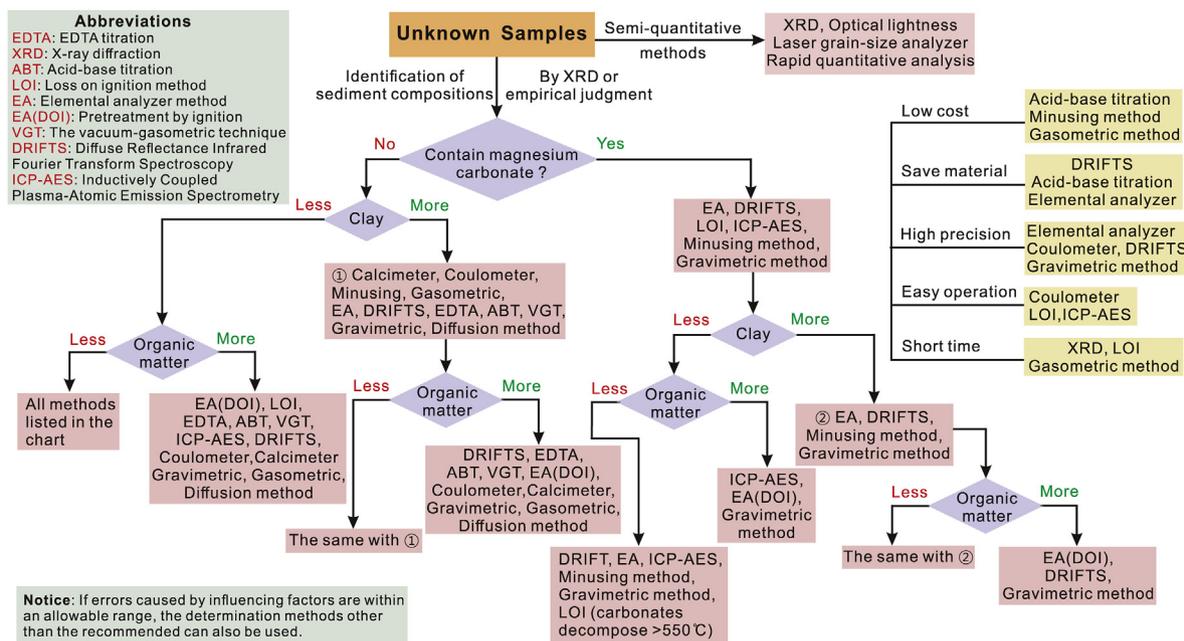
XRD analysis demonstrates that carbonate in sample 17WP-17 is dominated by dolomite, rather than calcite (Fig. 3a). The underestimation of carbonate content by using the gasometric method is probably due to the insufficient dissolution of dolomite in short time. The obviously high carbonate content for sample 17WP-19 measured by acid-base titration seems to be more reliable than those by gasometric and LOI methods due to the high bulk CaO concentration (14.19% wt, unpublished data) and peak intensity of calcite (Fig. 3a). Therefore, we propose that sediment compositions, particularly clay minerals and different carbonate species, have a certain impact on the determination of carbonate content by these methods.

#### 4.3. A comprehensive summary of the different determination methods

Numerous methods have been proposed to determine the carbonate content in sediments and sedimentary rocks over the last decades. Here, a comparative table, which shows methodology, operation, cost, advantages and disadvantages, is summarized through references and the new data in this study (Table A. 1). XRD analysis is a qualitative to semi-quantitative method, which can quickly detect mineral compositions of sediments and estimate carbonate contents by the reference intensity ratio (RIR) method (Chung, 1974; Hubbard and Snyder, 1988; Snyder, 1992; Johnson and Zhou, 2000). Our findings suggest that acid-base titration has advantages of low sample consumption and high precision but with disadvantage of relatively low and unstable accuracy. The inaccuracy presumably comes from operational errors during the analytical process. Therefore, strict operations such as precise calibration of standard NaOH solution and exact judgement of titration endpoint are beneficial for optimizing the accuracy of results. The gasometric method is convenient, short time consuming and can be routinely applied to measure sediments or sedimentary rocks in which calcite is the dominant carbonate species. Besides, appropriate sample sizes for sediments with different quantities of carbonate are important to improve and stabilize the precision in the gasometric measurements. The LOI method is easy to operate and is suitable for batch determinations. Results by the LOI method demonstrate relatively good precision and accuracy, but LOI measurement requires more sample amounts than other two methods. Note that the LOI method is not appropriate to determine carbonate for sediments with complex mineral compositions, especially those with low carbonate contents and abundant clay minerals. Dehydroxylation of hydrous layered silicate minerals possibly influence carbonate measurements during the high-temperature

**Table 2**  
Comprehensive summary of the acid-base titration, gasometric and LOI methods.

Method	Precision (RSD)	Sample size	Time-consuming	Cost	Operation
Acid-base titration	1–3%; > 3% (low CaCO <sub>3</sub> content)	0.1 g	3 days for one batch (2 days for reaction and 1 day for operation)	Low	Skilled chemical operation
Gasometric method	1–3%	< 1 g	8 min for each sample	Low	Easy, no skill required
LOI method	< 1%; > 3% (low CaCO <sub>3</sub> content)	3 g	1 day for one batch (most time for dry and combustion)	Low	Easy, no skill required



**Fig. 9.** A flow chart for selecting carbonate content determination methods. Most of the selections are based on sediment compositions and operation properties. We suggest that all the methods can be employed for determining samples with only calcium carbonate and extremely low clay and organic matter content.

combustion process. Therefore, it is recommended that sediment compositions should be investigated by XRD analysis before combustion. Table 2 is a comprehensive summary of the properties of the acid-base titration, gasometric and LOI methods.

This study highlights that carbonate determination by all the methods can be significantly affected by mineral compositions of the targeted samples and carbonate components therein. We propose a flow chart for method selection (Fig. 9) depending on different sample features, including carbonate species, clay mineral content and organic matter abundance, on basis of references and this study. The environments where sediments or sedimentary rocks formed (marine facies or continental facies) have flexibly and variably indirect impacts on carbonate determination. Hence, methods for determining carbonate content in marine or terrestrial sediments are not unique. The determination methods should be selected by comprehensive consideration of experimental purposes, accuracy requirements, laboratory conditions and sediments properties.

## 5. Conclusions

This study compares carbonate content measurement data for marine sediments and terrestrial sedimentary rocks by three non-instrumental methods, i.e., acid-base titration, gasometric method, LOI method, combine mineral phase identification by XRD analysis, and obtains the following findings.

Carbonate content result accuracies by all the determining methods are closely related to two major factors, i.e., the operation of analytical procedure and mineral (especially carbonate) compositions in unknown samples. We suggest that the complexity of sediment compositions,

instead of formation environments of the sediments (marine or terrestrial), plays a crucial role in the selection of carbonate determination approaches.

Result precisions by non-instrumental methods are generally low (ca. avg. RSD of 3.36%) when measuring carbonate-poor (< 20% wt) sediments. However, the LOI method (avg. RSD and recovery of 0.27% and 99.79%, respectively, same as below) is more preferred than the acid-base titration (1.73%, 108.64%) and gasometric methods (2.76%, 101.85%) when determining carbonate-rich (> 20% wt), clay-poor sediments. In this case, using the LOI method is expected to obtain as good results as instrumental approaches at a lower cost and in less time.

Our pre-experimental results indicate that the analytical processes such as selection of sample sizes, reaction time, combustion temperature, weighing, calibration of reagent concentration, and judgement of titration endpoint warrant more attention in those non-instrumental methods. Taking care of the analytical process is especially beneficial for improving result precisions and accuracies by the acid-base titration and gasometric methods.

## CRediT authorship contribution statement

**Hanjing Fu:** Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. **Xing Jian:** Conceptualization, Resources, Writing - original draft, Writing - review & editing, Supervision, Funding acquisition. **Wei Zhang:** Resources, Writing - original draft, Project administration, Writing - review & editing. **Fei Shang:** Writing - original draft, Writing - review & editing.

## Declaration of competing interest

We declare that we don't have any conflict of interest.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpetgeo.2020.104337>.

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